Unlike structural steel, most of the metals to be discussed this month are prepared for painting by chemical cleaning, pickling, and etching, not mechanical scarification. Most require some form of pretreatment cleaning before applying chemical conversion (or paint bonding) coatings. These cleaning processes are often broadly grouped under the general heading solvent or detergent cleaning, although several different mechanisms may be involved. The effects of these cleaning techniques, the subsequent etching and deoxidizing procedures, and, where applicable, the use of conversion coatings are of great consequence to the adhesion or de-adhesion of subsequently applied organic coatings on these metals. This is similar to the case with aluminum, discussed last month. This month’s column provides an overview to coating other non-ferrous metals.

Magnesium
As a structural material, magnesium has limited general use. It is not as strong as aluminum and is much more sensitive to corrosion. Like aluminum, the corrosion resistance of magnesium depends heavily on the purity of the metal. Its corrosion resistance suffers from alloying, but alloying generally increases strength. Distilled magnesium loses about 0.01 mil (0.25 µm) of metal per year in seawater. The commercial metal corrodes up to 500 times as fast in the same environment.

The natural hydrated oxide-carbonate film that forms in air does not provide good barrier value under most moist conditions, especially where chloride ions are present. Like zinc, magnesium produces an alkaline corrosion product (pH of about 10.5), which will saponify and cause de-adhesion of alkali-sensitive paints such as alkyds. To mitigate reactivity and aid in painting, conversion coatings or anodized pretreatments are necessary. Generally one of a variety of chromate-based pretreatments is employed to improve improve paint adhesion and reduce corrosion. Pretreatments are reviewed in many standard texts. Some are anodizing processes and are considered to give maximum corrosion resistance.

An alternative to anodizing, chromate conversion coatings may be

Noble Metals
The noble metals (such as gold, platinum, rhodium, and silver) are rarely coated. They may, however, be used in cladding or plating type applications over other metals for both decorating and engineering applications (e.g., electrical contacts). Perhaps the earliest example of this type of approach is the use of gold leaf (fine leaves of beaten gold applied over structural supports) for decorative purposes. The technique is still occasionally used on cupolas and domes of public buildings. In these applications, where the support is metal sheet, the gold must be well insulated from contact with the base metal. The base metal must be well primed with several coats of insulating material (paint) in addition to the oil-based sizing treatments and adhesives employed to fix gold leaves in place. In the early 1980s, the author was involved in litigation where a contractor had eliminated the necessary primer coat on a gold-leaved cupola of a church in a humid area in the southern U.S. In this case, the unprotected areas of the steel supports corroded so severely and rapidly in the presence of the huge gold cathode that several of the steel members had to be entirely replaced.

Silver will tarnish, especially in sulfide-bearing atmospheres (or after contact with sulfide-bearing foods such as eggs and onions). Chromate treatments and the use of vapor phase inhibitors in storage will reduce this; clear coatings may also be used. Silver plate may also develop white corrosion spots in the dishwasher. If unsightly corrosion spots are to be avoided on silver plate, it is necessary for the silver coating to be non-porous. This is difficult with silver coatings less than 1 mil (25 µm) in thickness. To combat the problem, it is usual to apply a copper or nickel "strike" beneath the silver coat. A 1-mil (25-micrometer) coat of copper allows good performance from a 0.1-mil (2.5-micrometer) silver plate.

Electroplated gold has also been understruck with nickel for use over steel. Continued
applied to magnesium as pre-paint treatments. Most paint primers for magnesium are chromate-based. Magnesium, especially magnesium alloys, find most use in the aircraft and aerospace industries. Its use and pretreatment in these applications is discussed by Lewin.5

**Terne-Coated Steel**
Terne-coated steel is often confused with tin-coated and tin-milled product. In fact, terne coat is primarily a lead alloy, with rarely more than 25% tin, and optimally about 8%. Tin levels below 3 or 4% show a large increase in the rate of dissolution of the alloy in 5% brine. Terne coatings are generally applied by hot dipping, although electrolytic terne coatings are used. In some cases, an electrolytic nickel coating may be applied beneath the hot dipped terne application. The nickel improves the wettability of the surface
being plated and produces a terne coat with fewer discontinuities.

Terne-coated steel has been successfully used over many years as roofing panels, furnace components, radio and TV chassis, and lab benches, and in a variety of automotive applications including gasoline tanks, air filters, and valve covers. As a substrate, the material accepts paint readily, and in roofing service, the substrate should always be kept painted. Performance of the painted substrate drops off dramatically in immersion service. Excessive moisture at the interface of the coating and the terne plate may result in the production of hydrogen, which will gradually force the paint from the substrate. As with zinc-coated steel, passive surface treatments are applied at the coating mill to prevent storage stain. In this case, adhesion of paint to the substrate is markedly reduced. Before a coating is applied, the surface is best cleaned, lightly sanded, or even sweep-blasted as is the case with galvanized steel.

Tin Plate

Although tin coatings were long applied to steel through a hot dipping process similar to galvanizing, electrolytic tin plating is now the more common process. The switch has been fostered by an easier application. It also allows the control of quality coatings at the low film thickness that the process affords, particularly when used in a coil process. These factors are of some criticality to the major market for tin plate, the container industry.

Like zinc, hot dipped tin coatings consist of a layer of pure tin over an intermetallic layer of FeSn₂. Films are much thicker than is the case with the electrolytically plated tin. In the latter, there is no alloy layer, unless the tin plate is subsequently heated (annealed), a process known as reflowing. During reflowing, an intermetallic layer of the same FeSn₂ begins to form. As is the case with terne plate, the deposition of a thin 0.001-mil (0.025-micrometer) film of nickel beneath tin plate is said to produce a significant improvement in corrosion resistance.

There are three principal types of construction in can manufacture: drawn wall iron cans, three-piece cans and draw-redraw cans. Materials and practices in the canning industry vary widely, however.7,8,9

Epoxy phenolics have the broadest applications as interior lining materials on many drawn cans, as well as pails, drums, and three-piece cans for paints, cleaners and aerosols, and food cans. The linings combine good formability with impermeability. High levels of phenolic favor corrosion resistance and impermeability...
but suffer in food applications because of a stronger tendency to taint the taste of food. Epoxies add flexibility and formability, allowing thicker films to be applied with less danger of cracking and delamination in service. Oldring et al. present an excellent comprehensive overview of the can coating industry and in-depth discussions of the type of materials currently in use.9,11,12

The composition of can coatings for food contact is carefully controlled. The industry itself is very conservative and is self-policing. In addition, the U.S. Department of Agriculture and the U.S. Food and Drug Administration control all raw materials that are used in interior linings.6,8,10 The raw materials that may be used are listed in the Code of Federal Regulations (21CFR 175.300). Regulatory concerns center on the possibility of extractives from the coating contaminating the food. Contamination may occur directly from the interior coatings or indirectly by transfer from other coatings (e.g., from exterior coatings by face contact with interior faces of blanks and stacks).

**Copper and Copper Alloys**

Copper, cupronickel, and other copper alloys including the brasses are appreciably more corrosion-resistant than the light metals (such as aluminum, magnesium, and tin) and mild steel. Some are, however, sensitive to tarnishing, especially when handled. For this reason, many decorative articles that are made from these metals (bathroom fixtures, furniture, outdoor hardware, etc.) are coated with clear water white finishes such as the acrylics and urethanes. These coatings preserve the appearance of metal, especially when the coatings are modified with small amounts of active inhibitors, generally benzotriazole or tolyltriazole. Decorative acrylic coatings of this type have been successfully used on copper roofs. Coatings for copper are described by Spindel.13

Clear oxidizing coatings should not be used over bright copper, because of a tendency to darken on aging. Color changes may also occur from sulfur-based contaminants and excessive baking temperatures.

Uncoated copper surfaces develop an aesthetically pleasing green patina of mixed sulfates and carbonates. In marine environments, chlorides may also be present in the patina, whereas in desert areas, sulfate salts are minimized. These salts increase in basicity over time. The patinas may take years to develop, although processes are accelerated in industrial environments. The patina is often
considered aesthetically desirable and is not normally coated. Copper corrosion does not advance appreciably in non-chemical environments, and patina-coated surfaces, hundreds, even thousands, of years old, are still in good condition.

Copper and copper alloys are more susceptible to attack under specific conditions. While neither moisture nor SO₂ has much effect separately, at relative humidities above 75%, attack of SO₂ is much accelerated because the gas is catalytically oxidized to sulfuric acid under these conditions.

Copper has good resistance to seawater. The metal is used for ship propellers; copper compounds are widely used as anti-fouling agents. In brackish water, sewage or polluted seawater, sulfides and nitrogenous compounds readily attack both copper and cupronickel alloys. In these environments, ammonia, carbon dioxide, and sulfides destroy the protective film on cupronickel alloys. Brady, for example, reports that within six months of installation, sewage pipes on aircraft carriers showed aggressive interior corrosion from sulfuric acid produced by aerobic bacteria or from sulfides produced under anaerobic conditions. Lining the interior surfaces of these pipes with a methylene di-aniline-based low molecular weight epoxy reportedly lengthens pipe lifetimes to six years or more. The product is patented and licensed by the Navy.

Pigmented coating systems over brass and copper are applied after surface treatment with proprietary chromate conversion coatings or black oxide treatments. Solvent cleaning alone is not considered an acceptable surface preparation for copper, except for light-duty service, although it is an important adjunct to most cleaning processes. Abrasive blasting (using non-metallic abrasives) and etching solutions (after degreasing) have been used.

Snogren reports adhesive difficulties with paint on copper. Much of what is known about surface preparation of titanium is derived from preparation procedures for adhesive application. Coatings may on occasion be necessary to eliminate the possibilities of galvanic corrosion of other metals from titanium cathodes. Additionally, while the passive films protect in most environments (including oxidizing acids), hydrofluoric acid and aluminum chloride will break down this film.

Mechanical scarification (using nylon pads) and nitric acid pickling are used as surface preparation devices for titanium together with chromate conversion coatings. Wash primers are also said to give good adhesion over the abraded substrate, after which a variety of coatings, including epoxies, polyurethanes, and alkyds, may be used. The metal may also be anodized using sulfuric acid.

Titanium

Titanium is a relatively lightweight metal of great strength and high melting point. The material and its alloys with aluminum and vanadium are used in supersonic aircraft construction (on landing gears, firewalls, and skin sections subject to extreme temperatures). The metal is also used in the chemical process industry and for pressure-resistant vessels in deep water diving applications. The metal is initially very reactive with air but within a very short time forms a passive film that provides an exceptionally high degree of corrosion resistance. A marked enhancement of the electrochemical potential indicates the change from active to passive state.

Titanium is, therefore, rarely coated. Because of this, data on paintability are minimal. Much of what is known about surface preparation of titanium is derived from preparation procedures for adhesive application. Coatings may on occasion be necessary to eliminate the possibilities of galvanic corrosion of other metals from titanium cathodes. Additionally, while the passive films protect in most environments (including oxidizing acids), hydrofluoric acid and aluminum chloride will break down this film.

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ties on copper when coatings based on amines (or coatings that may form amines) are used. Presumably, these include two-pack epoxies, and possibly certain latex paints. These residues attack the copper, forming an embrittled surface. The effect is analogous to that of acidic degradation products of oxidizing systems on zinc. In most cases, however, dwell time from any amine (or ammonia) reactions must be much briefer. It is also reported that baked finishes on brass surfaces have longer cure requirements and lower gloss than do the same coatings applied to either iron or aluminum. 

There are engineering applications of coated copper and copper alloys in addition to the primarily decorative ones. In some of these, the presence of a coating is vital to the utility. In wire coatings, for example, the coating must serve as an electrical insulator to prevent short circuits, especially in windings. Polyimide coatings for copper wire are said to be superior to all other coatings except for perhaps abrasion resistance, where the polyesters and urethanes are preferred. For high temperature wire, polyimides are said to give 20 to 50 times the service life at 250 °C (482 °F) as is possible from silicone-based coatings. 

A variety of electrical applications is detailed by Carter.

**Cadmium**

Cadmium and cadmium-plated surfaces are sacrificial to iron, although the potential difference is much less than is the case with the zinc/iron couple. Unlike zinc coatings, virtually all cadmium coatings are applied by electroplating from cyanide baths. Compared to zinc, cadmium is much less reactive in marine (chloride) environments. The metal is, however, more sensitive than zinc to industrial (sulfate) environments. The difference is most probably related to the relative solubility of the chloride and sulfate salts of the two metals. Relative to zinc, cadmium gives a more insoluble chloride and a more soluble sulfate.

The adhesion of organic surface coatings to cadmium has been evaluated at some length by Walker. Like zinc, cadmium was found to be unusually inhospitable to oxidizing-type binders, with poor initial adhesion values, which deteriorated further with exposure. Epoxy esters and short oil alkyds gave poorer performance than long oil alkyds, although both chlorinated rubber-based lacquers and chemically curing thermosets (epoxy/polyamides, epoxy/amines, and blocked aromatic polyurethane finishes) were much
better. Loss of adhesion of oxidizing systems was ascribed to the same phenomena that are found on zinc surfaces, i.e., reactivity of the metal with aliphatic acid breakdown products from the binder's curing and aging processes. Cadmium is known to be attacked by alkalies as well as organic acids. Even volatile acidic organic species emitted by certain woods and plastics have been known to attack the metal. Walker found that passivation treatments on cadmium gave largely unfavorable (even harmful) results. However, when these surfaces were painted with alkyds and epoxy ester-based systems, the use of two-pack wash primers greatly improved the adhesion with these oxidizing systems.

Cadmium may also be phosphatized using zinc phosphate. Phosphated pretreatments give good surfaces for subsequent paint adhesion.

**Stainless Steel**

Alloys of iron with chromium, with and without the presence of nickel, comprise a class of steel alloys known as the stainless steels. There are four principal types of alloys. All of these stainless steels are protected with passive films that readily form in oxygen and give the alloys extremely high corrosion resistance. Under special conditions, the metal may be subject to localized corrosion such as pitting (from concentration cells beneath deposits), intergranular attack, and stress corrosion cracking (especially the austenitic and martensitic alloys) in chloride and other halide environments.

Where any portion of a stainless steel surface becomes active (i.e., when the oxygen availability is insufficient to maintain the passive film), corrosion will initiate. Where there are subsequent galvanic effects (from the juxtaposition of more noble metals), the galvanic corrosion of stainless steel may become aggressive.

In other and more usual cases, stainless steel cathodes may themselves initiate galvanic corrosion of less noble metals.

Because of these reactions, or where chloride-initiated stress corrosion cracking is likely, stainless steel may be coated. Surface preparation techniques include abrasive blasting or phosphoric acid treatments after solvent cleaning. Nitric acid with small amounts of hydrofluoric acid is often used for scale removal and pickling. Phosphate conversion coatings using manganese phosphate baths (with oxalic acid and sulfide additions) have also been used as paint binding treatments, as have oxalate coatings (used also to assist...
lubrication when the metal is drawn).

A variety of coatings, including epoxies, phenolics, and silicones, has been used over properly prepared stainless steel surfaces. The wash primer may be useful especially when vinyls are to be used for recoating. The possibility of dehydrochlorination of a vinyl next to (and accelerated by the presence of) stainless steel is particularly concerning because of the possibility of subsequent stress corrosion cracking of the steel as a result of the formation of chlorides at the interface.

Conclusion

This completes our review of coating systems on metal. Next, we will consider coating films on calcereous and other cementitious surfaces and the peculiar problems encountered with coatings in these applications.

References