Chapter

9

Protective Coatings

9.1 Introduction 781
9.2 Coatings and Coating Processes 782
9.2.1 Metallic coatings 782
9.2.2 Inorganic coatings 805
9.2.3 Organic coatings 810
9.3 Supplementary Protection Systems 829
9.3.1 Jointing compounds and sealants 830
9.3.2 Water displacing compounds 830
9.4 Surface Preparation 831
References 831

9.1 Introduction

Protective coatings are probably the most widely used products for corrosion control. They are used to provide long-term protection under a broad range of corrosive conditions, extending from atmospheric exposure to the most demanding chemical processing conditions. Protective coatings in themselves provide little or no structural strength, yet they protect other materials to preserve their strength and integrity. The main function of a protective coating is to isolate structural reactive elements from environmental corrosives. The fact that protective coatings occupy only a very small fraction of the total volume of a system is quite telling of the heavy requirements imposed on these materials. A coating must provide a continuous barrier to a substrate, and any imperfection can become the focal point for degradation and corrosion of the substrate.

Metal finishing comprises a wide range of processes that are practiced by most industries engaged in manufacturing operations using metal parts. Typically, metal finishing is performed on manufactured parts after

they have been shaped, formed, forged, drilled, turned, wrought, cast, and so forth. A "finish" can be defined as any final operation applied to the surface of a metal article to alter its surface properties and achieve various goals. The quality of a coating depends on many factors besides the nature of the materials involved. Metal finishing operations are intended to increase corrosion or abrasion resistance, alter appearance, serve as an improved base for the adhesion of other materials, enhance frictional characteristics, add hardness, improve solderability, add specific electrical properties, or improve the utility of the product in some other way.

9.2 Coatings and Coating Processes

Coating fundamentals makes reference to a multitude of concepts and properties. A critical property of antifouling paint is, for example, the inhibition of living organism growth on the coating. A fire-resistant coating, on the other hand, should resist or retard the burning of the substrate. From a corrosion point of view a coating is rated on the resistance it provides against corrosion in a specific environment, and because there are many variations in environment corrosivity, there is also a great variety of corrosion protective coatings. These can be broadly divided into metallic, inorganic, and organic coatings. A general description of how the main elements are used in metallic and inorganic coatings is given in Table 9.1.

9.2.1 Metallic coatings

Metallic coatings provide a layer that changes the surface properties of the workpiece to those of the metal being applied. The workpiece becomes a composite material exhibiting properties generally not achievable by either material if used alone. The coatings provide a durable, corrosion-resistant layer, and the core material provides the load-bearing capability.

The deposition of metal coatings, such as chromium, nickel, copper, and cadmium, is usually achieved by wet chemical processes that have inherent pollution control problems. Alternative metal deposition methods have replaced some of the wet processes and may play a greater role in metal coating in the future. Metallic coatings are deposited by electroplating, electroless plating, spraying, hot dipping, chemical vapor deposition, and ion vapor deposition. Some important coatings are cadmium, chromium, nickel, aluminum, and zinc. Copper, gold, and silver are also used in electrical equipment and occasionally for specialty fastener applications. Copper is used as a base layer in multiple-plate electroplating, silver is used for antifretting purposes, and both silver and gold are sometimes used to provide electrical conductivity in waveguides and at contacts.

TABLE 9.1 Properties and Applications of the Main Metallic Elements Used for Protective Coatings

Aluminum
Aluminum coatings can be applied to steel by hot dipping, cementation, ion vapor deposition, and spraying. Ion vapor deposition is a relatively new process, and spraying is the only process that has been used extensively over a long period of time. Pack cementation is widely used for gas turbine components. In soft waters aluminum is cathodic with respect to steel; however, in seawater or some fresh waters containing chloride ions or sulfate ions, aluminum may become anodic to steel, and aluminum coatings should therefore corrode sacrificially and provide cathodic protection to steel. However, as noted below, this may not always be the case.
Sprayed aluminum coatings provide an adherent, somewhat absorbent film about 100 to 150 μm thick. They provide very good protection to steel, and they may be sealed with organic lacquers or paints to provide further protection and delay the formation of visible surface rust. The surface of the steel must first be grit-blasted to provide a rough surface to aid adhesion. Unfortunately the thickness and relative roughness of the coatings make them unsuitable for close tolerance parts.
Ion vapor-deposited aluminum coatings have been used on a variety of parts including steel and titanium fasteners, electrical connectors, engine mounts and stator vanes, landing gear components, integrally machined wing skins, and a large number of miscellaneous components. These coatings are soft and ductile and are prepared using commercially available aluminum (1100 alloy) feed wire that is melted, vaporized, and ionized in a glow discharge created by an inert gas. The process is applied in a batch mode, where parts to be coated are held at a high negative potential relative to the evaporation source. The positively charged gas ions bombard the surface of the part and perform a final cleaning action. When this is done the aluminum is vaporized and ionized, and the ionized aluminum is accelerated toward the part surface where it plates as a dense, tightly adherent coating.
Minimum coating thickness are in the range 8 to 25 μm, and coatings may be used as prepared or with a supplementary chromate treatment. The thinner coatings are used when close tolerances are required such as on threads, intermediate thickness coatings (> 13 μm) are used on interior parts or where only mildly corrosive environments are expected, and the thicker coatings (> 25 μm) are used for exterior parts operating in highly corrosive environments and for engine parts. Ion vapor-deposited aluminum has been considered as a replacement for diffused nickel cadmium and aluminum pigmented paints for use in the cooler sections of gas turbines, where temperatures are less than 454°C. The process has also been considered as an alternative to pack cementation for the preparation of aluminide coatings on hot-section components. In this case the ion vapor-deposited aluminum is diffused into the nickel-based superalloy substrates to form the nickel aluminide coating.
Ion vapor deposition of aluminum is attractive because it avoids the environmental and toxicological problems associated with cadmium. It does not cause hydrogen embrittlement of steel or solid metal embrittlement of steel or titanium, and it should be more galvanically compatible with aluminum alloy structure and avoid the exfoliation corrosion of sensitive aluminum alloy structure. However, views on the ability of aluminum to protect steel fasteners appear to vary. A view is that the presently available pure aluminum coatings are not able to provide adequate sacrificial protection to steel in a chloride ion environment, and for this reason a recommendation is made for the development of aluminum coatings containing small amounts of zinc or other elements for improved protection.

TABLE 9.1 Properties and Applications of the Main Metallic Elements Used for Protective Coatings (*Continued*)

Cadmium
Cadmium is widely used by the aircraft industry for electroplating steel fasteners and bearing assemblies because it provides a galvanically acceptable couple with aluminum. Cadmium is also anodic to steel and will cathodically protect the substrate at scratches or gaps in the coating and at cut edges. It also exhibits surface lubricity and conductivity and resists fretting and fatigue, and its corrosion products do not cause binding. Platings are usually deposited from cyanide baths, but baths containing fluoroborates or sulfamates are also used. The baths may contain special additives to reduce hydrogen penetration, and the coatings are usually 5 to 25 μm thick. The use of cadmium introduces four problems. The first problem is that it is highly toxic, and environmental protection agencies have been concerned about its release into the environment. Disposal of wastes from cyanide baths is therefore a problem, as is the eventual disposal of the finished coated part. The second problem is that the electroplating process also exposes parts to cathodically produced hydrogen, and because many of the high-strength steels involved are highly susceptible to hydrogen embrittlement, stringent requirements exist to bake parts immediately after plating to remove this hydrogen. Most process specifications for cadmium plating include requirements for baking and subsequent testing of coupons to demonstrate absence of embrittlement. The problem of hydrogen embrittlement can be avoided by applying cadmium coatings by an ion vapor deposition process, which does not produce hydrogen. This process is sometimes used on very high strength steels where hydrogen would be difficult to remove by baking. Once deposited, these coatings are essentially similar to electrodeposited coatings and should receive the same type of additional paint protection. The third problem is that cadmium has been reported to cause solid metal embrittlement of steel and titanium alloys. Finally, cadmium has also been reported to cause exfoliation corrosion of susceptible aluminum alloys when used on fasteners in contact with these alloys in a riveted or bolted structure. Many alternatives to cadmium plating exist, with no single universal substitute available. Some cadmium plating alternatives are zinc plating, tin or tin alloy plating, cobalt-zinc plating, zinc-nickel plating, zinc-iron plating, zinc-flake dispersion coating, metallic ceramic coating, and ion vapor deposition of aluminum. The most successful of these alternatives has been zinc-nickel plating, which has a long history in the electroplating industry. Generally, for alternatives to be successful, they must provide sufficient corrosion resistance, as measured by standard tests. For certain military and aerospace applications, the alternative deposits must also provide other desired characteristics, such as lubricity. Many electroplating job shops have eliminated cadmium plating because of a reduced market and the enforcement of local discharge standards.
Chromium
Chromium is used as a protective coating, providing resistance to wear, abrasion, and corrosion. It has hardness in the range 900 to 1100 HV, low-friction characteristics, and high reflectivity. It is used as a thin coating, usually in the range 0.2 to 1 μm thick, as the final layer in a multipleplate copper-nickel-chromium electroplating or as a thick coating up to 300 μm to provide wear resistance. When used as a constituent of a multiple-plate coating, chromium provides hardness, reflectivity, and tarnish resistance. The corrosion resistance is derived primarily from the barrier effect of the thick nickel plate under the chromium. However, copper, nickel, and chromium are all cathodic with respect to steel, and corrosion can be accelerated once the coating is breached and the underlying steel is exposed. For this reason these coatings are not chosen where corrosion protection is the primary concern.

TABLE 9.1 Properties and Applications of the Main Metallic Elements Used for Protective Coatings (*Continued*)

Hard chromium plating is usually applied directly to steel parts in thickness up to about 300 μm to provide resistance to wear, abrasion, and corrosion. It is also used to build up worn or undersized parts. In the thicker applications it may be impervious but is subject to microcracks. Chromium is a metal with low cathode efficiency, and substantial amounts of hydrogen are deposited on the part along with the metal being plated. Because of this, parts must be baked as soon as possible after plating to drive off the hydrogen and prevent embrittlement.

Chromium plating is traditionally performed with a hexavalent chromium bath, but trivalent chromium plating has increased in use, especially during the past 10 years. With either process, an undercoat of nickel/copper or nickel is usually applied. Trivalent chromium plating is an economically attractive alternative to hexavalent plating for some applications. However, its use has been limited due to a difference in appearance from the standard hexavalent bath. The trivalent bath chemistry is more expensive to purchase than the hexavalent bath. The cost savings are a result of reduced metal loading on the treatment system (the trivalent bath contains less total chromium) and the avoidance of the hexavalent chromium reduction step during treatment. The total cost of trivalent chromium plating is about one-third of the costs for hexavalent solution.

Hard chromium plating is applied to tools, hydraulic cylinders, and other metal surfaces that require wear resistance. It is widely used in the mining industry. The major difference between the hard chromium and decorative deposits is their thickness. The hard chromium deposit is typically hundreds of times thicker than decorative ones. Although research efforts have aimed at a trivalent chromium substitute for hard chromium plating, no solutions are available commercially. Input material changes for hard chromium have focused on alternative deposits. Alternative processes have also been used. The most successful alternative input material is electroless nickel. Other alternative input materials under investigation are electroplated nickel alloys and nickel alloy composites. Alternative processes to hard chromium plating include brush plating, vacuum coating, and metal sprays.

Chromium use with aluminum finishing is perhaps most common in the aerospace industry. Chromium combines with aluminum on the surface of parts to provide corrosion and wear resistance and a chemically active surface for painting or coloring. The two most common processes are chromic acid anodizing and chromate conversion coating. Both processes are presently performed in hexavalent chromium baths. The anodizing process is electrolytically performed, and the conversion coating process involves simple immersion. Significant research efforts have been undertaken during the past 10 years to find alternatives to these processes. For many applications, alternatives have been identified and implemented. For example, chromic acid anodizing has been partially replaced by common sulfuric acid anodizing and sulfuric/boric acid anodizing, and chromium baths have been replaced to a lesser extent by nonchromium conversion coatings (e.g., permanganate, rare earth metals, and zirconium oxide).

Another use of chromium during aluminum finishing is for deoxidizing/desmutting. These preliminary processes (sometimes a combined single step) remove oxides and other inorganics that would interfere with aluminum processing (e.g., anodizing). Alternatives to the chromium-based products include iron and ammonium salts and amines mixed with various oxidizers and/or etchants. Owing to the extent of research for nonchromium aluminum finishing and the success rate of these efforts, it is possible that chromium use will eventually be eliminated from the aluminum finishing area. One would expect to see large-scale substitutions during the next 10 years. However, total elimination will take considerable longer because of small residual uses of chromium for which no satisfactory substitute exists.

TABLE 9.1 Properties and Applications of the Main Metallic Elements Used for Protective Coatings (*Continued*)

Nickel
By far the greatest use of nickel plating is on steel in conjunction with copper and chromium as described above. However, nickel can also be deposited, both on metals and nonmetals by an electroless or nonelectrolytic process. The metal is deposited spontaneously on the surface of a catalytic substrate immersed in an aqueous solution containing the metal ion and a reducing agent together with a compound (frequently the salt of an organic acid) that acts as a buffer and a complexing agent for the metallic ion. The baths often contain phosphorous or boron, and they provide coatings of uniform thickness even over sharp corners and into deep recesses. The coatings have low internal stress and are less magnetic than electrodeposited nickel platings, and they have hardness values of about 500 HV. The coatings can be heat treated to higher hardness of about 1000 HV, which provides wear and abrasion resistance. This increase in hardness is achieved by a precipitation hardening process involving the phosphorous, which is usually present in amounts of 5 to 10%. The heat treatment is carried out at temperatures of about 400°C. Electroless nickel coatings about 25 μm thick are often used after baking to remove hydrogen and to provide protection against stress corrosion cracking of precipitation hardenable stainless steels.
Zinc
Zinc coatings may be applied either by electroplating or spraying. Electroplatings are normally less than 25 μm thick and may be as thin as 5 μm on threaded parts. However, although they provide good protection to steel in rural atmospheres, they do not perform as well in marine or industrial environments. Zinc coatings 30 μm thick last about 11 years or longer in rural or suburban locations, about 8 years in marine locations, and only 4 years in industrial atmospheres. The short life in industrial atmospheres was attributed to attack by sulfuric acid in polluted atmospheres. Zinc plating does not perform as well as cadmium in tropical and marine atmospheres, and therefore cadmium is preferred for aircraft use. Where thicker coatings are permissible, zinc may be deposited by spraying but must compete with aluminum, which is usually the preferred material.

Plating and surface treatment processes are typically batch operations, in which metal objects are dipped into and then removed from baths containing various reagents to achieve the desired surface condition. The processes involve moving the object being coated through a series of baths designed to produce the desired end product. These processes can be manual or highly automated operations, depending on the level of sophistication and modernization of the facility and the application. Plating operations can generally be categorized as electroplating and electroless plating processes.

Electroplating. Electroplating is achieved by passing an electrical current through a solution containing dissolved metal ions and the metal object to be plated. The metal object serves as the cathode in an electrochemical cell, attracting metal ions from the solution. Ferrous and

nonferrous metal objects are plated with a variety of metals, including aluminum, brass, bronze, cadmium, copper, chromium, iron, lead, nickel, tin, and zinc, as well as precious metals, such as gold, platinum, and silver. The process is regulated by controlling a variety of parameters, including the voltage and amperage, temperature, residence times, and the purity of bath solutions. Plating baths are almost always aqueous solutions; therefore, only those metals that can be reduced from aqueous solutions of their salts can be electrodeposited. The only major exception is aluminum, which can be plated from organic electrolytes. The sequence of unit operations in an electroplating operation typically involves various cleaning steps, stripping of old plating or paint, electroplating steps, and rinsing between and after each of these operations. Electroless plating uses similar steps but involves the deposition of metal on a substrate without the use of external electrical energy.

Electroless plating. Electroless nickel (EN) plating is a chemical reduction process that depends upon the catalytic reduction process of nickel ions in an aqueous solution (containing a chemical reducing agent) and the subsequent deposition of nickel metal without the use of electrical energy. Thus in the EN plating process, the driving force for the reduction of nickel metal ions and their deposition is supplied by a chemical reducing agent in solution. This driving potential is essentially constant at all points of the surface of the component, provided the agitation is sufficient to ensure a uniform concentration of metal ions and reducing agents. The electroless deposits are therefore very uniform in thickness all over the part's shape and size. The process thus offers distinct advantages when plating irregularly shaped objects, holes, recesses, internal surfaces, valves, threaded parts, and so forth.

Electroless (autocatalytic) nickel coating provides a hard, uniform, corrosion-, abrasion-, and wear-resistant surface to protect machine components in many industrial environments. EN is chemically deposited, making the coating exceptionally uniform in thickness. Careful process control can faithfully reproduce the surface finish, eliminating the need for costly machining after plating.

In a true electroless plating process, reduction of metal ions occurs only on the surface of a catalytic substrate in contact with the plating solution. Once the catalytic substrate is covered by the deposited metal, the plating continues because the deposited metal is also catalytic. As a result, electroless plating processes are widely used in industry to meet the end-use functional requirements and are only rarely used for decorative purposes. Distinct advantages of EN plating are

- Uniformity of the deposits, even on complex shapes. The electroplated coatings are thinner in recessed areas and thicker on projecting areas.

- Deposits are often less porous and thus provide barrier corrosion protection to steel substrates that is much superior to that of electroplated nickel and hard chrome.
- Deposits cause about one-fifth as much hydrogen absorption as electrolytic nickel and about one-tenth as much as hard chrome.
- Deposits can be plated with zero or compressive stress. Fatigue strength debit on the substrate material is thus zero or positive.
- Deposits have inherent lubricity and nongalling characteristics, unlike electrolytic nickel.
- Deposits have good wetability for oils.
- Deposits have good solderability, braze weldability, and weldability.
- Deposits are much harder with as-plated microhardness of 450 to 600 HV, which can be increased to 1000 to 1100 HV by a suitable heat treatment, the increase being due to the precipitation of Ni3P, which causes general hardening of the alloy.

Deposits have unique magnetic properties. EN deposits containing more than 8% P are generally considered to be essentially nonmagnetic in the as-plated condition. In Ni-P coatings, phosphorus is present as supersaturated solution in fine microcrystalline solid solution, bordering on amorphous or liquidlike (glasslike) metastable structure, and is responsible for nonferromagnetic behavior of as-plated Ni-P deposits (with $P > 8\%$).

A second generation of EN plating has been developed by codepositing micrometer-sized particles of silicon carbide with the nickel, thereby creating an extremely wear- and corrosion-resistant coating. The nickel alloy matrix provides corrosion resistance, and the silicon carbide particles, which are actually the contacting surface, add wear resistance.

Hot dip galvanizing. Hot dip galvanizing is the process of applying a zinc coating to fabricated iron or steel material by immersing the material in a bath consisting primarily of molten zinc. The simplicity of the galvanizing process is a distinct advantage over other methods of providing corrosion protection. The automotive industry depends heavily on this process for the production of many components used in car manufacturing, as illustrated in Table 9.2.

The recorded history of galvanizing goes back to 1742 when a French chemist named Melouin described, in a presentation to the French Royal Academy, a method of coating iron by dipping it in molten zinc. In 1836 another French chemist, Sorel, obtained a patent for a means of coating iron with zinc after first cleaning it with 9% sul-

furic acid and fluxing it with ammonium chloride. A British patent for a similar process was granted in 1837. By 1850, the British galvanizing industry was using 10,000 tons of zinc a year for the protection of steel.[1]

Galvanizing can be found in almost every major application and industry where iron or mild steel is used. The utilities, chemical process, pulp and paper, automotive, and transportation industries, to name just a few, have historically made extensive use of galvanizing for corrosion control. They continue to do so today. For over 140 years, galvanizing has had a proven history of commercial success as a method of corrosion protection in a myriad of applications worldwide.

The electrochemical protection provided to steel by zinc coatings is a vital element in the effectiveness of galvanized coatings in protecting steel from corrosion. All pregalvanized products rely on the cathodic protection provided by zinc to prevent corrosion of exposed steel at cut edges. While the potential difference between metals is the prime driving force providing the corrosion current, it is not a reliable guide to the rate and type of corrosion occurring at a particular point. The severity of galvanic corrosion also depends on the ratio of the areas of metals in contact, the duration of wetness (galvanic corrosion can only occur in the presence of a conductive solution), and the conductivity of the electrolyte. The presence of oxide films on the surface of one or both of the metals can greatly inhibit galvanic corrosion.

In any situation where zinc is corroded sacrificially to protect exposed steel, the mass of available zinc will determine the corrosion protection performance. Corrosion rates of zinc coatings required to cathodically protect uncoated steel in aggressive environments (saltwater/marine) may be 25 times higher than the normal zinc corrosion rate.

Pack cementation. Diffusion coatings are formed by depositing a layer of aluminum on the metal surface and then heating the component in a furnace for a period of time. During this heat treatment, the aluminum and metal atoms migrate, or diffuse, into each other, which is the reason these coatings are called diffusion coatings. This processing is usually performed by a pack cementation process in which the aluminum deposition and the heat treatment occur simultaneously.

Pack cementation is widely used to confer oxidation resistance on ferrous alloys. Usually relatively expensive aluminum or binary alloys grade reagent is used during the pack process with aluminum as a source. Pack cementation processes include aluminizing, chromizing, and siliconizing. Components are packed in metal powders in sealed heat-resistant retorts and heated inside a furnace to precisely controlled temperature-time profiles. In the aluminizing process, a source

TABLE 9.2 Coatings for Automotive Sheet Steels

Steel coating	Description	Typical applications
Hot dipped, zinc coated (regular and minimized spangle)	Made on hot-dipped galvanizing lines and supplied in coils and cut lengths. Includes regular and minimized spangle in a wide range of coating designations and is available in extra smooth finish.	Rocker panels, wheelhouse and inner and outer panels, luggage compartment floor pans, bumper reinforcement, body structure inner reinforcements, floor pans
Hot dipped, zinc coated (fully alloyed zinc-iron coated)	Hot-dipped, zinc-coated product that is heat treated or wiped to produce a fully alloyed zinc-iron coating.	Body rails, cross members, light truck box beds
Hot dipped, zinc coated (differentially zinc coated)	Hot-dipped, zinc-coated product that is produced with different specified coating weights on opposite sheet surfaces. Both surfaces are zinc.	Cross members, hoods, fenders, door outer panels, quarter panels, wheelhouses, various underbody components
Hot dipped, zinc coated (differentially zinc-iron coated)	Same as above, except that the coating on the lighter surface is heat treated or wiped to produce a fully alloyed zinc-iron coating.	Fenders, doors, outer body panels, quarter panels, hoods, floor pans, door inner panels, dash panels
Hot dipped, zinc coated, one side	Produced with continuous hot-dipped, zinc coating on one side and a zinc-free, cold-rolled steel surface on the other for superior paint adhesion.	Fenders, door outer panels, quarter panels, deck lids, lower back panels, roofs, hoods
Electrolytic zinc, flash coated	Produced by continuously flash electroplating with zinc—30 to 60 g/m^2 total on both sides. It is used when minimal corrosion resistance is required.	Window guides, wiper blade frames, radio speaker baskets, head rest supports
Electroplated zinc coated	Produced by continuously electroplating zinc. Two side coatings can be produced on an equal basis or differentially. One side of the product has a standard cold-rolled surface.	Exposed and unexposed body panels
Electroplated iron-zinc alloy coated	Produced by the simultaneous electroplating of zinc and iron to form an alloy coating. One and two side coatings can be produced on an equal basis or differentially coated.	Exposed and unexposed body panels

Electroplated zinc-nickel alloy coated	Produced by the simultaneous electroplating of zinc and nickel to form an alloy coating. One and two side coatings can be produced on an equal basis or differentially coated.	Exposed and unexposed body panels
Aluminum coated	Produced by hot-dip coating cold-rolled sheet steel on continuous lines. It provides a material with the superior strength of steel and the surface properties of aluminum.	Exhaust systems, chassis components
Aluminum-zinc coated	Produced by hot-dip coating cold-rolled sheet steel on continuous lines. It has the superior strength of steel and excellent corrosion resistance.	Exhaust systems, air cleaner covers, core plugs, brake shields, floor pan covers
Zinc-aluminum mischmetal coated	Produced by hot-dip coating cold-rolled sheet steel on continuous lines. It provides maximum formability and excellent corrosion resistance.	Fuel-tank shields, fuel oil-filter shields, motor housings, shock towers and other deep-drawn underbody parts
Long terne	Cold-rolled sheet steel coated on both sides with a lead-tin alloy by a continuous hot-dip process.	Fuel tanks, fuel lines, brake lines, radiator and heater parts, air cleaners
Nickel terne	Cold-rolled sheet steel electrolytically nickel flash-plated and then coated on both sides with a lead-tin alloy by a continuous hot-dip process. Corrosion resistance is superior to standard long terne.	Fuel tanks, fuel lines, brake lines, radiator and heater parts, air cleaners
Tin coated	Cold-rolled sheet steel coated with tin by a continuous electrolytic process.	Oil filter and heater components
Zincrometal	A cold-rolled steel product with a base coat containing primarily chromium and zinc, top coated by a weldable zinc-rich primer for corrosion resistance—generally only to one side. The other side is typically a standard cold-rolled surface for superior paint adhesion.	Door inner and outer panels, fenders, quarter panels, hoods, deck lids, lift gate outers, lower back panels

of aluminum reacts with a chemical activator on heating to form a gaseous compound (e.g., pure Al with NaF to form AlF). This gas is the transfer medium that carries aluminum to the component surface. The gas decomposes at the substrate surface, depositing aluminum and releasing the halogen activator. The halogen activator returns to the pack and reacts with the aluminum again. Thus, the transfer process continues until all of the aluminum in the pack is used or until the process is stopped by cooling. The coating forms at temperatures ranging from 700 to 1100°C over a period of several hours.[2]

Pack cementation is the most widely used process for making diffusion aluminide coatings. Diffusion coatings are primarily aluminide coatings composed of aluminum and the base metal. A nickel-based superalloy forms a nickel-aluminide, which is a chemical compound with the formula NiAl. A cobalt-based superalloy forms a cobalt-aluminide, which is a chemical compound with the formula CoAl. It is common to incorporate platinum into the coating to improve the corrosion and oxidation resistance. This is called a platinum-aluminide coating. Diffusion chrome coatings are also available.

Diffusion aluminide coatings protect the base metal by forming a continuous, aluminum oxide layer, Al_2O_3, which prevents further oxidation of the coating. (Actually, oxidation continues but at much slower rates than without a continuous aluminum oxide scale.) When part of the Al_2O_3 scale spalls off, the underlying aluminide layer is exposed to form a new Al_2O_3 scale. Thus, the coating is self-healing.

Pack cementation can also be used to produce chromium-modified aluminide coatings. The addition of chromium is known to improve the hot corrosion resistance of nickel-based alloys. Although chromium can be codeposited with aluminum in a single-step process, a duplex process is frequently used to form the chromium-modified aluminide. The component is first chromized using either pack cementation or a gas phase process, and this is then followed by a standard aluminizing treatment. The final distribution of the chromium in the coating will depend on whether a low- or high-activity aluminizing process is employed.

For a platinum-aluminide coating, a thin (typically 8-μm) layer of platinum is first deposited onto the substrate, usually by a plating process. The second step involves aluminizing for several hours using the conventional packed cementation process to form the platinum-aluminide coating.

Conventional pack cementation processes are unable to effectively coat internal surfaces such as cooling holes. The coating thickness on these internal surfaces is usually less than on the surface due to limited access by the carrier gas. Access can be improved by pulsing the carrier gas,[3] or by use of a vapor phase coating process.

Another method of coating both the internal and external surfaces involves generating the coating gases in a reactor that is separate from the vessel the parts are in. The coating gases are pumped around the outside and through the inside of the parts by two different distribution networks. Internal passages can be coated by filling them with the powder used in the pack (actually a variation of this powder).[4]

Slurry processes can also be used to deposit the aluminum or the aluminum and other alloying elements. The slurry is usually sprayed on the component. The component is then given a heat treatment, which burns off the binder in the slurry and melts the remaining slurry, which reacts with the base metal to form the diffusion coating. After coating, it is usually necessary to heat treat the coated component to restore the mechanical properties of the base metal.

Cladding. Corrosion resistance can be improved by metallurgically bonding to the susceptible core alloy a surface layer of a metal or an alloy with good corrosion resistance. The cladding is selected not only to have good corrosion resistance but also to be anodic to the core alloy by about 80 to 100 mV. Thus if the cladding becomes damaged by scratches, or if the core alloy is exposed at drilled fastener holes, the cladding will provide cathodic protection by corroding sacrificially.

Cladding is usually applied at the mill stage by the manufacturers of sheet, plate, or tubing. Cladding by pressing, rolling, or extrusion can produce a coating in which the thickness and distribution can be controlled over wide ranges, and the coatings produced are free of porosity. Although there is almost no practical limit to the thickness of coatings that can be produced by cladding, the application of the process is limited to simple-shaped articles that do not require much subsequent mechanical deformation. Among the principal uses are lead and cadmium sheathing for cables, lead-sheathed sheets for architectural applications, and composite extruded tubes for heat exchangers. Because of the cathodic protection provided by the cladding, corrosion progresses only to the core/cladding interface and then spreads laterally, thus helping to prevent perforations in thin sheet. The cut edges of the clad product should be protected by the normal finish or by jointing-compound squeezed out during wet assembly.

For aluminum-copper alloys (2000 series) dilute aluminum alloys such as 1230, 6003, or 6053, containing small amounts of manganese, chromium, or magnesium, may be used as cladding material. These have low-copper contents, less than 0.02%, and low-iron content, less than 0.2%. However these alloys are not sufficiently anodic with respect to the Al-Zn-Mg-Cu alloys of the 7000 series, and they do not provide cathodic protection in these cases. The 7000 series alloys are

therefore usually clad with aluminum alloys containing about 1% zinc, such as 7072, or aluminum-zinc-magnesium alloys such as 7008 and 7011, which have higher zinc contents.

The thickness of the cladding is usually between 2 and 5% of the total sheet or plate thickness, and because the cladding is usually a softer and lower-strength alloy, the presence of the cladding can lower the fatigue strength and abrasion resistance of the product. In the case of thick plate where substantial amounts of material may be removed from one side by machining so that the cladding becomes a larger fraction of the total thickness, the decrease in strength of the product may be substantial. In these cases the use of the higher-strength claddings such as 7008 and 7011 is preferred.

Thermal spraying. Energy surface treatment involves adding energy into the surface of the work piece for adhesion to take place. Conventional surface finishing methods involve heating an entire part. The methods described in this section usually add energy and material into the surface, keeping the bulk of the object relatively cool and unchanged. This allows surface properties to be modified with minimal effect on the structure and properties of the underlying material.[5] Plasmas are used to reduce process temperatures by adding energy to the surface in the form of kinetic energy of ions rather than thermal energy. Table 9.3 shows the main metallic materials that have been used for the production of spray coatings and Table 9.4 contains a brief description of the main advanced techniques. Similarly, Table 9.5 describes briefly the applications and costs of these advanced techniques, and Table 9.6 summarizes the limits and applicability of each technique.

Advanced surface treatments often require the use of vacuum chambers to ensure proper cleanliness and control. Vacuum processes are generally more expensive and difficult to use than liquid or air processes. Facilities can expect to see less-complicated vacuum systems appearing on the market in the future. In general, use of the advanced surface treatments is more appropriate for treating small components (e.g., ion beam implantation, thermal spray) because the treatment time for these processes is proportional to the surface areas being covered. Facilities will also have to address the following issues when considering the new techniques:[5]

- *Quality control methods.* Appropriate quality assurance tests need to be developed for evaluating the performance of the newer treatment techniques.
- *Performance testing.* New tribological tests must be developed for measuring the performance of surface engineered materials.

TABLE 9.3 Spray-Coating Materials

Type coating	General qualities
Aluminum	Highly resistant to heat, hot water, and corrosive gases; excellent heat distribution and reflection
Babbitt	Excellent bearing wearability
Brass	Machines well, takes a good finish
Bronze	Excellent wear resistance; exceptional machinability; dense coatings (especially Al, bronze)
Copper	High heat and electrical conductivity
Iron	Excellent machining qualities
Lead	Good corrosion protection, fast, deposits and dense coatings
Molybdenum (molybond)	Self-bonding for steel surface preparation
Monel	Excellent machining qualities; highly resistant to corrosion
Nickel	Good machine finishing; excellent corrosion protection
Nickel-chrome	High-temperature applications
Steel	Hard finishes, good machinability
Chrome steel (tufton)	Bright, hard finish, highly resistant to wear
Stainless	Excellent corrosion protection and superior wearability
Tin	High purity for food applications
Zinc	Superior corrosion resistance and bonding qualities

- *Substitute cleaning and coating removal.* The advanced coatings provide excellent adhesion between the substrate and the coating; as a result, these coatings are much more difficult to strip than conventional coatings. Many coating companies have had to develop proprietary stripping techniques, most of which have adverse environmental or health risks.
- *Process control and sensing.* The use of advanced processes requires improvements in the level of control over day-to-day production operations, such as enhanced computer-based control systems.

Coatings can be sprayed from rod or wire stock or from powdered materials. The material (e.g., wire) is fed into a flame, where it is melted. The molten stock is then stripped from the end of the wire and atomized by a high-velocity stream of compressed air or other gas, which propels the material onto a prepared substrate or workpiece. Depending on the substrate, bonding occurs either due to mechanical interlock with a roughened surface, due to localized diffusion and alloying, and/or by means of Van der Waals forces (i.e., mutual attraction and cohesion between two surfaces).

TABLE 9.4 Description of the Main Advanced Techniques for Producing Metallic Coatings

Combustion torch/flame spraying
Flame spraying involves the use of a combustion flame spray torch in which a fuel gas and oxygen are fed through the torch and burned with the coating material in a powder or wire form and fed into the flame. The coating is heated to near or above its melting point and accelerated to speeds of 30 to 90 m/s. The molten droplets impinge on the surface, where they flow together to form the coating.
Combustion torch/high-velocity oxy-fuel (HVOF)
With HVOF, the coating is heated to near or above its melting point and accelerated in a high-velocity combustion gas stream. Continuous combustion of oxygen fuels typically occurs in a combustion chamber, which enables higher gas velocities (550 to 800 m/s). Typical fuels include propane, propylene, or hydrogen.
Combustion torch/detonation gun
Using a detonation gun, a mixture of oxygen and acetylene with a pulse of powder is introduced into a water-cooled barrel about 1 m long and 25 mm in diameter. A spark initiates detonation, resulting in hot, expanding gas that heats and accelerates the powder materials (containing carbides, metal binders, oxides) so that they are converted into a plasticlike state at temperatures ranging from 1100 to 19,000°C. A complete coating is built up through repeated, controlled detonations.
Electric arc spraying
During electric arc spraying, an electric arc between the ends of two wires continuously melts the ends while a jet of gas (air, nitrogen, etc.) blows the molten droplets toward the substrate at speeds of 30 to 150 m/s.
Plasma spraying
A flow of gas (usually based on argon) is introduced between a water-cooled copper anode and a tungsten cathode. A direct current arc passes through the body of the gun and the cathode. As the gas passes through the arc, it is ionized and forms plasma. The plasma (at temperatures exceeding 30,000°C) heats the powder coating to a molten state, and compressed gas propels the material to the workpiece at very high speeds that may exceed 550 m/s.
Ion plating/plasma based
Plasma-based plating is the most common form of ion plating. The substrate is in proximity to a plasma, and ions are accelerated from the plasma by a negative bias on the substrate. The accelerated ions and high-energy neutrals from charge exchange processes in the plasma arrive at the surface with a spectrum of energies. In addition, the surface is exposed to chemically activated species from the plasma, and adsorption of gaseous species form the plasma environment.
Ion plating/ion beam enhanced deposition (IBED)
During IBED, both the deposition and bombardment occur in a vacuum. The bombarding species are ions either from an ion gun or other sources. While ions are bombarding the substrate, neutral species of the coating material are delivered to the substrate via a physical vapor deposition technique such as evaporation or sputtering. Because the secondary ion beam is independently controllable, the energy particles in the beam can be varied over a wide range and chosen with a very narrow window. This

TABLE 9.4 Description of the Main Advanced Techniques for Producing Metallic Coatings (*Continued*)

allows the energies of deposition to be varied to enhance coating properties such as interfacial adhesion, density, morphology, and internal stresses. The ions form nucleation sites for the neutral species, resulting in islands of coating that grow together to form the coating.

Ion implantation

Ion implantation does not produce a discrete coating; the process alters the elemental chemical composition of the surface of the substrate by forming an alloy with energetic ions (10 to 200 keV in energy). A beam of charged ions of the desired element (gas) is formed by feeding the gas into the ion source where electrons, emitted from a hot filament, ionize the gas and form a plasma. The ions are focused into a beam using an electrically biased extraction electrode. If the energy is high enough, the ions will go into the surface, not onto the surface, changing the surface composition. Three variations have been developed that differ in methods of plasma formation and ion acceleration: beamline implantation, direct ion implantation, and plasma source implantation. Pretreatment (degreasing, rinse, ultrasonic cleaner) is required to remove any surface contaminants prior to implantation. The process is performed at room temperature, and time depends on the temperature resistance of the workpiece and the required dose.

Sputtering and sputter deposition

Sputtering is an etching process for altering the physical properties of the surface. The substrate is eroded by the bombardment of energetic particles, exposing the underlying layers of the material. The incident particles dislodge atoms from the surface or near-surface region of the solid by momentum transfer form the fast, incident particle to the surface atoms. The substrate is contained in a vacuum and placed directly in the path of the neutral atoms. The neutral species collides with gas atoms, causing the material to strike the substrate from different directions with a variety of energies. As atoms adhere to the substrate, a film is formed. The deposits are thin, ranging from 0.00005 to 0.01 mm. The most commonly applied materials are chromium, titanium, aluminum, copper, molybdenum, tungsten, gold, silver, and tantalum. Three techniques for generating the plasma needed for sputtering are available: diode plasmas, RF diodes, and magnetron enhanced sputtering.

Laser surface alloying

The industrial use of lasers for surface modifications is increasingly widespread. Surface alloying is one of many kinds of alteration processes achieved through the use of lasers. It is similar to surface melting, but it promotes alloying by injecting another material into the melt pool so that the new material alloys into the melt layer. Laser cladding is one of several surface alloying techniques performed by lasers. The overall goal is to selectively coat a defined area. In laser cladding, a thin layer of metal (or powder metal) is bonded with a base metal by a combination of heat and pressure. Specifically, ceramic or metal powder is fed into a carbon dioxide laser beam above a surface, melts in the beam, and transfers heat to the surface. The beam welds the material directly into the surface region, providing a strong metallurgical bond. Powder feeding is performed by using a carrier gas in a manner similar to that used for thermal spray systems. Large areas are covered by moving the substrate under the beam and overlapping disposition tracks. Shafts and other circular objects are coated by rotating the beam. Depending on the powder and substrate metallurgy, the microstructure of the surface layer can be controlled, using the interaction time and laser parameters. Pretreatment is not as vital to successful performance of laser

TABLE 9.4 Description of the Main Advanced Techniques for Producing Metallic Coatings (*Continued*)

cladding processes as it is for other physical deposition methods. The surface may require roughening prior to deposition. Grinding and polishing are generally required posttreatments.
Chemical vapor deposition (CVD)
Substrate pretreatment is important in vapor deposition processes, particularly in the case of CVD. Pretreatment of the surface involves minimizing contamination mechanically and chemically before mounting the substrate in the deposition reactor. Substrates must be cleaned just prior to deposition, and the deposition reactor chamber itself must be clean, leak-tight, and free from dust and moisture. During coating, surface cleanliness is maintained to prevent particulates from accumulating in the deposit. Cleaning is usually performed using ultrasonic cleaning and/or vapor degreasing. Vapor honing may follow to improve adhesion. Mild acids or gases are used to remove oxide layers formed during heat-up. Posttreatment may include a heat treatment to facilitate diffusion of the coating material into the material.

The basic steps involved in any thermal coating process are substrate preparation, masking and fixturing, coating, finishing, inspection, and stripping (when necessary). Substrate preparation usually involves scale and oil and grease removal, as well as surface roughening. Roughening is necessary for most of the thermal spray processes to ensure adequate bonding of the coating to the substrate. The most common method is grit blasting, usually with alumina. Masking and fixturing limit the amount of coating applied to the workpiece to remove overspray through time-consuming grinding and stripping after deposition. The basic parameters in thermal spray deposition are particle temperature, velocity, angle of impact, and extent of reaction with gases during the deposition process. The geometry of the part being coated affects the surface coating because the specific properties vary from point to point on each piece. In many applications, workpieces must be finished after the deposition process, the most common technique being grinding followed by lapping. The final inspection of thermal spray coatings involves verification of dimensions, a visual examination for pits, cracks, and so forth. Nondestructive testing has largely proven unsuccessful.

There are three basic categories of thermal spray technologies: combustion torch (flame spray, high velocity oxy-fuel, and detonation gun), electric (wire) arc, and plasma arc. Thermal spray processes are maturing, and the technology is readily available.

Environmental concerns with thermal spraying techniques include the generation of dust, fumes, overspray, noise, and intense light. The metal spray process is usually performed in front of a “water curtain” or dry filter exhaust hood, which captures the overspray and fumes.

TABLE 9.5 Applications and Costs of the Main Advanced Techniques for Producing Metallic Coatings

Combustion torch/flame spraying
This technique can be used to deposit ferrous-, nickel-, and cobalt-based alloys and some ceramics. It is used in the repair of machine bearing surfaces, piston and shaft bearing or seal areas, and corrosion and wear resistance for boilers and structures (e.g., bridges).
Combustion torch/high velocity oxy-fuel (HVOF)
This technique may be an effective substitute for hard chromium plating for certain jet engine components. Typical applications include reclamation of worn parts and machine element buildup, abradable seals, and ceramic hard facings.
Combustion torch/detonation gun
This can only be used for a narrow range of materials, both for the choice of coating materials and as substrates. Oxides and carbides are commonly deposited. The high-velocity impact of materials such as tungsten carbide and chromium carbide restricts application to metal surfaces.
Electric arc spraying
Industrial applications include coating paper, plastics, and other heat-sensitive materials for the production of electromagnetic shielding devices and mold making.
Plasma spraying
This techniques can be used to deposit molybdenum and chromium on piston rings, cobalt alloys on jet-engine combustion chambers, tungsten carbide on blades of electric knives, and wear coatings for computer parts.
Ion plating/plasma based
Coating materials include alloys of titanium, aluminum, copper, gold, and palladium. Plasma-based ion plating is used in the production of x-ray tubes; space applications; threads for piping used in chemical environments; aircraft engine turbine blades; tool steel drill bits; gear teeth; high-tolerance injection molds; aluminum vacuum sealing flanges; decorative coatings; corrosion protection in nuclear reactors; metallizing of semiconductors, ferrites, glass, and ceramics; and body implants. In addition, it is widely used for applying corrosion-resistant aluminum coatings as an alternative to cadmium. Capital costs are high for this technology, creating the biggest barrier for ion plating use. It is used where high value-added equipment is being coated such as expensive injection molds instead of inexpensive drill bits.
Ion plating/ion beam enhanced deposition (IBED)
Although still an emerging technology, IBED is used for depositing dense optically transparent coatings for specialized optical applications, such as infrared optics. Capital costs are high for this technology, creating the biggest barrier for ion plating use. Equipment for IBED processing could be improved by the development of low-cost, high-current, large-area reactive ion beam sources.
Ion implantation
Nitrogen is commonly implanted to increase the wear resistance of metals because ion beams are produced easily. In addition, metallic elements, such as titanium, yttrium, chromium, and nickel, may be implanted into a variety of materials to produce a wider

TABLE 9.5 Applications and Costs of the Main Advanced Techniques for Producing Metallic Coatings (*Continued*)

range of surface modifications. Implantation is primarily used as an antiwear treatment for components of high value such as biomedical devices (prostheses), tools (molds, dies, punches, cutting tools, inserts), and gears and ball bearings used in the aerospace industry. Other industrial applications include the semiconductor industry for depositing gold, ceramics, and other materials into plastic, ceramic, and silicon and gallium arsenide substrates. The U.S. Navy has demonstrated that chromium ion implantation could increase the life of ball bearings for jet engines with a benefit-to-cost ratio of 20:1. A treated forming die resulted in the production of nearly 5000 automobile parts compared to the normal 2000 part life from a similar tool hard faced with tank plated chromium. The initial capital cost is relatively high, although large-scale systems have proven cost effective. An analysis of six systems manufactured by three companies found that coating costs range from \$0.04 to \$0.28/cm^2. Depending on throughput, capital cost ranges from \$400,000 to \$1,400,000, and operating costs were estimated to range from \$125,000 to \$250,000.

Sputtering and sputter deposition

Sputter-deposited films are routinely used simply as decorative coatings on watchbands, eyeglasses, and jewelry. The electronics industry relies heavily on sputtered coatings and films (e.g., thin film wiring on chips and recording heads, magnetic and magneto-optic recording media). Other current applications for the electronics industry are wear-resistant surfaces, corrosion-resistant layers, diffusion barriers, and adhesion layers. Sputtered coatings are also used to produce reflective films on large pieces of architectural glass and for the coating of decorative films on plastic in the automotive industry. The food packaging industry uses sputtering for coating thin plastic films for packaging pretzels, potato chips, and other products. Compared to other deposition processes, sputter deposition is relatively inexpensive.

Laser surface alloying

Although laser processing technologies have been in existence for many years, industrial applications are relatively limited. Uses of laser cladding include changing the surface composition to produce a required structure for better wear, or high-temperature performance; build up a worn part; provide better corrosion resistance; impart better mechanical properties; and enhance the appearance of metal parts. The high capital investment required for using laser cladding has been a barrier for its widespread adoption by industry.

Chemical vapor deposition (CVD)

CVD processes are used to deposit coatings and to form foils, powders, composite materials, free-standing bodies, spherical particles, filaments, and whiskers. CVD applications are expanding both in number and sophistication. The U.S. market in 1998 for CVD applications was \$1.2 billion, 77.6 percent of which was for electronics and other large users, including structural applications, optical, optoelectronics, photovoltaic, and chemical. Analysts anticipate that future growth for CVD technologies will continue to be in the area of electronics. CVD will also continue to be an important method for solving difficult materials problems. CVD processes are commercial realities for only a few materials and applications. Start-up costs are typically very expensive.

TABLE 9.6 Limits and Applicability of the Main Advanced Techniques for Producing Metallic Coatings

Combustion torch/flame spraying
Flame spraying is noted for its relatively high as-deposited porosity, significant oxidation of the metallic components, low resistance to impact or point loading, and limited thickness (typically 0.5 to 3.5 mm). Advantages include the low capital cost of the equipment, its simplicity, and the relative ease of training the operators. In addition, the technique uses materials efficiently and has low associated maintenance costs.
Combustion torch/high velocity oxy-fuel (HVOF)
This technique has very high velocity impact, and coatings exhibit little or no porosity. Deposition rates are relatively high, and the coatings have acceptable bond strength. Coating thickness range from 0.000013 to 3 mm. Some oxidation of metallics or reduction of some oxides may occur, altering the coating's properties.
Combustion torch/detonation gun
This technique produces some of the densest of the thermal coatings. Almost any metallic, ceramic, or cement materials that melt without decomposing can be used to produce a coating. Typical coating thickness range from 0.05 to 0.5 mm, but both thinner and thicker coatings are used. Because of the high velocities, the properties of the coatings are much less sensitive to the angle of deposition than most other thermal spray coatings.
Electric arc spraying
Coating thickness can range from a few hundredths of a millimeter to almost unlimited thickness, depending on the end use. Electric arc spraying can be used for simple metallic coatings, such as copper and zinc, and for some ferrous alloys. The coatings have high porosity and low bond strength.
Plasma spraying
Plasma spraying can be used to achieve thickness from 0.3 to 6 mm, depending on the coating and the substrate materials. Sprayed materials include aluminum, zinc, copper alloys, tin, molybdenum, some steels, and numerous ceramic materials. With proper process controls, this technique can produce coatings with a wide range of selected physical properties, such as coatings with porosity ranging from essentially zero to high porosity.
Ion plating/plasma based
This technique produces coatings that typically range from 0.008 to 0.025 mm. Advantages include a wide variety of processes as sources of the depositing material; in situ cleaning of the substrate prior to film deposition; excellent surface covering ability; good adhesion; flexibility in tailoring film properties such as morphology, density, and residual film stress; and equipment requirements and costs equivalent to sputter deposition. Disadvantages include many processing parameters that must be controlled; contamination may be released and activated in the plasma; and bombarding gas species may be incorporated in the substrate and coating.
Ion plating/ion beam enhanced deposition (IBED)
Advantages include increased adhesion; increased coating density; decreased coating porosity and prevalence of pinholes; and increased control of internal stress, morphology, density, and composition. Disadvantages include high equipment and

TABLE 9.6 Limits and Applicability of the Main Advanced Techniques for Producing Metallic Coatings (*Continued*)

processing costs; limited coating thickness; part geometry and size limit; and gas precursors used for some implantation species that are toxic. This technique can produce a chromium deposit 10 μm thick with greater thickness attained by layering. Such thickness is too thin for most hard chrome requirements (25 to 75 μm with some dimensional restoration work requiring 750 μm) and layering would significantly add to the cost of the process. IBED provides some surface cleaning when the surface is initially illuminated with a flux of high-energy inert gas ions; however, the process will still require precleaning (e.g., degreasing).

Ion implantation

Ion implantation can be used for any element that can be vaporized and ionized in a vacuum chamber. Because material is added to the surface, rather than onto the surface, there is no significant dimensional change or problems with adhesion. The process is easily controlled, offers high reliability and reproducibility, requires no posttreatment, and generates minimal waste. If exposed to high temperatures, however, implanted ions may diffuse away from the surface due to limited depth of penetration, and penetration does not always withstand severe abrasive wear. Implantation is used to alter surface properties, such as hardness, friction, wear resistance, conductance, optical properties, corrosion resistance, and catalysis. Commercial availability is limited by general unfamiliarity with the technology, scarcity of equipment, lack of quality control and assurance, and competition with other surface modification techniques. Areas of research include ion implantation of ceramic materials for high-temperature internal combustion engines, glass to reduce infrared radiation transmission and reduce corrosion, as well as automotive parts (piston rings, cylinder liners) to reduce wear.

Sputtering and sputter deposition

This technique is a versatile process for depositing coatings of metals, alloys, compounds, and dielectrics on surfaces. The process has been applied in hard and protective industrial coatings. Primarily TiN, as well as other nitrides and carbides, has demonstrated high hardness, low porosity, good chemical inertness, good conductivity, and attractive appearance. Sputtering is capable of producing dense films, often with near-bulk quantities. Areas requiring future research and development include better methods for in situ process control; methods for removing deposited TiN and other hard, ceramiclike coatings from poorly coated or worn components without damage to the product; and improved understanding of the factors that affect film properties.

Laser surface alloying

This technique can be used to apply most of the same materials that can be applied via thermal spray techniques; the powders used for both methods are generally the same. Materials that are easily oxidized, however, will prove difficult to deposit without recourse to inert gas streams and envelopes. Deposition rates depend on laser power, powder feed rates, and traverse speed. The rates are typically in the region of 2×10^{-4} cm^3 for a 500-W beam. Thickness of several hundred micrometers can be laid down on each pass of the laser beam, allowing thickness of several millimeters to accumulate. If the powder density is too high, this thermal cycling causes cracking and delamination of earlier layers, severely limiting the attainable buildup. Research has found that easily oxidized materials, such as aluminum, cannot be laser clad because the brittle oxide causes cracking and delamination. Some steels may be difficult to coat effectively.

TABLE 9.6 Limits and Applicability of the Main Advanced Techniques for Producing Metallic Coatings (*Continued*)

The small size of the laser's beam limits the size of the workpieces that can be treated cost effectively. Shapes are restricted to those that prevent line-of-sight access to the region to be coated.
Chemical vapor deposition (CVD)
CVD is used mainly for corrosion and wear resistance. CVD processes are also usually applied in cases where specific properties of materials of interest are difficult to obtain by other means. CVD is unique because it controls the microstructure and/or chemistry of the deposited material. The microstructure of CVD deposits depends on chemical makeup and energy of atoms, ions, or molecular fragments impinging on the substrate; chemical composition and surface properties of the substrate; substrate temperature; and presence or absence of a substrate bias voltage. The most useful CVD coatings are nickel, tungsten, chromium, and titanium carbide. Titanium carbide is used for coating punching and embossing tools to impart wear resistance.

Water curtain systems periodically discharge contaminated wastewaters. Noise generated can vary from approximately 80 dB to more than 140 dB. With the higher noise-level processes, robotics are usually required for spray application. The use of metal spray processes may eliminate some of the pollution associated with conventional tank plating. In most cases, however, wet processes, such as cleaning, are necessary in addition to the metal coating process. Therefore, complete elimination of tanks may not be possible. Waste streams resulting from flame spray techniques may include overspray, wastewaters, spent exhaust filters, rejected parts, spent gas cylinders, air emissions (dust, fumes), and wastes associated with the grinding and finishing phases.

Physical vapor deposition. Vapor deposition refers to any process in which materials in a vapor state are condensed through condensation, chemical reaction, or conversion to form a solid material. These processes are used to form coatings to alter the mechanical, electrical, thermal, optical, corrosion-resistance, and wear properties of the substrates. They are also used to form free-standing bodies, films, and fibers and to infiltrate fabric to form composite materials.[5] Vapor deposition processes usually take place within a vacuum chamber.

There are two categories of vapor deposition processes: physical vapor deposition (PVD) and chemical vapor deposition (CVD). In PVD processes, the workpiece is subjected to plasma bombardment. In CVD processes, thermal energy heats the gases in the coating chamber and drives the deposition reaction.

Physical vapor deposition methods are clean, dry vacuum deposition methods in which the coating is deposited over the entire object

simultaneously, rather than in localized areas. All reactive PVD hard coating processes combine:

- A method for depositing the metal
- Combination with an active gas, such as nitrogen, oxygen, or methane
- Plasma bombardment of the substrate to ensure a dense, hard coating[6]

PVD methods differ in the means for producing the metal vapor and the details of plasma creation. The primary PVD methods are ion plating, ion implantation, sputtering, and laser surface alloying.

Waste streams resulting from laser cladding are similar to those resulting from high-velocity oxy-fuels and other physical deposition techniques: blasting media and solvents, bounce and overspray particles, and grinding particles. Generally speaking, none of these waste streams are toxic.[6]

CVD is a subset of the general surface treatment process, vapor deposition. Over time, the distinction between the terms *physical vapor deposition* and *chemical vapor deposition* has blurred as new technologies have been developed and the two terms overlap. CVD includes sputtering, ion plating, plasma-enhanced chemical vapor deposition, low-pressure chemical vapor deposition, laser-enhanced chemical vapor deposition, active-reactive evaporation, ion beam, laser evaporation, and many other variations. These variants are distinguished by the manner in which precursor gases are converted into the reactive gas mixtures. In CVD processes, a reactant gas mixture impinges on the substrate upon which the deposit is to be made. Gas precursors are heated to form a reactive gas mixture. The coating species is delivered by a precursor material, otherwise known as a reactive vapor. It is usually in the form of a metal halide, metal carbonyl, a hydride, or an organometallic compound. The precursor may be in gas, liquid, or solid form. Gases are delivered to the chamber under normal temperatures and pressures, whereas solids and liquids require high temperatures and/or low pressures in conjunction with a carrier gas. Once in the chamber, energy is applied to the substrate to facilitate the reaction of the precursor material upon impact. The ligand species is liberated from the metal species to be deposited upon the substrate to form the coating. Because most CVD reactions are endothermic, the reaction may be controlled by regulating the amount of energy input.[7] The steps in the generic CVD process are

- Formation of the reactive gas mixture
- Mass transport of the reactant gases through a boundary layer to the substrate

- Adsorption of the reactants on the substrate
- Reaction of the adsorbents to form the deposit
- Description of the gaseous decomposition products of the deposition process

The precursor chemicals should be selected with care because potentially hazardous or toxic vapors may result. The exhaust system should be designed to handle any reacted and unreacted vapors that remain after the coating process is complete. Other waste effluents from the process must be managed appropriately. Retrieval, recycle, and disposal methods are dictated by the nature of the chemical. For example, auxiliary chemical reactions must be performed to render toxic or corrosive materials harmless, condensates must be collected, and flammable materials must be either combusted, absorbed, or dissolved. The extent of these efforts is determined by the efficiency of the process.[7]

9.2.2 Inorganic coatings

Inorganic coatings can be produced by chemical action, with or without electrical assistance. The treatments change the immediate surface layer of metal into a film of metallic oxide or compound that has better corrosion resistance than the natural oxide film and provides an effective base or key for supplementary protection such as paints. In some instances, these treatments can also be a preparatory step prior to painting.

Anodizing. Anodizing involves the electrolytic oxidation of a surface to produce a tightly adherent oxide scale that is thicker than the naturally occurring film. Anodizing is an electrochemical process during which aluminum is the anode. The electric current passing through an electrolyte converts the metal surface to a durable aluminum oxide. The difference between plating and anodizing is that the oxide coating is integral with the metal substrate as opposed to being a metallic coating deposition. The oxidized surface is hard and abrasion resistant, and it provides some degree of corrosion resistance.

However, anodizing cannot be relied upon to provide corrosion resistance to corrosion-prone alloys, and further protection by painting is usually required. Fortunately the anodic coating provides an excellent surface both for painting and for adhesive bonding. Anodic coatings break down chemically in highly alkaline solutions (pH $>$ 8.5) and highly acid solutions (pH $<$4.0). They are also relatively brittle and may crack under stress, and therefore supplementary protection, such as painting, is particularly important with stress corrosion-prone alloys.

Anodic coatings can be formed in chromic, sulfuric, phosphoric, or oxalic acid solutions. Chromic acid anodizing is widely used with 7000 series alloys to improve corrosion resistance and paint adhesion, and unsealed coatings provide a good base for structural adhesives. However these coatings are often discolored, and where cosmetic appearance is important, sulfuric acid anodizing may be preferred. Table 9.7 shows the alloys suitable for anodizing and describes some of the coating properties obtained with typical usage and finishing advice.

The Al_2O_3 coating produced by anodizing is typically 2 to 25 μm thick and consists of a thin nonporous barrier layer next to the metal

TABLE 9.7 Aluminum Alloys Suitable for Anodizing

Series	Coating properties	Uses	Finishing advice
1*xxx*	Clear bright	Cans, architectural	Care should be taken when racking this soft material; good for bright coatings susceptible to etch, staining.
2*xxx*	Yellow poor protection	Aircraft mechanical	Because copper content is >2%, these produce yellow, poor weather-resistant coatings.
3*xxx*	Grayish-brown	Cans, architectural, lighting	Difficult to match sheet to sheet (varying degrees of gray/brown). Used extensively for architectural painted products
4*xxx*	Dark gray	Architectural, lighting	Produces heavy black smut, which is hard to remove; 4043 and 4343 used for architectural dark gray finishes in past years.
5*xxx*	Clear good protection	Architectural, welding, wire lighting	For 5005, keep silicon < 0.1% and magnesium between 0.7 and 0.9%; maximum of ±20% for job; watch for oxide streaks
6*xxx*	Clear good protection	Architectural, structural	Matte: iron > 0.2%. Bright: iron < 0.1%. 6063 best match for 5005. 6463 best for chemical brightening.
7*xxx*	Clear good protection	Automotive	Zinc over 5% will produce brown-tinted coatings; watch zinc in effluent stream; good for bright coatings.

SOURCE: Aluminum Anodizers Council (AAC) Technical Bulletin 2-94, *Aluminum Alloy Reference for Anodizing,* March 1994.

with a porous outer layer that can be sealed by hydrothermal treatment in steam or hot water for several minutes. This produces a hydrated oxide layer with improved protective properties. Figure 9.1 illustrates a porous anodic film and its evolution during the sealing process. Improved corrosion resistance is obtained if the sealing is done in a hot metal salt solution such as a chromate or dichromate solution. The oxide coatings may also be dyed to provide surface coloration for decorative purposes, and this can be performed either in the anodizing bath or afterward. International standards for anodic treatment of aluminum alloys have been published by the International Standards Organization and cover dyed and undyed coatings. There are many reasons to anodize a part. Following are a few considerations and the industries that employ them

- *Appearance.* Products look finished, cleaner, and better, and this appearance lasts longer. Color enhances metal and promotes a solid, well-built appearance while removing the harsh metal look. Any aluminum product can be color anodized.
- *Corrosion resistance.* A smooth surface is retained and weathering is retarded. Useful for food handling and marine products.
- *Ease in cleaning.* Any anodized product will stay cleaner longer and is easier to clean when it does get dirty.
- *Abrasion resistance.* The treated metal is tough, harder than many abrasives, and is ideal for caul plates, tooling, and air cylinder applications.
- *Nongalling.* Screws and other moving parts will not seize, drag, or jam, and wear in these areas is diminished. Gun sights, instruments, and screw threads are typical applications.
- *Heat absorption.* This can provide uniform or selective heat-absorption properties to aluminum for the food processing industry.
- *Heat radiation.* This is used as a method to finish electronic heat sinks and radiators. Further, anodizing will not rub off, is an excellent paint base, removes minor scuffs, and is sanitary and tasteless.

There are many variations in the anodization process. The following examples are given to illustrate some of the processes used in the industry:

1. *Hardcoat anodizing.* As the name implies, a hardcoat finish is tough and durable and is used where abrasion and corrosion resistance, as well as surface hardness, are critical factors. Essentially, hardcoating is a sulfuric acid anodizing process, with the electrolyte concentration, temperature, and electric current parameters altered to

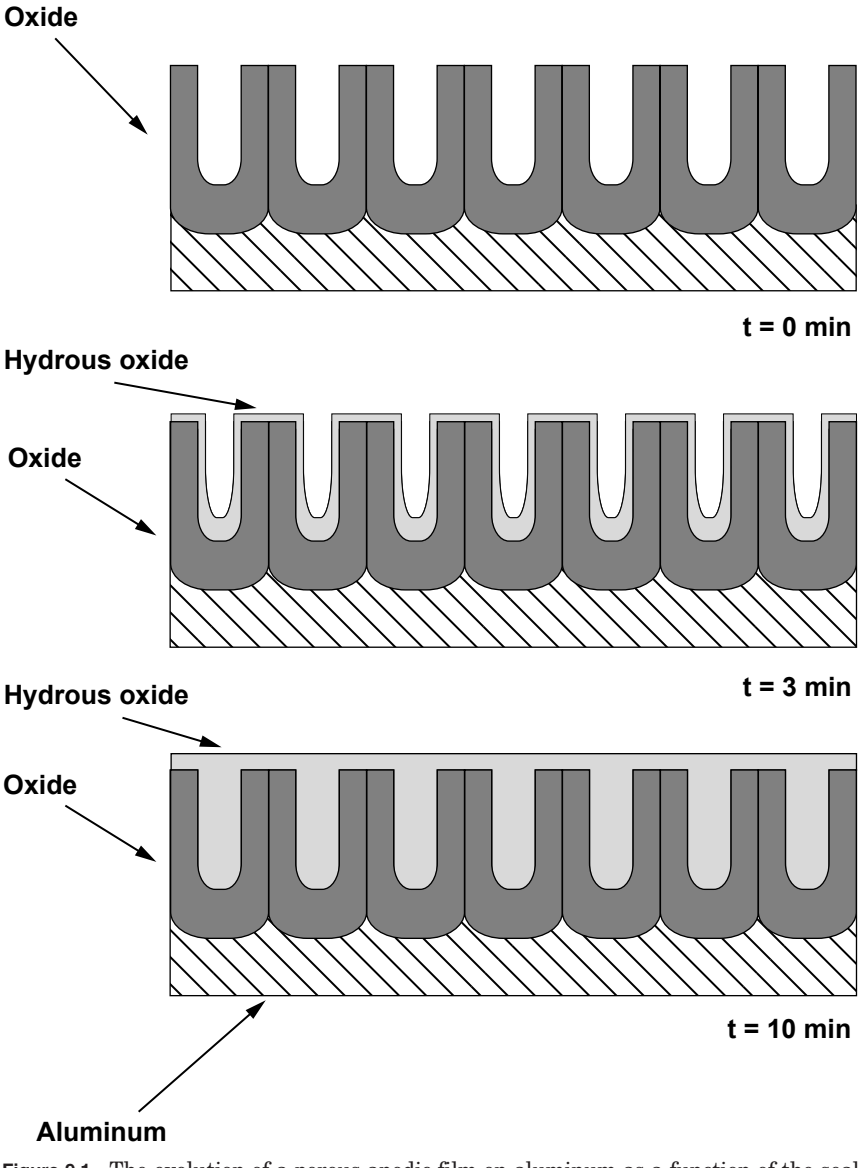


Figure 9.1 The evolution of a porous anodic film on aluminum as a function of the sealing time at 85°C.

produce the hardened surface. Wearing qualities have actually proven to be superior to those of case hardened steel or hard chrome plate.

2. *Bulk anodizing.* Bulk anodizing is an electrochemical process for anodizing small, irregularly shaped parts, which are processed in perforated aluminum, plastic, or titanium baskets. The tremendous

quantity of parts that can be finished in a relatively short time makes this technique highly economical. Another advantage in processing such large volumes at one time is the resulting consistency in color and quality. Finishing items such as rivets, ferrules, medical hubs, and so forth, using the bulk process make production economically feasible.

3. *Sulfuric acid anodizing.* This is the most common method of anodizing. The part is subjected to a specified electric current through a sulfuric acid electrolyte, converting the surface to an aluminum oxide coating capable of absorbing dyes in a wide range of colors. Abrasion and/or corrosion resistance is enhanced, and the surface may also be used as a base for applied coatings, such as paint, Teflon, and adhesives. Custom coloring is available to meet any specification, and through prefinish techniques, matte, satin, or highly reflective surfaces can be furnished.

Anodizing treatments are also available for magnesium and titanium alloys. The treatments commonly used with magnesium alloys involve several processing options to produce either thin coatings of about 5-μm thickness for flexibility and surfaces suitable for paint adhesion, or thick coatings, up to about 30 μm for maximum corrosion and abrasion resistance. When anodizing is used for the treatment of titanium and titanium alloys, it can provide limited protection to the less noble metals against galvanic corrosion, and when used together with solid film lubricants, it helps to prevent galling. The process produces a smooth coating with a uniform texture and appearance and a uniform blue-to-violet color.

Chromate filming. A number of proprietary chromate filming treatments are available for aluminum, magnesium, cadmium, and zinc alloys. The treatments usually involve short-time immersion in strongly acid chromate solutions, but spraying or application by brushing or swabbing can also be used for touchup of parts. The resulting films are usually about 5 μm thick and are colored depending on the base alloy, being golden yellow on aluminum, dull gold on cadmium and zinc, and brown or black on magnesium. The films contain soluble chromates that act as corrosion inhibitors, and they provide a modest improvement in corrosion resistance of the base metal. However, their main purpose is to provide a suitable surface for sealing resins or paints. Epoxy primer, for example, which does not adhere well to bare aluminum, adheres very well to chemical conversion coatings. Among the best-known coatings used with aluminum alloys are those produced by the Alodine 1200 and Alocrom 1200 processes.

A process for zinc alloys has been described to consist of immersion for a few seconds in a sodium dichromate solution at a concentration

of 200 g/L and acidified with sulfuric acid at 8 ml/L. The treatment is performed at room temperature and is followed by rinsing and drying to produce a dull yellow zinc chromate coating.

Phosphate coatings. A number of proprietary treatments such as Parkerizing and Bonderizing are available for use on steel. They are applied by brushing, spraying, or prolonged immersion in an acid orthophosphate solution containing iron, zinc, or manganese. For example a solution might contain $Zn(H_2PO_4)_2 \cdot 2H_2O$ with added H_3PO_4. The coatings consist of a thick porous layer of fine phosphate crystals, tightly bonded to the steel. The coatings do not provide significant corrosion resistance when used alone, but they provide an excellent base for oils, waxes, or paints, and they help to prevent the spreading of rust under layers of paint. Phosphating should not be applied to nitrided or finish-machined steel, and steel parts containing aluminum, magnesium, or zinc are subject to pitting in the bath. Some restrictions apply also to heat-treated stainless and high-strength steels.

Nitriding. Steels containing nitride-forming elements such as chromium, molybdenum, aluminum, and vanadium can be treated to produce hard surface layers, providing improved wear resistance. Many of the processes employed are proprietary, but typically they involve exposure of cleaned surfaces to anhydrous ammonia at elevated temperatures. The nitrides formed are not only hard but also more voluminous than the original steel, and therefore they create compressive residual surface stresses. Therefore, nitrided steels usually exhibit improved fatigue and corrosion fatigue resistance. Similar beneficial effects can be achieved by shot peening.

Passive films. Austenitic stainless steels and hardenable stainless steels such as martensitic, precipitation hardening, and maraging stainless steels are seldom coated, but their corrosion resistance depends on the formation of naturally occurring transparent oxide films. These films may be impaired by surface contaminants such as organic compounds or metallic or inorganic materials. Treatments are available for these materials to clean and degrease surfaces and produce uniform protective oxide films under controlled conditions. These usually involve immersion in an aqueous solution of nitric acid and a dichromate solution.

9.2.3 Organic coatings

Paints, coatings, and high-performance organic coatings were developed to protect equipment from environmental damage. Of prime importance in the development of protective coatings was the petroleum industry,

which produced most of the basic ingredients from which most synthetic resins were developed. The cracking of petroleum produced a multitude of unsaturated workable compounds that are important in the building of large resin polymers such as vinyls and acrylics. The solvents necessary for the solution of the resins were also derived from petroleum or natural gas. The building blocks for epoxies and modern polyurethane coatings are other derivatives produced by refining petroleum products.[8]

The Steel Structures Painting Council (SSPC) is the world's acknowledged resource and authority for protective coatings technology. SSPC's mission is to advance the technology and promote the use of protective coatings to preserve industrial marine and commercial structure components and substrates. Table 9.8 describes briefly most of the numerous standards and guides currently maintained by SSPC.

Some other concepts important for designing corrosion-resistant coatings include those of coating protection, component design, component function, and coating formulation. Many coatings contain as many as 15 to 20 ingredients with their own range of functionality. Some of the main variables used to design corrosion protective coatings are

- *Impermeability.* The ideal impermeable coating should be completely unaffected by the specific environment it is designed to block, be it most commonly humidity, water, or any other corrosive agent such as gases, ions, or electrons. This ideal impermeable coating should have a high dielectric constant and also have perfect adhesion to the underlying surface to avoid any entrapment of corrosive agents. Good impermeability has been the successful ingredient of many anticorrosion coatings.
- *Inhibition.* In contrast with coatings developed on the basis of impermeability, inhibitive coatings function by reacting with a certain environment to provide a protective film or barrier on the metallic surface. The concept of adding an inhibitor to a primer has been applied to coatings of steel vessels since these vessels were first constructed. Such coatings were originally oil based and heavily loaded with red lead.
- *Cathodically protective pigments.* As with inhibition, cathodic protection in coatings is mostly provided by additives in the primer. The main function of these additives is to shift the potential of the environment to a less-corrosive cathodic potential. Inorganic zinc-based primers are good examples of this concept.

The coating system approach. For serious corrosion situations, the coating system approach (primer, intermediate coat, and topcoat) provides all the ingredients for a long-lasting solution.[8]

TABLE 9.8 Reference, Purpose, and Brief Description of Painting Standards and Specifications

Guide to SSPC-VIS 1-89: Visual Standard for Abrasive Blast Cleaned Steel (Standard Reference Photographs)
This guide describes the use of standard reference photographs depicting the appearance of previously unpainted hot-rolled carbon steel prior to and after abrasive blast cleaning. These photographs are intended to be used to supplement the written SSPC blast cleaning surface preparation specifications. Because the written specifications are the primary means to determine conformance with blast cleaning requirements, the photographs shall not be used as a substitute for these specifications.
Guide to Visual Standard No. 2: Guide to Standard Method of Evaluating Degree of Rusting on Painted Steel Surfaces
This guide describes only the pictorial standard and does not constitute the standard. It is to be used for comparative purposes and is not intended to have a direct relationship to a decision regarding painting requirements.
Guide to SSPC-VIS 3: Visual Standard for Power-and Hand-Tool Cleaned Steel (Standard Reference Photographs)
This guide describes the use of standard reference photographs depicting the appearance of unpainted, painted, and welded hot-rolled carbon steel prior to and after power and hand tool cleaning. These photographs are intended to be used to supplement the written SSPC power and hand tool surface preparation specifications. Because the written specifications are the primary means to determine conformance with cleaning requirements, the photographs shall not be used as a substitute for the written specifications.
Surface Preparation Specification No. 1 (SSPC-SP 1): Solvent Cleaning
This specification covers the requirements for the solvent cleaning of steel surfaces—removal of all detrimental foreign matter such as oil, grease, dirt, soil, salts, drawing and cutting compounds, and other contaminants from steel surfaces by the use of solvents, emulsions, cleaning compounds, steam, or other similar materials and methods that involve a solvent or cleaning action.
Surface Preparation Specification No. 2 (SSPC-SP 2): Hand Tool Cleaning
This specification covers the requirements for the hand tool cleaning of steel surfaces—removal of all rust scale, mill scale, loose rust, and loose paint to the degree specified by hand wire brushing, hand sanding, hand scraping, hand chipping, or other hand impact tools or by a combination of these methods. The substrate should have a faint metallic sheen and also be free of oil, grease, dust, soil, salts, and other contaminants.
Surface Preparation Specification No. 3 (SSPC-SP3): Power Tool Cleaning
This specification covers the requirements for the power tool cleaning of steel surfaces—removal of all rust scale, mill scale, loose paint, and loose rust to the degree specified by power wire brushes, power impact tools, power grinders, power sanders, or by a combination of these methods. The substrate should have a pronounced metallic sheen and also be free of oil, grease, dirt, soil, salts, and other contaminants. Surface should not be buffed or polished smooth.

TABLE 9.8 Reference, Purpose, and Brief Description of Painting Standards and Specifications (*Continued*)

Joint Surface Preparation Standard (SSPC-SP 5/NACE No. 1): White Metal Blast Cleaning
This standard covers the requirements for white metal blast cleaning of steel surfaces by the use of abrasives—removal of all mill scale, rust, rust scale, paint, or foreign matter by the use of abrasives propelled through nozzles or by centrifugal wheels. A white metal blast cleaned surface finish is defined as a surface with a gray-white, uniform metallic color, slightly roughened to form a suitable anchor pattern for coatings. The surface, when viewed without magnification, shall be free of all oil, grease, dirt, visible mill scale, rust, corrosion products, oxides, paint, and any other foreign matter.
Joint Surface Preparation Standard (SSPC-SP 6/NACE No. 3): Commercial Blast Cleaning
This standard covers the requirements for commercial blast cleaning of steel surfaces by the use of abrasives—removal of mill scale, rust, rust scale, paint, and foreign matter by the use of abrasives propelled through nozzles or by centrifugal wheels, to the degree specified. A commercial blast cleaned surface finish is defined as one from which all oil, grease, dirt, rust scale, and foreign matter have been completely removed from the surface and all rust, mill scale, and old paint have been completely removed except for slight shadows, streaks, or discolorations caused by rust stain, mill scale oxides, or slight, tight residues of paint or coating that may remain; if the surface is pitted, slight residues of rust or paint may by found in the bottom of pits; at least two-thirds of each square inch of surface area shall be free of all visible residues and the remainder shall be limited to the light discoloration, slight staining, or tight residues mentioned above.
Joint Surface Preparation Standard (SSPC-SP 7/NACE No. 4): Brush-Off Blast Cleaning
This standard covers the requirements for brush-off blast cleaning of steel surfaces by the use of abrasives—removal of loose mill scale, loose rust, and loose paint, to the degree hereafter specified, by the impact of abrasives propelled through nozzles or by centrifugal wheels. It is not intended that the surface shall be free of all mill scale, rust, and paint. The remaining mill scale, rust, and paint should be tight and the surface should be sufficiently abraded to provide good adhesion and bonding of paint. A brush-off blast cleaned surface finish is defined as one from which all oil, grease, dirt, rust scale, loose mill scale, loose rust, and loose paint or coatings are removed completely, but tight mill scale and tightly adhered rust, paint, and coatings are permitted to remain provided that all mill scale and rust have been exposed to the abrasive blast pattern sufficiently to expose numerous flecks of the underlying metal fairly uniformly distributed over the entire surface.
Surface Preparation Specification No. 8 (SSPC-SP 8): Pickling
This specification covers the requirements for the pickling of steel surfaces—removal of all mill scale, rust, and rust scale by chemical reaction, or by electrolysis, or by both. It is intended that the pickled surface shall be completely free of all scale, rust, and foreign matter. Furthermore, the surface shall be free of unreacted or harmful acid or alkali or smut.
Joint Surface Preparation Standard (SSPC-SP 10/NACE No. 2): Near-White Blast Cleaning
This standard covers the requirements for near-white metal blast cleaning of steel surfaces by the use of abrasives—removal of nearly all mill scale, rust, rust scale, paint,

TABLE 9.8 Reference, Purpose, and Brief Description of Painting Standards and Specifications (*Continued*)

or foreign matter by the use of abrasives propelled through nozzles or by centrifugal wheels, to the degree hereafter specified. A near-white blast cleaned surface finish is defined as one from which all oil, grease, dirt, mill scale, rust, corrosion products, oxides, paint, and other foreign matter have been completely removed from the surface except for very light shadows, very slight streaks or slight discolorations caused by rust stain, mill scale oxides, or light, tight residues of paint or coating that may remain. At least 95 percent of each square inch of surface area shall be free of all visible residues, and the remainder shall be limited to the light discoloration mentioned above.
Surface Preparation Specification No. 11 (SSPC-SP 11): Power Tool Cleaning to Bare Metal
This specification covers the requirements for the power tool cleaning to produce a bare metal surface and to retain or produce a surface profile. This specification is suitable where a roughened, clean, bare metal surface is required, but where abrasive blasting is not feasible or permissible.
Joint Surface Preparation Standard (SSPC-SP 12/NACE No. 5): Surface Preparation and Cleaning of Steel and Other Hard Materials by High- and Ultrahigh-Pressure Water Jetting Prior to Recoating
This standard provides requirements for the use of high- and ultrahigh-pressure water jetting to achieve various degrees of surface cleanliness. This standard is limited in scope to the use of water only without the addition of solid particles in the stream.
Abrasive Specification No. 1 (SSPC-AB 1): Mineral and Slag Abrasives
This specification defines the requirements for selecting and evaluating mineral and slag abrasives used for blast cleaning steel and other surfaces for painting and other purposes.
Abrasive Specification No. 2 (SSPC-AB 2): Specification for Cleanliness of Recycled Ferrous Metallic Abrasives
This specification covers the requirements for cleanliness of recycled ferrous metallic blast cleaning abrasives used for the removal of coatings, paints, scales, rust, and other foreign matter from steel or other surfaces. Requirements are given for lab and field testing of recycled ferrous metallic abrasives work mix. Recycled ferrous metallic abrasives are intended for use in field or shop abrasive blast cleaning of steel or other surfaces.
Thermal Precleaning (NACE 6G194/SSPC-SP-TR 1): Specifications for Thermal Precleaning
This state-of-the-art report addresses the use of thermal precleaning for tanks, vessels, rail tank cars and hopper cars, and process equipment, when preparing surfaces for the application of high-performance or high-bake coating and lining systems.
Painting System Guide No. 1.00: Guide for Selecting Oil Base Painting Systems
These specifications cover oil base painting systems for steel cleaned with hand or power tools.

TABLE 9.8 Reference, Purpose, and Brief Description of Painting Standards and Specifications (*Continued*)

Painting System Specification No. 1.04: Three-Coat Oil-Alkyd (Lead- and Chromate-Free) Painting System for Galvanized or Non-Galvanized Steel (with Zinc Dust-Zinc Oxide Linseed Oil Primer)
This specification covers an oil-base, lead- and chromate-free painting system for new or weathered (white or red rusted) galvanized steel. It is also effective on nongalvanized steel cleaned with hand or power tools. This system is suitable for use on parts or structures exposed in Environmental Zone 1A (interior, normally dry) and Zone 1B (exterior, normally dry). The finish paint allows for a choice of durable, fade-resistant colors.
Painting System Specification No. 1.09: Three-Coat Oil Base Zinc Oxide Painting System (without Lead or Chromate Pigment)
This specification covers an oil-base, lead- and chromate-free painting system for steel cleaned with hand or power tools. This system is suitable for use on parts or structures exposed in Environmental Zones 1A (interior, normally dry) and 1B (exterior, normally dry). The finish paint allows for a choice of durable, fade-resistant colors.
Painting System Specification No. 1.10: Four-Coat Oil Base Zinc Oxide Paintin System (without Lead or Chromate Pigment)
This specification covers an oil-base, lead- and chromate-free painting system for steel cleaned with hand or power tools. This system is suitable for use on parts or structures exposed in Environmental Zones 1A (interior, normally dry) and 1B (exterior, normally dry). The finish paint allows for a choice of durable, fade-resistant colors.
Painting System Specification No. 1.12: Three-Coat Oil Base Zinc Chromate Painting System
This specification covers an oil-base, zinc-chromate painting system for steel cleaned with hand or power tools. This system is suitable for use on parts or structures exposed in Environmental Zones 1A (interior, normally dry) and 1B (exterior, normally dry). The finish paint allows for a choice of durable, fade-resistant colors.
Painting System Specification No. 1.13: One-Coat Oil Base Slow Drying Maintenance Painting System (without Lead or Chromate Pigments)
This specification covers a one-coat oil-base, lead- and chromate-free painting system for steel cleaned with hand or power tools. This system is suitable for use on parts or structures exposed in Environmental Zones 1A (interior, normally dry) and 1B (exterior, normally dry). This system is never used as a shopcoat because of its very long drying time. It is unsuitable for use where the slow drying, slippery paint film would be dangerous to workers when walking or climbing on painted surfaces.
Painting System Specification No. 2.00: Guide for Selecting Alkyd Painting Systems
These specifications cover alkyd painting systems for commercial blast cleaned or pickled steel. These systems are suitable for use on parts or structures exposed in Environmental Zones 1A (interior, normally dry) and 1B (exterior, normally dry). The color of the finish paint must be specified.

TABLE 9.8 Reference, Purpose, and Brief Description of Painting Standards and Specifications (*Continued*)

Painting System Specification No. 2.05: Three-Coat Alkyd Painting System for Unrusted Galvanized Steel (for Weather Exposure)
This specification covers an alkyd painting system for new, unrusted, untreated, galvanized steel. This system is suitable for use on parts or structures exposed in Environmental Zones 1A (interior, normally dry) and 1B (exterior, normally dry). The primer has good adhesion to clean galvanized steel but does not adhere properly to rusted galvanized steel. Painting System No. 1.04 should be specified for this condition. The finish paint allows for a choice of durable, fade-resistant colors.
Painting System Specification No. 3.00: Guide for Selecting Phenolic Painting Systems
These specifications cover phenolic painting systems for blast cleaned steel. These systems are suitable for use on parts or structures exposed in Environmental Zones 1A (interior, normally dry), and 1B (exterior, normally dry), and 2A (frequently wet by fresh water). Phenolic paints will normally dry in about 12 h. For optimum intercoat adhesion recoating should take place in less than 24 h. The color of the finish paint must be specified.
Painting System Specification No. 4.00: Guide for Selecting Vinyl Painting Systems
The guide covers vinyl painting system for blast cleaned or pickled steel. These systems are suitable for use on parts or structures exposed in Environmental Zones 1A (interior, normally dry), 2A (frequently wet by fresh water), 2B (frequently wet by salt water), 2C (fresh water immersion), 2D (salt water immersion), 3A (chemical, acidic), and 3B (chemical neutral). The color of the finish paint must be specified.
Painting System Specification No. 9.01: Cold-Applied Asphalt Mastic Painting System with Extra-Thick Film
This specification covers a cold-applied asphalt mastic painting system for above-ground steel structures. This system is suitable for use on parts or structures exposed in Environmental Zones 2A (frequently wet by fresh water), 2B (frequently wet by salt water), 3B (chemical, neutral), and 3C (chemical, alkaline). It should not be used in contact with oils, solvents, or other reagents which tend to soften or attack the coating.
Painting System Specification No. 10.01: Hot-Applied Coal Tar Enamel Painting System
This system is suitable for use on parts or structures exposed in Environmental Zones 2C (fresh water immersion), 3B (chemical, neutral), and 3C (chemical, alkaline). It has good abrasion resistance. It is also suitable for underground use. It must be used with discretion for immersion in corrosive chemicals because the coating is dissolved by some organic solvents and attacked by oxidating solutions. The coal tar enamel must be topcoated with coal tar emulsion when exposed to sunlight to prevent checking and alligatoring.
Painting System Specification No. 10.02: Cold-Applied Coal Tar Mastic Painting System
This specification covers a cold-applied coal tar painting system for underground and underwater steel structures, consisting of two cold-applied coats. This system is suitable for use on parts or structures exposed in Environmental Zones 2C (fresh water

TABLE 9.8 Reference, Purpose, and Brief Description of Painting Standards and Specifications (*Continued*)

immersion), 3B (chemical, neutral), and 3C (chemical, alkaline). It has fairly good abrasion resistance and is suitable for underground use. It must be used with discretion for immersion in corrosive chemicals because the coating is dissolved by some organic solvents and attacked by oxidating solutions. The coal tar mastic must be topcoated with coal tar emulsion when exposed to sunlight to prevent checking and alligatoring.

Painting System Specification No. 11.01: Black (or Dark Red) Coal Tar Epo Polyamide Painting System

This specification covers a complete coal tar epoxy-polyamide black (or dark red) painting system for the protection of steel surfaces that will be exposed to severely corrosive conditions. This system is suitable for use on parts or structures exposed in Environmental Zones 2A (frequently wet by fresh water), 2B (frequently wet by salt water), 2C (fresh water immersion), 2D (salt water immersion), 3A (chemical, acidic), 3B (chemical, neutral), and 3C (chemical, alkaline). Its resistance to chemical fumes, mists, and splashings is generally considered to be good, but its suitability for prolonged immersion in specific chemicals should be confirmed by trial tests in the absence of applicable case histories. It is also suitable for underground exposure and as a protective coating for sound concrete surfaces in marine and some chemical environments. Its good weathering properties can be improved by applying a finish coat of a compatible aluminum pigmented paint. Although it is self-priming and exhibits good adhesion to clean structural steel surfaces, it may also be used over suitable inhibitive primers. The color of paint is black unless red is specified.

Painting System Guide No. 12.00: Guide to Zinc-Rich Coating Systems

This guide provides general information on the description, selection, and applications of zinc-rich coatings and the selection of top coats. Zinc-rich coatings are highly pigmented primer coatings that are uniquely defined by their capability of galvanically protecting steel exposed at discontinuities such as narrow scratches and holidays. Although the major pigment component in a zinc-rich coating is zinc dust, the vehicle may be inorganic or organic. Zinc-rich coatings are classified as follows: Type IA—Inorganic: postcured, water-borne, alkali-silicates; Type IB—Inorganic: self-cured, water-borne, alkali-silicates; Type IC—Inorganic: self-cured, solvent-borne, alkyl-silicates; Type IIA—Organic: thermoplastic binders; Type IIB—Organic: thermoset binders. Certain zinc-rich coating systems are suitable for use in protecting steel surfaces either topcoated or untopcoated. Zinc-rich systems are not suitable for certain exposure conditions.

Painting System Specification No. 12.01: One-Coat Zinc-Rich Painting System

This specification covers a one-coat zinc-rich painting system to be used on steel in mild-to-moderately severe environments. This system is suitable for use on parts or structures exposed in Environmental Zone 3B (chemical, neutral). It is not recommended for environments where corrosive contaminants will have a pH below 5 or above 9 or in severely corrosive environments. The system is recommended as a durable shop primer or as a protective one-coat system for normal atmospheric weathering environments and certain immersion services. This specification does not pertain to weldable prefabrication zinc-rich primers that are applied at lower thicknesses [1 mil (25 μm) or less]. Further information regarding these and other zinc-rich primers can be found in SSPC-PS Guide 12.00, Guide for Selecting Zinc-Rich Painting Systems.

TABLE 9.8 Reference, Purpose, and Brief Description of Painting Standards and Specifications (*Continued*)

Painting System Specification No. 4.02: Four-Coat Vinyl Painting System (for Fresh Water, Chemical, and Corrosive Atmospheres)
This specification covers a complete vinyl painting system for structural steel. This system is suitable for use on parts or structures exposed in Environmental Zones 2C (fresh water immersion), 3A (chemical exposure, acidic), and 3B (chemical exposure, neutral). The finish paint allows for choice of colors.
Painting System Specification No. 4.04: Four-Coat White or Colored Vinyl Painting System (for Fresh Water, Chemical, and Corrosive Atmospheres)
This specification covers a complete vinyl painting system for structural steel. This system is suitable for use on parts or structures exposed in Environmental Zones 2B (frequently wet by salt water), 2C (fresh water immersion), 3A (chemical exposure, acidic), and 3B (chemical exposure, neutral). The finish paint allows for choice of colors.
Painting System Specification No. 7.00: Guide for Selecting One-Coat Shop Painting Systems
This guide covers one-coat shop painting systems for steel that will not be exposed to corrosive conditions for long periods. They are also suitable for steel encased in concrete in those cases where bonding of steel to concrete is not required. They can be used under fireproofing. These systems are suitable for use on parts or structures exposed in Environmental Zones 0 (encased in concrete or masonry, normally dry) and 1A (interior, normally dry). The paints covered by this guide are primers, and if a color other than the standard color is required, the color must be specified.
Painting System Specification No. 8.00: Guide to Topcoating Zinc-Rich Primers
This guide covers the selection and application (including surface preparation) of top coats to surfaces coated with a zinc-rich primer. Both organic and inorganic zinc-rich primers are included. The guide does not cover the selection and application of the zinc-rich primer.
Painting System Specification No. 13.01: Epoxy-Polyamide Painting System
This specification outlines a three-coat epoxy-polyamide painting system for the protection of steel surfaces subject to industrial exposure, marine environments, and areas subject to chemical exposure such as acid and alkali. This system, when properly applied and cured, is capable of giving excellent protection to steel surfaces in Environmental Zones 2A (frequently wet by fresh water), 2B (frequently wet by salt water), 3A (chemical, acidic), 3B (chemical, neutral), and 3C (chemical, alkaline) but not in potable water tanks. Although the coating herein specified has exhibited good chemical protection, its resistance against specific chemicals should, in the absence of applicable case histories, be appropriately tested.
Painting System Specification No. 14.01: Steel Joist Shop Painting System
This specification covers a one-coat shop joist primer that will provide temporary protection to the steel joists during delivery and erection. This system is intended as a one-coat shop paint for open web and long-span steel joists that may be either enclosed or exposed in the interiors of buildings (Environmental Zone 1A, interior, normally dry) where the temperature rarely falls below the dew point, the humidity rarely exceeds 85%, and corrosive protection is not necessary.

TABLE 9.8 Reference, Purpose, and Brief Description of Painting Standards and Specifications (*Continued*)

Painting System Specification No. 15.00: Guide for Selecting Chlorinated Rubber Painting Systems
These specifications cover chlorinated rubber painting systems for blast cleaned or pickled steel. These coatings are not recommended for areas exposed to strong organic solvents, oxidating acids, or the areas where the surface temperature exceeds 74°C). Straight chain unsaturated acids and fats and oils of animal or vegetable origin will cause softening and swelling of these coatings. These systems are suitable for use on parts or structures exposed in Environmental Zones 1A (interior, normally dry), 1B (exterior, normally dry), 2A (frequently wet by fresh water), 2B (frequently wet by salt water), 2C (fresh water immersion), 2D (salt water immersion), 3A (chemical, acidic), 3B (chemical, neutral), and 3C (chemical, alkaline). Chlorinated rubber paints are single-package systems that dry to solvent evaporation and have low permeability to water vapor and oxygen. After drying, they are nonflammable and resistant to mildew growth. The color of the finish must be specified.
Painting System Specification No. 15.01: Chlorinated Rubber Painting System for Salt Water Immersion
This specification covers a complete chlorinated rubber painting system for structural steel. This system is suitable for use on parts or structures exposed in Environmental Zones 2B (frequently wet by salt water) and 2D (salt water immersion). The finish paint allows for a choice of colors.
Painting System Specification No. 15.02: Chlorinated Rubber Painting System for Fresh Water Immersion
This specification covers a complete chlorinated rubber painting system for structural steel. This system is suitable for use on parts or structures exposed in Environmental Zones 2A (frequently wet by fresh water) and 2C (fresh water immersion). It may also be used in nonsolvent chemical atmospheres. The finish paint allows for a choice of colors.
Painting System Specification No. 15.03: Chlorinated Rubber Painting System for Marine and Industrial Atmospheres
This specification covers a complete chlorinated rubber painting system for structural steel. This system is suitable for use on parts or structures exposed in Environmental Zones 1A (interior, normally dry), 1B (exterior, normally dry), 2A (frequently wet by fresh water), 2B (frequently wet by salt water), 3A (chemical, acidic), 3B (chemical, neutral), and 3C (chemical, alkaline). The finish paint allows for a choice of colors.
Painting System Specification No. 15.04: Chlorinated Rubber Painting System for Field Application over a Shop Applied Solvent Base Inorganic Zinc-Rich Primer
This specification covers a field-applied chlorinated rubber painting system for structural steel shop-primed with a solvent base inorganic zinc-rich primer. This system is suitable for use on parts or structures exposed in Environmental Zones 1A (interior, normally dry), 1B (exterior, normally dry), 2A (frequently wet by fresh water), 2B (frequently wet by salt water), 3A (chemical exposure, acidic), 3B (chemical exposure, neutral), and 3C (chemical exposure, alkaline). The finish paint allows for a choice of colors.

TABLE 9.8 Reference, Purpose, and Brief Description of Painting Standards and Specifications (*Continued*)

Painting System Specification No. 16.01: Silicone Alkyd Painting System for New Steel
This specification covers a complete silicone alkyd painting system for structural steel. This system is suitable for use on parts or structures exposed in Environmental Zone 2A (frequently wet by fresh water), including high humidity, infrequent immersion, and mild chemical atmospheres. The primary virtue of this system is the exterior durability and minimum deterioration of the silicone alkyd finish as shown by chalk resistance, gloss retention, and color retention. In addition, the finish paint allows for a choice of colors.
Painting System Guide No. 17.00: Guide for Selecting Urethane Painting Systems
This guide outlines urethane painting systems for structural steel surfaces. There are three types of urethane coatings covered by the guide. They are Types II, IV, and V, as classified by ASTM Standard D 16. These painting systems are suitable for use on parts or structures exposed in varied types of environments ranging from severely corrosive environments to mild atmospheric conditions. These painting systems are intended principally for structural steel where excellent weathering, color retention, and chemical resistance is desired. The color of the finish must be specified.
Painting System Specification No. 18.01: Three-Coat Latex Painting System
This specification covers a complete latex painting system for structural steel. This system is suitable for use on parts or structures exposed in Environmental Zones 1A (interior, normally dry) and 1B (exterior, normally dry) and high-humidity or mild chemical atmospheres. The finish paint is semigloss and chalk resistant and allows for a choice of colors.
Painting System Guide No. 19.00: Guide for Selecting Painting Systems for Ship Bottoms
This guide covers painting systems for ship bottoms from the keel to the light load line on steel ships. The area from the light load line to the deep load line, more commonly called the boot-top area, may also be coated with these systems; however, SSPC-PS Guide 20.00 covers painting systems for this area. It should be noted that boot tops are rarely used with today's commercial ships, and bottom systems may extend up to the deep load line. These coating systems may also be used for other floating or stationary structures exposed to or submerged in salt or brackish water. This would include barges, buoys, oceanographic installations, and so forth.
Painting System Guide No. 20.00: Guide for Selecting Painting Systems for Boottoppings
This guide covers painting systems for the protection of the exterior boot-top areas (the area from the light load line to the deep load line) of steel ships. It should be noted that boottops are rarely used with today's commercial ships, and bottom systems may extend up to the deep load line. In general, the anticorrosive and antifouling paints covered in SSPC-PS Guide 19.00 are applicable to boot-top areas.
Painting System Guide No. 21.00: Guide for Selecting Painting Systems for Topsides
This guide covers painting systems for the protection of the topside or exterior area of steel ships. This includes the area from the deep load line to the rail, more commonly

TABLE 9.8 Reference, Purpose, and Brief Description of Painting Standards and Specifications (*Continued*)

called the freeboard, decks, and superstructure. These systems can also be used for above-water parts of floating structures exposed to salt or fresh water and the normal marine environment. They also cover all above-water areas on ships such as deck equipment or machinery, booms, mast, and bulwarks.

Painting System Guide No. 22.00: Guide for Selecting One-Coat Preconstruction or Prefabrication Painting Systems

This guide covers those shop primers used in today's modern commercial shipyards for preconstruction and prefabrication priming of abrasive blast cleaned structural steel and steel plates. To maximize efficiency in new construction, all ships' steel plates, shapes, and angles are abrasive blast cleaned, shop primed, and stored for future use in preparation of sections of ships, called modules or units. Shop primers are covered by generic classification.

Coating System Guide No. 23.00: Guide for Thermal Spray Metallic Coating Systems

This guide covers the requirements for thermal spray metallic coatings, with and without sealers and topcoats, as a means to prevent corrosion of steel surfaces. Types of metallic coatings included are pure zinc, pure aluminum, and zinc/aluminum alloy, 85% zinc/15% aluminum by weight. This system is suitable for use on structures or parts thereof exposed in SSPC Environmental Zones 1A (interior, normally dry), 1B (exterior, normally dry), 2A (frequently wet by fresh water), and 2C (fresh water immersion). It may be used in Environmental Zones 2B (frequently wet by salt water), 2D (salt water immersion), 3A (chemical exposure, acidic), 3B (chemical exposure, neutral), and 3C (chemical exposure, alkaline) with proper sealing/topcoating (see Section 6 and Note 11.2 of the Guide. This document is intended to serve as a guide for preparing specifications for thermal spray applications.

Painting System Specification No. 24.00: Latex Painting System for Industrial and Marine Atmospheres, Performance-Based

This specification covers a painting system for steel surfaces based on multiple coats of air-drying, single-component latex paints having a total dry film thickness of a minimum of 6 mil (152 μm). The painting system is categorized according to its performance level over blast-cleaned steel, the intended substrate. The painting system is also categorized according to the volatile organic compound (VOC) classes of the latex paints comprising it. The system is suitable for exposure in Environmental Zones 1A (interior, normally dry), 1B (exterior, normally dry), 2A (frequently wet by fresh water), 2B (frequently wet by salt water), 3A (chemical exposure, acidic), 3B (chemical exposure, neutral), 3C (chemical exposure, alkaline), and 3D (chemical exposure, mild solvent). The system is not intended for immersion service.

Paint Specification No.5: Zinc Dust, Zinc Oxide, and Phenolic Varnish Paint

This specification covers a quick-drying zinc dust, zinc oxide, and phenolic varnish paint for steel or galvanized surfaces. It has very good rust inhibitive characteristics but only fair wetting ability for rusting, greasy, or oily surfaces. It has a drying time of about 12 h, good durability even when weathered before finish coating, and may be used for intermediate and finish coats. This paint is supplied in two-package kits: one package contains the liquid vehicle (component A) and the other contains the zinc dust zinc oxide pigment (component B). This paint is suitable for exposure in Environmental Zones 1A (interior, normally dry) and 1B (exterior, normally dry) and is particularly

TABLE 9.8 Reference, Purpose, and Brief Description of Painting Standards and Specifications (*Continued*)

suited for exposure in Environmental Zone 2A (frequently wet by fresh water). It is intended for brush or spray application over steel surfaces prepared in accordance with SSPC-SP 6, Commercial Blast Cleaning; SSPC-SP 10, Near-White Blast Cleaning; SSPC-SP 5, White Metal Blast Cleaning; and SSPC-SP 8, Pickling; or over clean galvanized steel. This paint is suitable as a shop primer, field primer, maintenance primer, or intermediate coat and is to be applied in accordance with SSPC-PA 1, Shop, Field, and Maintenance Painting. This paint will dry in about 12 h and should be recoated within 24 h for optimum intercoat adhesion.
Surface Preparation Specification No. 4 (SSPC-SP 4): Flame Cleaning
Removal of all loose scale, rust, and other detrimental foreign matter by passing high-temperature, high-velocity oxy-acetylene flames over the entire surface, followed by wire brushing. Surface should also be free of oil, grease, dirt, soil, salts, and other contaminants.

Primers. The primer is a universal component of all anticorrosive coatings and is considered to be one of the most important element of a protective system. A good primer generally provides the ability to stifle or retard the spread of corrosion discontinuities such as pinholes, holidays, or breaks in the film. To perform satisfactorily they must themselves adhere well to the base metal or any surface conversion coating that might be present. They should also contain an adequate concentration of a leachable inhibitor, where this is considered an important feature of the protection system, and this is usually a chromate pigment. The primary functions of a primer are

- Adhesion or strong bond to the substrate
- Cohesion or internal strength
- Inertness to the environment
- High bond to intermediate coat
- Appropriate flexibility

Intermediate or body coats. Intermediate or body coats are usually used in coating systems designed for specific applications where coating thickness and structure are advantageous. Intermediate coats with red lead and inert pigments have been giving coatings a heavy body that is impervious to the most demanding applications. The primary purposes of an intermediate coat are to provide

- Thickness to a protective coating
- Strong chemical resistance
- Resistance to moisture vapor transfer

- Increased coating electrical resistance
- Strong cohesion
- Strong bond to primer and topcoat

Topcoats. In the coating system approach, the topcoat provides a resinous seal over the intermediate coats and the primer. The first topcoat may in fact penetrate into the intermediate coat, thus providing the coating system with an impervious top surface. The topcoat is the first line of defense of many coatings against aggressive chemicals, water, or the environment. It is generally more dense than intermediate coats because topcoats are formulated with a lower pigment-to-vehicle (solvent) ratio. The topcoats commonly used include air-drying paints and oil-based varnishes which harden by oxidation; acrylics and other lacquers, which dry by solvent evaporation; and polyurethane and epoxy paints, which dry by cold curing chemical reactions. High-temperature curing or stoving can also be used with certain types of epoxy to produce a harder finish, but this also makes them more difficult to remove.

Polyurethane paints have been widely used in marine applications worldwide. However, these paints are quite brittle and tend to chip and crack, and for these reasons many prefer solvent-drying acrylic paints for the exterior finish. These paints can be removed locally by chemical solvents down to the primer and are reported to be easier to touch up. Whichever paint system is selected for exterior use, it is usual to qualify the system on the basis of its ability to prevent filiform corrosion. Topcoats main functions are to provide

- A resistant seal for the coating system
- An initial barrier to the environment
- Resistance to chemicals, water, and weather
- Toughness and wear resistance to the surface
- A pleasant appearance

However, there are a number of situations where the intermediate coats provide the primary barrier to the environment, and the finish coat is applied for entirely different purposes. The topcoat can be used, for example, to provide a nonskid surface, and the intermediate coat and the primer provide the barrier to the environment, as in a marine environment.

Basic coating components

Binders. To perform in a practical environment, a coating must convert, after its application, into a dense, solid, and adherent membrane

that has all the properties discussed previously. The binder is the material that makes this possible. It provides uniformity and coherence to the coating system. Not all binders are corrosion resistant, so only a few serve in the formulation of protective coatings. The binder's ability to form a dense, tight film is directly related to its molecular size and complexity. Binders that have the highest molecular weight will form films by the evaporation of the vehicle, whereas binders with smaller molecular weight will generally be reacted in situ. Binders can be classified according to their essential chemical reactions.

Oxygen-reactive binders. Oxygen-reactive binders are generally low molecular weight resins that are only capable of producing coatings through an intermolecular reaction with oxygen. This reaction is often catalyzed by metallic salts of cobalt or lead. Examples are

- *Alkyds.* Alkyds are produced by chemically reacting natural drying oils to form a synthetic resin with good film curability, chemical resistance, and weather resistance.
- *Epoxy esters.* Epoxy resins react chemically with drying oils to form epoxy esters. The drying oils' part of the molecule determines the basic properties of the epoxy ester coatings. The coating dries by oxidation in the same manner as an alkyd.
- *Urethane alkyds.* Epoxy resins are also chemically combined with drying oils as part of the molecule that further reacts with isocyanates to produce urethane alkyds. Upon application as a liquid coating, the resin-oil combination converts by oxidation to a solid.
- *Silicone alkyds.* Alkyd resins are combined with silicone molecules to form an excellent weather-resistant combination known as silicone alkyds.

Lacquers. Lacquers are coatings that are converted from a liquid material to a solid film by the evaporation of solvents alone. Lacquers have generally a low volume of solids. Examples are

- *Polyvinyl chloride polymers.* This principal corrosion-resistant lacquer is made from polyvinyl chloride copolymers. The vinyl molecule is relatively large and will effectively dissolve in solvent in the 20% range.
- *Chlorinated rubbers.* To be effective, chlorinated rubbers have to be modified by other resistant resins to obtain higher solids, decreased brittleness, and increased adhesion.
- *Acrylics.* Acrylics are also of high molecular weight and may be combined with vinyls to improve exterior weatherability and color retention.

- *Bituminous materials.* Bituminous asphalts and coal tars are often combined with solvents to form lacquer-type films. They can provide good corrosion resistance but can only be applied where appearance is not a factor.

Heat-conversion binders. Examples of heat-conversion binders are

- *Hot melts.* Hot melts normally involve asphalt or coal tar and are melted and applied as 100% solids in the hot-liquid condition.
- *Organisols and plastisols.* These are high molecular resins (organisols) or vinyl materials (plastisols) that are dispersed in a solvent or plasticizer to solvate them into a filming material upon heating.
- *Powder coatings.* Powder coatings are high molecular weight thermoplastic resins or semithermoset resins applied to a substrate as a very fine powder that is melted to form a coating. Powder coatings can be applied by using an electrostatic field with the coating and substrate charged with opposing polarities. Such an application method is very efficient because the coated section of a substrate becomes insulating, therefore making the uncoated section the only one electrostatically attractive to the powder being applied.

Coreactive binders. Coreactive binders are formed from two low molecular weight resins that are combined prior to the application to the substrate, where they react to form a very adherent and solid film. Examples are

- *Epoxies.* Epoxy binders are made of relatively low molecular weight resins in which the epoxy group is at the end of each molecule. The epoxy resins are then reacted with amines of various molecular weight and cured to form high molecular weight binders with good solvent and chemical resistance.
- *Polyurethanes.* Polyurethanes are coreactive binders in which low molecular weight resins containing alcohol or amine groups are reacted with di-isocynates into an intermediate resin prepolymer that is then capable of reacting with other groups containing amines, alcohol, or even water.

Condensation binders. Condensation binders are based primarily on resins that interact to form cross-linked polymers when subject to sufficient thermal energy. These binders are also called high-baked materials and are commonly used as tank and pipe linings. Condensation is essentially the release of water during the polymerization process.

Coalescent binders. Coalescent binders are coatings where binders of various resin types are emulsified to form a liquid binder. They are

primarily emulsified with water or less commonly with some other solvent dispersions. When applied to the surface, the medium evaporates, leaving the coating in such a way that the binder resin gradually flows into itself, or coalesces, to form a continuous film.

Inorganic binders. Inorganic binders are mostly inorganic silicates dissolved in water or solvent that react with moisture in the air after their application to a surface. The type of inorganic binder depends on the form of the silicate during the curing period. Examples are

- *Postcured silicates.* Soluble silicates are combined with zinc dust to form very hard rocklike films that are further stabilized by reacting them with an acidic curing agent.
- *Self-curing water silicates.* In this case, the soluble alkali silicates are combined with colloidal silica to improve the curing speed. Once applied to a surface they develop water insolubility by reacting with carbon dioxide and moisture from the air.
- *Self-curing solvent-based silicates.* These binders are organic esters of silica that are converted from a liquid form to a solid by reaction with moisture from the air, forming a very hard and corrosion-resistant binder. A major advantage of these materials is their conversion to rain- or moisture-resistant form shortly after their application.

Pigments. Pigments are essentially dry powders that are insoluble in the paint medium and that consequently need to be mixed in it by a dispersion technique. They range from naturally occurring minerals to artificial organic compounds. Pigments contribute several properties essential to the effective use of protective coatings. Several different pigments may be used within the same coating, all of them contributing to the coating's general characteristics to perform important functions such as providing

- Color
- Protection to resin binder
- Corrosion inhibition
- Corrosion resistance
- Film reinforcement
- Nonskid properties
- Sag control
- Increased coverage
- Hide and gloss control
- Adhesion

Zinc phosphates are now probably the most important pigments in anticorrosive paints. The selection of the correct binder for use with these pigments is very important and can dramatically affect their performance. Red lead is likely to accelerate the corrosion of nonferrous metals, but calcium plumbate is unique in providing adhesion to newly galvanized surfaces in the absence of any pretreatment and is claimed to behave similarly on other metals.

Solvents. Most coatings are made with multiple solvents and rarely with a single solvent. The choice of solvents influences viscosity, flow properties, drying speed, spraying and brushing characteristics, and gloss. There is no universal solvent for protective coatings, the best solvent in one system being often impractical for another. Asphalts, for example, can be readily dissolved by hydrocarbons but are insoluble in alcohols. One of the most serious problems associated with coatings is the wrong choice of solvent because it can severely affect the curing and adhesion characteristics of the final coating. One convenient way to describe solvents is to regroup them into the following categories:

- *Aliphatic hydrocarbons.* Aliphatic hydrocarbons or paraffins such as naphtha or mineral spirits are typically used with asphalt-, oil-, and vinyl-based coatings.
- *Aromatic hydrocarbons.* Aromatic hydrocarbons, such as toluene, xylene, or some of the higher-boiling homologs, are typically used with chlorinated rubbers, coal tars, and certain alkyds.
- *Ketones.* Ketones such as acetone, methyl ethyl ketone, methyl isobutyl or amyl ketone, and many others, are very effectively used with vinyls, some epoxies, and other resin formulations.
- *Esters.* Esters such as ethyl, *n*-propyl, *n*-butyl, and amyl acetates are used commonly as latent solvents (a type of solvent that just swells the binder at room temperature) with epoxy and polyurethane formulations.
- *Alcohols.* Alcohols such as methyl, propyl, iso-propyl or butyl alcohols, and cyclo-hexanol are good solvents for highly polar binders such as phenolics. Some alcohols are used in connection with epoxies.
- *Ethers and alcohol ethers.* Ethers such as ethyl ether are excellent solvents for some of the natural resins, oils, and fats. The usual forms of ether used in protective coatings are alcohol ethers such as ethylene glycol mono methyl ether, known commonly as cellosolve. Cellosolve is a good solvent for many oils, gums, natural resins, and synthetic resins such as alkyds, ethyl-cellulose, nitro-cellulose, polyvinyl acetate, polyvinyl butyryl, and phenolics. Cellosolve is a slow solvent that is used in many lacquers to improve flow-out and gloss.

- *Water.* The recent regulations to reduce the emission of volatile organic compounds (VOCs) produced by organic solvents are forcing the coating industry to reconsider the applicability of water as a solvent. The most common water-borne coatings used for application to metals are air dried or force dried at temperatures below 90°C. A wide range of coating formulations falls into this category. The most commonly available technologies are water-reducible alkyds and modified alkyds, acrylic latexes, and acrylic epoxy hybrids.

Nonstick coatings. Nonstick coatings for industrial, architectural, automotive, and marine use are widespread. Hull coatings that resist the formation of strong bonds to marine organisms keep ships free from marine growth without needing heavy metal toxins that accumulate in the environment. Maintaining sanitation in health-care facilities and food processing plants is eased by surfaces that resist microbial attachment.

Investigations of nonstick surfaces have usually focused on the surface and overlooked the adherent. The free energy of a surface or its critical surface tension has long been believed to be the dominant factor in adhesion. Surface free energy is the excess energy of the groups, atoms, or molecules on the surface compared with their counterparts in the bulk material. The size of the free energy represents the capability of the surface to interact spontaneously with other materials. Organic polymers possess surface free energies typically between 11 and 80 $mJ \cdot m^{-2}$. Many commercial polymers with surface energies at the lower end of this range (Table 9.9) have been studied in the search for nonstick coatings.

Hydrocarbons such as polyethylene and polypropylene are readily available and inexpensive, but they are not sufficiently soluble to cast as films. Unsubstituted hydrocarbons are easily oxidized and their nonstick properties rapidly deteriorate in exterior usage. Halogenated

TABLE 9.9 Surface Free Energy of Some Polymers

Polymer	Surface energy, $mJ \cdot m^{-2}$
Polyethylene	34
Polychlorotrifluoroethylene	31
Polypropylene	30
Polyvinyl fluoride	28
Polyethylene-co-tetrafluoroethylene	27
Polyvinylidene fluoride	25
Polydimethylsiloxane	22
Polytetrafluoroethylene	19
Polytetrafluoroethylene-co-hexafluoropropylene	18
Poly[3,3,3-trifluoropropylmethylsiloxane]	18
Polyethylene-co-chlorotrifluoroethylene	15

polymers containing chlorine and especially fluorine have also received a great deal of attention. There are at least half a dozen commodity homopolymers and copolymers containing vinyl fluoride, vinylidene fluoride, tetra-fluoroethylene, hexa-fluoropropylene or chlorotrifluoroethylene. All of these have surface energies between 15 and 31 $mJ \cdot m^{-2}$ and show excellent resistance to chemicals.[9]

Fluorinated precursors are now commercially available to help overcome the obstacles of solubility and adhesion to the substrate. These oligomers have molecular weights of 2000 to 7000 and contain fluorine to impart low surface energy and hydroxyl groups to confer reactivity and adhesion. They are formulated with polyisocyanates to produce urethane coatings. The dominant fluorinated polyols used today are copolymers of chlorotrifluoroethylene and assorted nonhalogenated vinyl ethers. The latter are functionalized to provide reactivity, adhesion, and solubility, and their structure and proportions vary widely. The materials are known generically as *fluorinated ethylene vinyl ether* (FEVE) resins.[10]

Fluorinated polyols derived from hexafluoroacetone (HFA) are also produced for surface coatings. The surface energy of these polyols is close to that of poly(tetrafluoroethylene) (PTFE), and PTFE can be dispersed in the resin as any conventional paint pigment. Flakes of PTFE overlap in the dry film, improving the barrier properties of the coating. These coatings are used as interior linings in large fuel storage tanks and have been used as anticorrosion coatings for ship bilges and tanks and as nontoxic fouling release coatings on small boats.

Industrial and marine coatings containing either FEVE- or HFA-based fluoropolyurethanes are applied as a topcoat over a urethane or epoxy primer. When topcoating is done before the basecoat has fully cured, chemical reaction between the two coats takes place and ensures good adhesion and durability. Fluorinated groups preferentially migrate to the upper surface, where they demonstrate their nonstick behavior.

However, some drawbacks to fluorocarbon surfaces persist. For example, pure PTFE is quite porous and accumulates marine fouling rapidly, in spite of its low surface free energy, because marine organisms inject their adhesive and achieve a mechanical interlock. In addition, fluorine atoms impart stiffness to fluoropolymer chains by raising the barrier to rotation about the backbone bond. In addition, fluorourethane coatings are highly cross-linked thermosets with little or no significant molecular mobility.[9]

9.3 Supplementary Protection Systems

Supplementary protection is provided to surfaces that already have some form of permanent or semipermanent protection such as cladding or conversion coating. The supplementary protection may be in the form

of a material that can be easily applied and removed and that will be replaced periodically during the life of the system. Jointing compounds and sealants are examples of this type.

9.3.1 Jointing compounds and sealants

Jointing compounds are used for protection at joints where they act by excluding dirt and moisture and by providing a reservoir of soluble passivators that act as inhibitors. Sealants are applied to joints to prevent the escape of fluids, such as fuel, but they also exclude moisture. Jointing compounds must remain flexible to allow easy disassembly of parts. Various synthetic resins are used for this purpose. The compounds harden sufficiently at edges to take paint, but they remain tacky within the joint so that flexure does not cause cracking. Sealants of the type now being specified are also elastomeric, and the most popular are polysulphide sealants containing corrosion inhibitors. The inhibitive sealants are very effective when used in faying surfaces and butt joints, for wet installation of fasteners, and over fastener patterns. They are also effective in insulating dissimilar metals.

9.3.2 Water-displacing compounds

Water-displacing compounds may be useful in providing supplementary protection for paint systems that have deteriorated or become damaged in service. They are applied as fluids by wiping, brushing, spraying, or dipping, and they are usually immiscible with water and displace water from surfaces and crevices. A number of fluids used are based on lanolin and contain various solvents and inhibitors. The evaporation of the solvents leaves either thin soft films, semihard films, or hard resin films that provide varying degrees of protection. Some of these fluids may be used to provide short-term protection. They should then exhibit excellent water-displacing characteristics and leave a thin oily film, providing short-term corrosion protection.

Two typical water displacement products used in North America by aircraft maintainers are AML-350 and AMLGUARD. AML350 is a petroleum sulfonate in a mineral spirit solvent. When applied to a metal surface, it spreads over the surface and under water droplets, and as the solvent evaporates, it leaves a soft oillike film of sulfonate, which isolates the metal from the environment and acts as a corrosion inhibitor. The film is built up to a thickness of 2 to 5 μm.

AMLGUARD is a water-displacing compound containing solvents, silicone and silicone alkyd resins, barium petroleum sulfonate, and several other additives. It dries to the touch in about 18 h, but continues to cure for 1 to 3 months to form a hard, dry, but flexible finish between 25 and 50 μm thick. It not only displaces water, but it also

leaves a protective barrier coating containing barium petroleum sulfonate and alkyl ammonium organic phosphate as inhibitors. AML350 is intended for use on internal metallic parts and electrical connectors. AMLGUARD is intended for temporary use on external aircraft parts, such as wheels, wheel wells, cables, landing gear parts, wing leading edges, and helicopter blades.

9.4 Surface Preparation

It is well recognized that you can make a poor coating perform with excellent pretreatment, but you cannot make an excellent coating perform with poor pretreatment. Surface pretreatment by chemical or mechanical means is also important in painting, and the methods used are designed to ensure good adhesion of the paint to the alloy surface. Surface engineering for increased material performance is one important element in the world of metal finishing. Refer to Table 9.8 for the main specifications concerning surface preperation. Most metal surface treatment and plating operations have three basic steps:

1. Surface cleaning or preparation, which involves the use of solvents, alkaline cleaners, acid cleaners, abrasive materials, and/or water
2. Surface modification, which involves some change in surface properties, such as application of a metal layer or hardening
3. Rinsing or other workpiece finishing operations to produce the final product

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