Shop Talk

Selection & Applications Of Inorganic Finishes: Metal Deposits*

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Vib	VIIb		VIII		ID	lib	Illa	iVa	Va	Via
Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
Мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
w	Re	Os	tr	Pť	Au	Hg	Te	Pb	81	Po

Fig. 1—Portion of the Periodic Table showing metal elements electrodeposited from aqueous solutions. Elements in the blue-gray area are of greatest commercial importance; those in yellow are plated only as alloys [as of 1979].

Metal deposits provide corrosion/tarnish resistance, decorative appeal, wear resistance, lubricity, solderability, electrical/heat conductivity and adhesion. This article focuses on the most commonly applied metal deposits for obtaining these and other properties, and considers other important selection factors.

Many metallic elements can be deposited in essentially pure form from aqueous solutions (Fig. 1). In addition, a large number of binary and ternary alloys have been electrodeposited.¹ It is usually more difficult to control alloy plating baths than those from which single elements are deposited, but some alloys provide useful and unique properties not otherwise obtainable and therefore find important commercial applications.

Non-aqueous solvent solutions or fused-salt baths can be used to electrodeposit many metals that cannot be deposited from aqueous solution; however, few such applications have achieved importance. Metal deposits are also applied by a hot-dip in molten metal, and by metal spraying, diffusion coating, thermal decomposition of vapors or liquids, vacuum metallizing/ion vapor

*Based on an original article from the "AES Update" series [Plating, **66**, 28 (April 1979)]

deposition/sputtering, cladding, mechanical (peen) plating and metalliding.

Dissimilar Metal Cells & Galvanic Corrosion

The use of metal deposits presents a situation differing from the use of nonconductive conversion coatings because dissimilar metal cells are formed in the presence of an electrolyte (*e.g.*, moisture film) when the deposit contains or develops pores or defects that expose the underlying metal. The difference in the electrode potentials of the two metals produces a flow of electrons from the more "active" metal (which becomes an anode) to the less active metal (cathode). The flow of electrons within the metal

Table 1 Galvanic Series of Metals in Seawater**

ACTIVE (Anodic) END

Magnesium alloys Zinc (plated) Aluminum (pure) Cadmium (plated) Aluminum alloys (most) Mild steel Stainless steel, 410 (active) Stainless steel, 304 (active) Tin (plated) Lead (plated) Copper (plated) Brass (plated) Nickel (plated; passive) Monel Titanium Stainless steel, 410 (passive) Stainless steel, 304 (passive) Silver Graphite Gold Platinum

INACTIVE (Cathodic) END **Note: Order of metals may change in another environment.

Plating & Surface Finishing • February 2003

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Fig. 2—Cathodic protection of a steel pipeline by impressed current and insoluble anode.



Figure 3—Cathodic protection of a steel pipeline by current generated from corrosion of a soluble (sacrificial) anode.

is accompanied by chemical reactions at the electrolyte interface that result in the accelerated rate of corrosion of the more active member of the couple. The less active metal tends to be prevented from corroding, as compared to the behavior of the individual metals not in contact. The more active metal is said to *sacrificially protect* the less active metal, though, in more general terms, corrosion prevention of the less active metal by flow of electrons into the metal is said to be by cathodic protection. Examples of cathodic protection by galvanic action and by use of a dc-power supply are shown in Figs. 2 and 3.

A list of metals in order of their single electrode potential in seawater is shown in Table 1 and is called the Galvanic Series. In general, the further apart the metals are in the series, the greater the potential difference between them and the more pronounced will be the accelerated corrosion rate of the more active metal in contact. However, the degree of galvanic (dissimilar metal) corrosion is not only dependent on potential difference but also on the polarization characteristics and the ratio of exposed metal areas. A small anode area and large cathode area will usually result in intensive corrosion of the more active member. Metals close to each other in the galvanic series are likely to be relatively compatible in the presence of a seawater environment.

When it is necessary to plate corrosion-susceptible substrates such as steel, zinc or aluminum, protection of the substrate is a fundamental requirement regardless of what other characteristics may be required. The corrosion-preventive coatings can be divided into those that function by sacrificial protection and those that provide barrier-layer protection.

Sacrificially Protective Coatings

Table I indicates that coatings of magnesium, aluminum, cadmium or zinc would be anodic to steel in a seawater environment and

Table 2				
Corrosion Rate of Zinc in Various Environments				

Environment type	Location	Corrosion Rate		
Environment-type	Location	μm/y	mil/y	
Semi-arid	Phoenix, AZ	0.3	0.01	
Rural	State College, PA	1.3	0.05	
Marine	La Jolla, CA	2.0	0.08	
Industrial	Altoona, PA	5.3	0.21	
Industrial-marine	New York, NY	5.3	0.21	

Plating & Surface Finishing • February 2003

therefore provide sacrificial protection. Of these, magnesium can be eliminated as a practical coating since it would be difficult and expensive to deposit and would probably corrode too rapidly. Zinc is the least expensive metal of the group and is readily coated by a number of methods, but mainly by galvanizing or electroplating.

When a continuous zinc coating is present on steel, the zinc simply corrodes at its characteristic rate which, incidentally, is considerably lower than that of steel, despite its greater activity in the galvanic series. When the coating is discontinuous from pores or defects in the coating, the exposed steel areas are protected as illustrated in Fig. 4. The exposed steel becomes the cathodic member of the couple where oxygen discharge occurs and alkalinity is formed. The zinc is, of course, anodic and corrodes at a faster rate than normal, particularly in the vicinity of the exposed steel. Any tendency for the steel to corrode is counteracted by the flow of electrons from the corroding zinc to the steel surface (cathodic protection). The steel exposed at cut edges of galvanized sheet is prevented from rusting during exposure to marine or industrial environments by this mechanism. The duration of protection provided by zinc coatings is a function of coating thickness (regardless of method of application) and exposure conditions. The rate of corrosion of zinc at various exposure sites is shown in Table 2. A 25- μ m (1.0-mil) zinc coating might thus be expected to protect a steel substrate for almost five years of exposure at industrial or industrial-marine environments, but allowance must be made for nonuniformity of coating and the fact that the rate of zinc corrosion increases from galvanic action when any steel is exposed. For example, zinc tends to corrode more rapidly from the edges of cut galvanized sheet than from the interior until so much steel area is exposed that rusting occurs. Sacrificial protection usually does not extend to a distance of more than a millimeter or so during atmospheric exposure.

Zinc-plated Steel

Some of the innumerable applications of zinc-plated steel are fasteners, wire products, tools, shelves, tubular furniture, insect screens, military equipment, bicycle parts, plumbing fittings, washers, hinges, hooks and conduct pipes. Bright zinc can be electrodeposited on smooth substrates and a single-dip clear chromate applied to provide a blue-white luster that has important decorative applications. For outdoor exposures, deposits of 13 to more than 25 μ m (0.5 to 1.0 mil) are applied and a visible (*e.g.*, iridescent, bronze or olive-drab) chromate coating is applied to delay the onset of zinc corrosion.

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Fig. 4—Diagrammatic representation of corrosion in neutral salt solution. Substrate is protected with a more active metal deposit, though it is discontinuous.

Hot-dip galvanizing in molten zinc at 450°C (850°F) is usually more economical than electroplating to produce heavy coatings of zinc and is commonly applied continuously on coil steel and wire. Fabricated articles such as pails and trash cans are galvanized to produce the familiar bright spangled finish. Concrete reinforcing bars, chicken wire, wire rope, roofing and siding, treads and gratings, barbed wire, highway guardrails and various hardware are commonly zinc-coated by galvanizing. Galvanized steel sheet has been used for the fabrication of Army vehicles and painted to provide a high degree of corrosion resistance with minimum maintenance. The minimized-spangle variety is recommended for this military application because the spangles of a conventional galvanized finish may be visible through the paint.2 A commercial galvanized finish (G90) is approximately 19 μ m (0.75 mil) thick, but a 50- μ m-thick (2-mil-thick) coating is recommended for items subjected to severe exposure conditions. A zinc-rich surface is produced on small steel parts by a diffusion process ("Sherardizing") during which the parts are slowly rotated in powdered zinc and heated.

Mechanical (peen) plating involves tumbling of small articles with impact media (*e.g.*, glass beads) in a liquid slurry containing powdered metal that is deposited. The operation is considered nonembrittling and is used to coat high-strength steel items that could be adversely affected by electroplating. Lock-washers in large quantities have been peen plated for this reason and have not required heat treatment to relieve hydrogen embrittlement.

Zinc coatings may also be applied by flame-spray metallizing, *i.e.*, by fine spray of molten metal. Such coatings are normally 100 μ m (4 mil) or more in thickness but are porous and not as adherent as plated or galvanized coatings. Flame-sprayed zinc coatings are applied to large steel structures such as bridges and storage tanks. The zinc is applied to a "white-metal" sandblasted surface and is usually sealed with organic coatings for long-term corrosion resistance.

Zinc-rich paint primers, of organic (MIL-P-26915) or inorganic (MIL-P-38336) base, are finding a great many applications for protecting large structures. There is sufficient zinc dust in the coating to provide particle-to-particle contact and thus to sacrificially protect the steel substrate at those areas exposed because of damage from impact or scratches. The zinc-rich primer is usually over-coated with an organic finish.

One company has developed a process, competitive with galvanizing, to coat one side of coil steel with a zinc-rich baked finish* that can withstand forming operations. This coated steel has been adopted by the auto industry for fabrication of hoods and quarter panels, with the protected side forming the inner surfaces of the components.

Limitations of Zinc

Zinc should not be used on critical steel parts that will reach temperatures of 260°C (500°F) or higher as zinc may diffuse into grain boundaries to embrittle the steel. Zinc coatings can produce bulky corrosion products during exposure to marine or tropical environments and should not be used where the products may cause binding and prevent functioning of equipment that has moving parts in contact. Rapid corrosion of zinc can occur in confined atmospheres where repeated condensation of moisture is likely and where certain organic vapors containing halogen can accumulate. It should be recognized that in hot aqueous solutions, the potentials of zinc and steel may reverse. Therefore, for exposures at temperatures above about 60°C (140°F), it cannot be assumed without experi-

Table 3 Suggested standards for cadmium-plated steel products

Exposure conditions	Minimum Thickness μm (mil)	Typical applications
MILD: Exposure to indoor atmospheres with rare condensation and subject to minimum wear or abrasion.	5.1 (0.2)	Springs, lock washers, fasteners, tools and electronic and electrical parts.
MODERATE: Exposure mostly to dry indoor atmospheres but subjected to occasional condensation, wear or abrasion.	7.6 (0.3)	TV and radio chassis, threaded parts, screws, bolts, radio parts, instruments, aerospace fasteners.
SEVERE: Exposure to condensation, perspiration, infrequent wetting by rain, cleaners.	13 (0.5)	Washing-machine parts, military hardware, electronic parts for tropical service.
VERY SEVERE: Exposure to bold atmospheric conditions, frequent exposure to moisture, cleaners and saline solutions plus likely damage by denting, scratching or abrasive wear.	25 (1.0)	[None given]

mental tests that steel will be sacrificially protected by zinc.

Cadmium

[Note: Since the original publication of this article, concerns about toxicity have led to curtailment in the use of cadmium in many applications, including automobiles. However, substitutes for the metal have never quite been equal to cadmium in <u>all</u> of the properties for which it is selected. So it is still used in some quarters and the information in this section remains relevant.—JHL]

Next to zinc, cadmium is probably the most widely used metal for coating steel to provide sacrificial (cathodic) protection. Cadmium deposits are produced almost exclusively by electrodeposition and are normally chromated to inhibit corrosion. In marine environments and at equal thicknesses, cadmium outperforms zinc in protecting steel by a factor of about two, whereas zinc is somewhat superior to cadmium in industrial environments.³ However, cadmium has other valuable char-

Plating & Surface Finishing • February 2003

^{*}Zincrometal[®], Diamond Shamrock Corp., Cleveland, OH (1979); Metal Coatings International, Chardron, OH (2002).

acteristics that zinc does not have. For example, cadmium excels in lubricity, solderability, compatibility with aluminum, electrical conductivity and in producing relatively nonbinding corrosion products. When these properties are required, zinc is not normally a viable alternative.

In order to provide galvanic compatibility, cadmium is often applied to parts comprised of copper alloys or their substrates that are to be placed in contact with aluminum or magnesium.

Applications of Cadmium

Cadmium appears to be the best available deposit for aircraft and aerospace fasteners, according to data generated by SPS Technologies, Jenkintown, PA. It provides high lubricity, predictable high tension at low tightening torque (even with multiple removals), low binding tendency and galvanic compatibility with aluminum. The military requires cadmium deposits on assorted steel hardware, wire springs, self-tapping screws, bearing rings and aerospace/aircraft fasteners of all types. The automotive industry [used] cadmium coatings on disc-brake components, radiator-hose fittings, door latches and torsion-bar bolts, primarily for lubricity and corrosion resistance.

The electronics industry uses cadmium-because of its solderability, low contact resistance and corrosion resistance, on chassis, connectors and relays. Household applications include washingmachine parts requiring resistance to alkaline solutions; unlike zinc, cadmium is not amphoteric. Assorted hardware (*e.g.*, hinges) and fasteners with cadmium deposits are commonly used. The thickness of cadmium suggested for various applications is shown in Table 3.⁴

Limitations of Cadmium

The toxicity of cadmium precludes its application on any kind of food-handling equipment and imposes severe limitations on the disposal of electroplating rinsewater. This has prompted considerable interest in alternative coatings for cadmium. Zinc and aluminum appear to be the most viable alternatives for many applications, though some organic-metallics, ceramic-metallics and alloy deposits have been considered.

Though sacrificial coatings are usually monolithic deposits, a 2.5-µm (0.1-mil) tin strike on steel prior to zinc or cadmium deposition considerably improves corrosion resistance in marine environments. Alloy electrodeposits of 78% tin/zinc have been applied⁵ from a cyanide-based bath to steel nuts and bolts which were fastened to aluminum alloy. From the standpoints of protection to steel and compatibility with aluminum, the tin-zinc alloy deposit was equal or superior to either zinc or cadmium in marine or industrial environments. The tin-zinc alloy deposit also has excellent solderability characteristics and thus appears to be a potentially suitable alternative to cadmium. An alloy deposit of 86% zinc/nickel⁶ produced from a noncyanide bath was significantly more corrosion resistant than a zinc deposit and retained the ability to sacrificially protect steel.

An organic-metallic coating* is being used increasingly as a replacement for cadmium and zinc deposits. This pollution-free and nonembrittling process is normally applied by immersing parts in a composition containing dispersed zinc flake and organic chromate. The coating is highly protective to steel or aluminum alloys and can be used at service temperatures up to 340°C (650°F). A 7.6- µm (0.3-mil) coating prevents basis-metal corrosion for more than 336 hr of salt-spray exposure.

Cadmium should not be applied to or placed in contact with titanium or with steel that may reach temperatures of 230°C (450°F) or higher in service, as severe embrittlement may result. Hand-tools that may contact these materials should not be cadmium plated. In general, steel parts that have a tensile strength greater than 1660 MPa (240,000 psi) should not be coated by electrodeposition because of the risk of irreversible hydrogen embrittlement. Instead, cadmium may be deposited by vacuum deposition or by mechanical (peen) plating without danger of hydrogen embrittlement. Special high-strength steel bolts for aircraft are coated by the vacuum process. The high-strength steel is abrasive-blasted to remove any rust or scale; acid pickling, of course, is not permitted.

The nonaqueous methods of deposition are more expensive and produce lower-quality deposits than electrodeposition. However, in addition to their nonembrittling characteristics, the nonaqueous methods eliminate disposal problems with waste solutions containing cadmium. There have been some fears that, although ultrahighstrength steels are cadmium-plated by nonembrittling processes, embrittling hydrogen may be released during service as a result of corrosion processes involving the cadmium and basis metal.⁷

Aluminum

Aluminum has useful coating properties but suffers from the drawback that the metal cannot be electrodeposited from aqueous solutions, which is usually the most convenient and inexpensive method of applying high-quality deposits. Like zinc and cadmium, aluminum coatings are sacrificially protective at marine environments to small areas of steel exposed at pores, defects or cut edges. However, in industrial or rural environments, aluminum is passivated by a natural oxide film that reduces its activity to the point that sacrificial protection is not provided and rusting will occur at any exposed steel.

Aluminum coatings are applied by the hot-dip process on steel sheet, strip or wire in continuous lengths or to fabricated parts. Aluminum coatings considerably outperform galvanized coatings of the same thickness in all environments except on cut edges and bare areas at nonsaline exposure sites. A hot-dip coating of 55% Al/Zn** combines some of the best properties of galvanizing and aluminizing, that is, sacrificial protection and long-term corrosion resistance. Hot-dip aluminized steel (or aluminum-rich diffusion coatings—"Calorizing") is particularly effective for retarding hightemperature corrosion/oxidation and, because of this characteristic, has been used on auto mufflers, furnace parts and heater tubes. Aluminum coatings on steel may be used for exposures up to 500°C (925°F), whereas cadmium and zinc deposits may be used only up to 230° and 260°C (446° and 500°F), respectively. Aluminized steel has been widely used for coating chain-link fencing, barbed wire and guy wires for outdoor corrosion resistance.

A process for the ion vapor deposition of a pure aluminum coating has replaced conventional cadmium plating for applications on structural aircraft components (landing gear and arresting-gear mechanisms, horizontal tail spindles) and fasteners on the F-18 aircraft. The aluminum deposit is adherent and said to be more compatible than cadmium in contact with structural aluminum alloys. Exfoliation corrosion of aluminum alloy is retarded. The aluminum coating is also applied to fatigue-sensitive aluminum alloys and to stainless steels and titanium alloys for compatibility with structural aluminum. Ion vapor deposition can also be used on high-strength steels without introducing embrittlement, but a high capital investment for equipment is required.

Aluminum can be electrodeposited from organic solvent (*e.g.*, ethyl ether, alkyl benzene, hydrocarbons) baths. There have been

^{*}Dacromet 320, Diamond Shamrock Corp., Cleveland, OH (1979); Metal Coatings International, Chardron, OH (2002).

^{**}Galvalume, Bethlehem Steel Corp., Bethlehem, PA

some applications reported,⁸ including deposition on titanium springs and fasteners, on Kovar lead frames for integrated circuits, and on reinforcing fibers (*e.g.*, boron, graphite) used for making metal-matrix composite materials. Deposits of aluminum can also be produced by chemical vapor deposition (MIL-C-81740), vacuum deposition (MIL-C-23217) or flame spraying. Ceramic-bonded particulate aluminum (MIL-C-81751) and electrophoretically deposited aluminum (MIL-C-81797) coatings are used by the military to prevent corrosion and high-temperature oxidation.

Sheets of high-strength aluminum alloy are sometimes clad with layers of pure aluminum on a commercial basis ("alclad"). The pure aluminum is much more resistant to corrosion than the alloy, yet is more active in equilibrium potential (see Table 1) so that sacrificial protection is provided after long exposure results in perforation of the cladding.

Tin Coatings (Food & Beverage Cans)

That tin deposits will not provide sacrificial protection to steel under seawater exposure is evident from their positions in the galvanic series. However, in the presence of food acids (*e.g.*, citric, oxalic) and other tin-complexing acids (*e.g.*, hydrochloric, hydrofluoric), the potentials of steel and tin reverse. This is the main basis for the application of tin electrodeposits for food and beverage canning stock.

Continuous coils of steel strip are electroplated with thin tin deposits, usually 0.4 to 1.5 μ m (0.015 to 0.060 mil) for use as can stock. The electroplating process has replaced the thicker hot-dip tin coating of steel for cans except for use with highly corrosive food products. The tin electrodeposits are usually heat flow-brightened, which results in the formation of an Fe₂Sn compound at the interface that improves corrosion resistance. The interior surface of the container is often organic-coated ("enameled") to further improve corrosion resistance and maintain the original taste and color of food products that would otherwise be adversely affected.

Cans used for holding pineapple, grapefruit or some tomato products are usually tin-plated without any organic coating. Exposure of the plated steel to the acidic contents does not cause pitting of the steel because the tin deposit provides cathodic protection to both the Fe₂Sn layer and the steel substrate. However, unlike the systems described earlier, the anaerobic conditions inside a can preclude discharge of oxygen as the local cathodic reaction. Normally, the only reaction that can occur is that involving formation of atomic or molecular hydrogen. The high hydrogen overvoltage of tin explains the resistance of tin to acid dissolution. Also, trace quantities of stannous ions serve as an effective inhibitor of galvanic corrosion between the tin deposit and steel exposed at pores.⁹ The ambient storage temperature of canned foods affects the shelf life. The corrosion rate approximately doubles for each $10C^{\circ}$ (18F^o) increase in storage temperature.

The solderability of tin is an additional factor in its broad application for food cans because seams can readily be sealed by soldering.

"Tin-free steel," which describes an electrolytic treatment resulting in deposition on steel strip of chromium plus chromium oxide to a total thickness of only 0.01 μ m (0.0004 mil), apparently functions as effectively as tin for the organic-coated interior of beverage cans.

The exterior of a tin-plated food can is susceptible to rusting since the tin deposit may not be continuous and cannot sacrificially protect the steel at normal environmental exposures. The coating is adequate for mild indoor exposure conditions, but, when subjected to high humidity and periodic condensation, surface rusting and eventual perforation can be expected. *P&SF*

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Editor s note: The preceding article is based on material contributed by Fred Pearlstein for the "AES Update" series that ran in this journal. Since this article was written, much has changed. Indeed, the outlook for hexavalent chromate has drastically changed. Nevertheless, these processes remain revelant to a large portion of the finishing community. The reader may benefit both from that information and the historical perspective of the technology in 1979. The Update series was begun and coordinated by the late Dr. Donald Swalheim, and brought practical information to the metal finisher. In some cases here, words were altered for context.

Specifications

Specifications for coating processes discussed in this article include:

- Electroplated zinc on steel: QQ-Z-325C, "Zinc Coating, Electrodeposited."
- Commercial galvanizing: ASTM A-525, "Steel Sheet, Zinc-Coated (Galvanized) by the Hot-Dip Process, General Requirements."
- Mechanical plating: Mil-C-81562A, "Coatings, Cadmium, Tin-Cadmium and Zinc (Mechanically-deposited)."
- Electroplated cadmium: QQ-P-416C, "Plating, Cadmium (Electrodeposited)."
- Organic-metallic coating (Dacromet 320) for steel or aluminum alloys: MIL-C-87115, "Coating, Immersion Zinc Flake/ Chromate Dispersion."
- Vacuum deposition of cadmium: MIL-C-8837A, "Coating, Cadmium(Vacuum Deposited)."
- Aluminum coatings applied by hot-dip process on steel sheet, strip or wire in continuous lengths: ASTM A-463, "Steel Sheet, Cold-Rolled, Aluminum Coated Type I."
- Aluminum coatings applied by hot-dip process on fabricated parts: ASTM A-676, "Hot-Dipped Aluminum Coatings on Ferrous Articles."
- Ion vapor deposition of aluminum: MIL-C-83488A, "Coating, Aluminum, Ion Vapor Deposited."
- Other aluminum-coating processes: MIL-C-81740 (AS), "Coatings, Aluminum and Aluminum Alloys (Metallic Compound Decomposition)"; MIL-C-23217B, "Coating, Aluminum, Vacuum Deposited"; MIL-C-81751B, "Coating, Metallic-Ceramic"; MIL-C-81797, "Coating, Inorganically Bonded Aluminum (Electrophoretically Deposited)."
- Electrodeposited tin for food cans: ASTM A-624, "Single-Reduced Electrolytic Tin Plate"; ASTM A-626, "Double-Reduced Electrolytic Tin Plate."
- Tin-free steel for beverage cans: ASTM A-657, "Steel, Cold-Rolled, Single- and Double-Reduced Tin Mill Black Plate Electrolytic Chromium Coated."