

# Chromate Conversion Coatings

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**CHROMATE CONVERSION COATINGS** are formed on metal surfaces as a result of the chemical attack that occurs when a metal is immersed in or sprayed with an aqueous solution of chromic acid, chromium salts such as sodium or potassium chromate or dichromate, hydrofluoric acid or hydrofluoric acid salts, phosphoric acid, or other mineral acids. The chemical attack facilitates the dissolution of some surface metal and the formation of a protective film containing complex chromium compounds.

A variety of metals and electrodeposited metal coatings, including zinc, cadmium, magnesium, and aluminum, can be chromate conversion coated. Several articles in this Volume contain details about the procedures used to apply chromate coatings to specific metals and metal coatings. The conversion coating of cadmium electrodeposits is discussed in the article "Cadmium Plating"; the articles "Surface Engineering of Aluminum and Aluminum Alloys" and "Surface Engineering of Magnesium Alloys" contain information relating to the application of chromate conversion coatings to these metals; and procedures for applying conversion coatings to electrodeposited zinc are described in the article "Zinc Plating." A comprehensive summary of literature sources related to chromate conversion coatings is available in a detailed review of surface treatments for aluminum alloys (Ref 1). In addition, processing and testing details for application of chromium conversion coatings to aluminum, magnesium, cadmium, copper, silver, and zinc are continuously updated and presented in concise form (Ref 2).

Chromate conversion coatings are generally used to increase the corrosion resistance of the metal to which they are applied. Most conversion coatings slowly dissolve in water and provide limited protection in this medium; however, they furnish excellent protection in marine atmospheres and in high-humidity environments. The protection provided by chromate coatings increases directly with thickness up to a certain point, after which the protective nature is sacrificed due to the formation of a porous, nonadherent film. Chromate conversion coatings are also used for a variety of decorative and functional

applications. They can be produced in a variety of colors, ranging from the very bright coatings obtained on zinc and cadmium, which simulate the appearance of bright nickel and chromium, to the olive drab frequently applied to military equipment. Chromate coatings provide an excellent nonporous bonding surface for all paints that have good molecular adhesion. A summary of general uses for chromate conversion coatings is given in Table 1; more detailed information is provided in the section "Chromating Processes and Applications" in this article.

Most of the formulations used in chromating today are of a proprietary nature, and many of the patents in this area expired long ago. Some specific formulations are given in Ref 1, but details about solution control are difficult to find. This is unfortunate, because understanding solution replenishment chemistry is key to extending the life of chromating solutions and enhancing their versatility. This article briefly describes the basic attributes of chromate conversion and the processes for applying them. It also provides information about the influence of substrate microstructure on the performance of coating deposits, the mechanism of substrate protection supplied by chromate coatings, and the development of new replacement technologies in response to the environmental constraints that have developed around the use of chromium-base compounds. (Information related to this last item is also available in the article "Chromium Elimination" in

this Volume.) Most of the information provided in this article relates specifically to the chromating of aluminum and aluminum alloys, for these metals are by far the chief recipients of chromated films. However, most of the information is generally applicable to chromating of other metals as well.

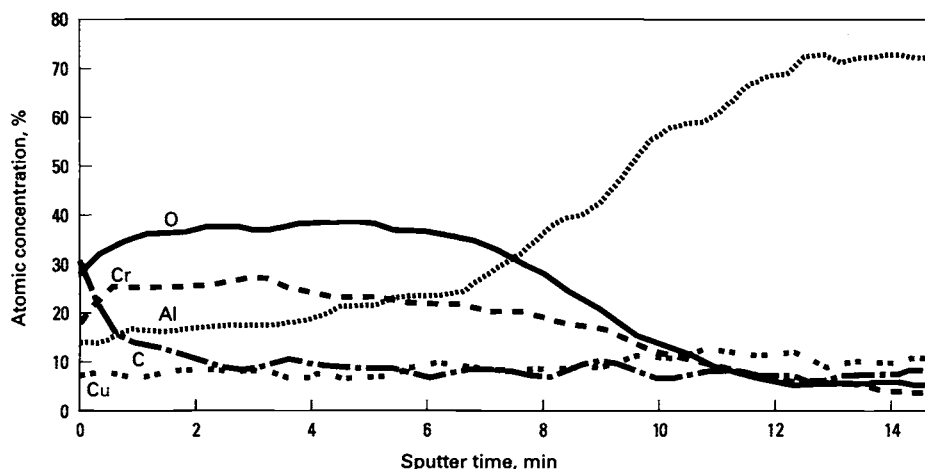
## Characteristics of a Chromate Conversion Coating

Conversion coating does not simply involve the deposition of a thin layer of, for example, hydrated metal oxide that "converts" a surface to a corrosion resistant state (Ref 3). As illustrated in Fig. 1, an Auger electron spectroscopy (AES) depth profile for a typical chromated layer on aluminum alloy 2024-T3, the film contains not only chromium and oxygen, but also part of the substrate (in this case aluminum) and the principal alloying element (copper). The profile was taken on the solid solution matrix, off any of the intermetallic second-phase particulates that typically form in the aluminum-copper alloy system. In the case of chromate coatings, the amorphous hydrated oxide mixture that is formed on the surface must involve oxidation of the substrate, followed by precipitation of the dissolved metal ions. Precipitation arises from an increase in pH at the surface due to reaction with excess hydroxyl ions produced as a result of the cathodic

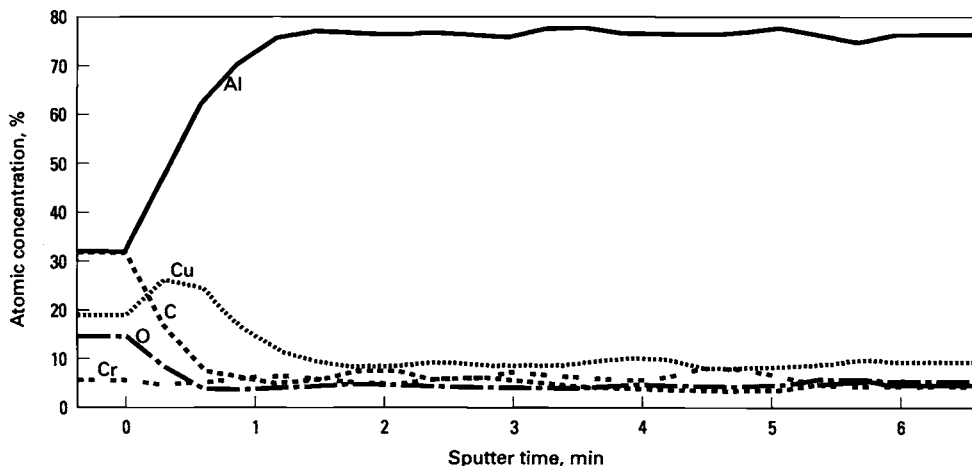
**Table 1 Common uses of chromate conversion coatings**

Metal	General use				Remarks
	Corrosion resistance	Paint base	Chemical polish	Metal coloring	
Aluminum	X	X	...	X	Economical replacement for anodizing if abrasion resistance is not required Used to "touch-up" damaged areas on anodized surfaces
Cadmium	X	X	X	X	...
Copper	X	X	X	X	Thin coatings prevent "spotting out" of brass and copper electrodeposits. No fumes generated during chemical polishing
Magnesium	X	X	...	...	...
Silver	X	...	...	...	...
Zinc	X	X	X	X	...

Source: Ref 2



**Fig. 1** Auger electron spectroscopy depth profile of polished aluminum alloy 2024-T3 solid solution matrix exposed to Alodine 1200S conversion coating solution for 5 min. Sputter rate approximately 300 Å/zmin (vs. SiO<sub>2</sub>). Experiment details in Ref 7. Source: Ref 4



**Fig. 2** Auger electron spectroscopy depth profile of polished aluminum alloy 2024-T3 solid solution matrix exposed for 5 min to the same solution as in Fig. 1 without fluoride ion present. Sputter rate approximately 300 Å/min (vs. SiO<sub>2</sub>). Experiment details in Ref 7. Source: Ref 4

(i.e., reduction) half reaction. Either reduction of dissolved oxygen or reduction of water itself will cause such an increase in pH at the surface. A similar mechanism is postulated for the formation of crystalline phosphate conversion coatings on steel, in which two principal crystalline phases have been identified: hopeite, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, and phosphophillite, Zn<sub>2</sub>Fe(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O (Ref 5). The latter compound involves incorporation of the main element in the substrate (i.e., iron) through oxidation of the surface in the presence of acidic zinc phosphate.

As evidenced by the above discussion, a conversion coating is simply a film that contains a mixture of the corrosion-resistant species and the major elements found in the substrate. The mixture promotes strong adhesion of the conversion coating to the substrate. This is unlike a film formed by physical vapor deposition, where there is a very clear interface between the film and the

substrate and where essentially none of the substrate is distributed through the deposited film. Poor film adhesion can result at such an interface, and if water and/or oxygen reach the interface region, corrosion can readily occur and cause delamination of the film. Because no clear interface exists in conversion coating films, a certain amount of oxygen and water can be tolerated; the substrate concentration gradient is observed through the protective film.

### Chromate Conversion Coating Processes and Applications

Although the beginning of chromium-based conversion coatings can be traced back to 1915 (Ref 6), the advent of modern-day chromating treatments is dated from 1945 to the early 1950s, when tradenames such as Alodine (American

Chemical Paint Co., later Amchem Products Co.), Alocrom (ICI Ltd.), Bonderite (Parker Rust Proof Co.), and Iridite (Allied Chemical Co.) were synonymous with the formation of highly corrosion-resistant conversion coatings. Unlike their predecessors, these coatings could be applied at or near room temperature for short times (a few seconds to several minutes, depending on the thickness and degree of corrosion resistance desired), and good results could be obtained on difficult-to-treat alloys such as aluminum-copper alloys and magnesium alloys. The use and solution control of surface activators (most notably fluoride ion) allowed chromating reactions to proceed at a very rapid rate. In addition, when maximum corrosion resistance was required, accelerators such as the ferricyanide ion were used, especially on difficult-to-treat alloys (Ref 3).

The importance of having fluoride present in the chromium-containing bath is illustrated in the AES depth profile of a conversion coating applied in the absence of fluoride (Fig. 2). Comparison of this profile with Fig. 1 indicates that, all other conditions being constant, the presence of fluoride increases film thickness by a factor of at least 30. With fluoride present (Fig. 1), the surface was found to contain 18 at.% Cr, whereas only 5 at.% Cr was observed without fluoride in solution (Fig. 2). Without fluoride present, very little chromium is deposited, and the enriched copper interface observed on the cleaned but untreated sample remains intact (data not shown; see Ref 7 for details).

The fluoride-based treatments can be divided into two principal classes whose names reflect the predominant color of the conversion coating: "green" or amorphous phosphate treatment and "gold" or amorphous chromate treatment. The green treatments are obtained from solutions containing mixtures of chromic, phosphoric, and hydrofluoric acids; coatings ranging in weight from 5 to 10 mg/ft<sup>2</sup> (colorless) to 200 to 500 mg/ft<sup>2</sup> (deep green) can be produced. Monitoring of cation concentration in chromium phosphate baths is critical to maintaining bath life and coating performance since sludging can occur very easily due to precipitation of NaK<sub>2</sub>AlF<sub>6</sub> and Na<sub>3</sub>AlF<sub>6</sub>. The gold treatments are obtained from solutions containing only chromic acid and a fluoride ion source; coating weights of 5 to 80 mg/ft<sup>2</sup> ranging in color from a light iridescence to a golden tan can easily be obtained.

In general, these treatments provide better unpainted corrosion resistance than the phosphate-based treatments and are much easier to control. The critical parameter for replenishment chemistry is control of the ratio of free-to-complexed fluoride ion. Many different fluoride ion sources have been used to affect this control. In addition to improving corrosion performance, these treatments serve as desirable substrates for promoting good paint adhesion and preventing underpaint corrosion. Corrosion performance can be enhanced by addition of accelerators such as the ferricyanide ion, which increases coating weight and also serves to complex copper in aluminum-copper alloys (see the section "Chromating

Mechanism," below). Aluminum-copper alloys are some of the most difficult metals to protect against corrosion but are also some of the most often used aluminum-base alloys due to their strength. Similar fluoride-ion-based treatments are used for magnesium and its alloys, with the Dow No. 7 treatment being the most often used where maximum corrosion protection is desired (Ref 8).

Chromate conversion coating treatments are used on five principal types of aluminum parts: aircraft and aerospace structural components, coil (for construction applications such as guttering and siding), extrusions (for window and door frames), heat exchanger parts, and containers (mainly beverage cans). A considerable amount of aluminum is also used in the automotive industry, but most receives a crystalline phosphate treatment because the aluminum is treated at the same time as the steel frame. As with chromating, fluoride ion is added to the phosphating bath to promote phosphate film growth on aluminum.

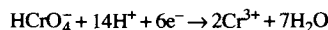
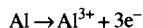
The major specifications that cover the performance of chromate conversion coatings are listed in Ref 2. The type of specifications used will depend on the end use of the fabricated part, which in turn will dictate the properties of the coating being sought. For example, in order to be used on military aircraft, aluminum alloy parts (such as those made from highly corrosive copper-containing aluminum alloy 2024-T3 or 7075-T6) must pass government specifications MIL-C-5541 and MIL-C-81706, which require that the unpainted chromated alloy must survive 336 h of salt fog testing (ASTM B 117). In addition, various tests are used to ascertain paint adhesion and underpaint corrosion under salt fog conditions. Aerospace companies use specifications similar to those used by the government. A boiling water test is often used in the container industry to detect the effectiveness of the chromate treatment in preventing discoloration caused by underpaint corrosion. Because the alloys used for manufacturing containers are not nearly as active, in a corrosive sense, as those used in aerospace, and because the specifications are not as severe, thin unaccelerated treatments are often used.

## Chromating Mechanism

Next to the alkali metals, the metals that chromate coatings must protect against corrosion (i.e., aluminum, magnesium, zinc, and cadmium) are the most active metals in the periodic table. In fact, from the large negative standard electrode reduction potentials for aluminum and magnesium dissolution, one would expect these metals to dissolve when immersed in water. This does not occur, of course; upon exposure to water or air, these metals immediately form a hydrated oxide film that is itself somewhat protective.

Chromate conversion treatments actually take advantage of this high surface activity. Through use of a strong oxidizing agent such as chromic acid,  $\text{CrO}_3$ , a redox reaction occurs at acidic pH (pH  $\approx$  2) where hexavalent chromium, either in

the form of  $\text{Cr}_2\text{O}_7^{2-}$  or  $\text{HCrO}_4^-$ , is reduced to trivalent chromium while aluminum is oxidized to trivalent aluminum:



Probably due to the presence of fluoride ion (see next paragraph), another reduction reaction besides that involving chromic acid can occur. This reaction involves the reduction of either water, hydronium ion, or dissolved oxygen to form hydroxyl ions at the metal surface. This surface-localized increase in pH results in the precipitation of an amorphous mixture of hydrated aluminum plus chromium oxides.

As described in the previous section, the presence of fluoride ion is important for building films of significant thickness; without its presence, film growth is extremely slow. Fluoride presumably serves two roles. First, it solubilizes the aluminum oxide initially present on the surface and allows the redox and deposition reactions to proceed. Second, it solubilizes a portion of the growing film, which allows penetration of the electrolyte to the surface and ion transport from the surface into the growing film. Fluoride has been characterized as a unique monodentate ligand that enhances the dissolution rate of aluminum oxide (Ref 9).

The high corrosion resistance offered by chromate films is attributed to the presence of both hexavalent and trivalent chromium in the coating. Analyses of coatings by wet chemical methods (Ref 10) and with surface-sensitive techniques (Ref 7, 11, 12) have shown that both Cr(VI) and Cr(III) are present in the films. The trivalent chromium is believed to be present as an insoluble hydrated oxide, whereas the hexavalent chromium imparts a "self-healing" character to the film during oxidative (corrosive) attack by species such as chloride ion. The hexavalent chromium is reduced during corrosion to form an insoluble trivalent chromium species that terminates the oxidative attack.

The enhanced corrosion resistance attributed to accelerated chromate conversion coatings has been ascribed to the increase in coating weight that is due to incorporation of the accelerator into the growing coating (Ref 3, 13, 14). Recent studies on ferricyanide-accelerated chromate coatings deposited on a high-copper-containing aluminum alloy indicate that ferricyanide is distributed throughout the film only on the high-copper-containing intermetallic phases such as  $\text{CuAl}_2$  (Ref 7). Because these phases are known to accelerate greatly the corrosion rate of aluminum (Ref 15), the decrease in corrosion rate offered by the accelerator is believed to be due to the formation of copper ferricyanides on the intermetallic surface, which alters its activity with respect to the solid solution matrix. At adequate treatment times, corrosion resistance is also believed to be enhanced by the uniform surface composition of chromium and oxygen and the

absence of aluminum and copper in the near-surface region.

## Effects of Substrate Microstructure

Because of specific physical property requirements, metal fabricators rely on a "mixed substrate," such as an alloy, rather than a pure metal. An alloy is typically of higher strength than a pure component because of the synergistic effect of the alloying element (e.g., a small amount of copper greatly strengthens aluminum for aerospace applications). The disadvantage of the alloy substrate from a conversion coating standpoint is twofold:

- The conversion coating must be tolerant of all the alloying elements. Formulating a conversion coating that can simultaneously treat all the elements present in an alloy can be difficult, depending on the elements' relative reactivity.
- The alloying elements may impart an accelerated corrosion rate to the metal. For example, when exposed to identical sodium-chloride-containing solutions, high-purity (99.999%) aluminum corrodes very slowly, whereas copper-containing aluminum alloys (e.g., the 2000-series alloys) corrode extremely rapidly (Ref 4). (On the other hand, alloying elements such as magnesium and zinc have very little effect on the corrosion rate of aluminum.) Aluminum used for alloying is typically of 99+% purity, and this aluminum will corrode at a faster rate than higher-purity material due to the presence of impurities, such as iron, that form intermetallic phases (e.g.,  $\text{FeAl}_3$ ). A few parts per million of iron, copper, or nickel in magnesium and magnesium alloys can also greatly accelerate the corrosion rate (Ref 16).

One of the principal difficulties in attempting to form a uniform conversion coating on an alloy surface is that alloys are seldom of homogeneous composition (i.e., they are not perfectly solid solutions). With the base metal and with themselves, the alloying elements often form second-phase particulates or "intermetallics" within the solid solution matrix (Ref 17). The intermetallics develop during the alloying process (as is found with precipitation hardening of a supersaturated alloy solution) and render the surface inhomogeneous. These intermetallics can form galvanic couples between themselves and the alloy solid solution matrix, and depending on their relative activity with respect to the matrix, they can either cause acceleration of the matrix or their own dissolution rate.

For example, the  $\text{CuAl}_2$  that is found in aluminum-copper alloys is typically less active than (i.e., lies cathodic to) the solid solution matrix, which enhances the solid solution dissolution rate. In addition to enhancing the corrosion rate, this can have a profound effect on the uniformity achieved with a particular conversion coating process. As has been noted in a previous study (Ref 7), the activity difference between  $\text{CuAl}_2$

intermetallics and the solid solution results in the application of a nonuniform (in thickness) conversion coating. A much thicker layer is found on the solid solution matrix because of its enhanced activity. The thinnest layers are found on the  $(\text{Fe,Mn})_3\text{SiAl}_{12}$  intermetallics, which appear to be less active than the  $\text{CuAl}_2$  phases.

Alloy temper can also affect microstructure, which in turn can influence coating performance. For example, one study found that chromate treatments that were effective in protecting aluminum alloy 7075-T6 were not effective in treating the same alloy in the T73 (overaged) temper (Ref 18).

The pretreatment process, which usually includes cleaning and deoxidizing or desmutting steps, can have a strong effect on the surface microstructure and thus on the formation of a coherent conversion coating. In the case of the copper-aluminum alloys cited above, surface pretreatments involving either acid etching (Ref 4) or final polishing in a basic silicate electrolyte (Ref 7) produce a surface that contains a relatively uniform layer of copper, as detected by spatially resolved AES. The enriched copper found on the solid solution matrix results from either selective dissolution of the aluminum and/or redeposition of the copper that was dissolved from the intermetallics and/or solid solution. The chromate solution "sees" the homogeneous surface and readily forms a chromate conversion coating over the copper-rich interface, leaving the interface intact (Ref 7). As indicated by transmission electron microscopy studies of electropolished and acid-etched samples of high-purity aluminum that were subsequently chromated, the hydrated chromium oxide coating initially deposits on the metal ridges (the cathodic sites, produced by the pretreatment process) while the anodic sites, where the aluminum oxide was continuously attacked by fluoride ion, lie between the metal ridges (Ref 19). These studies illustrate the importance of the pretreatment steps in producing a homogeneous surface layer before application of the conversion coating.

## Environmental Concerns

The use and disposal of chromium and chromium compounds have received much regulatory attention because of the toxicity of chromium and indications that it is a cancer-causing agent. A summary of studies on the mutational effects of chromium compounds in bacteria, mammalian cells, and human cultures was published in 1986 (Ref 20). In 1993, a listing of hazardous chemicals stated that "Chromate salts are suspected human carcinogens producing tumors of the lungs, nasal cavity and paranasal sinus" (Ref 21). This list indicates that some type of mutational data was reported for all chromium compounds. Hexavalent chromium compounds appear to be the most severe; most are designated as "confirmed carcinogens." One trivalent chromium salt,  $\text{Cr(III)}$  acetate, is now also a confirmed carcinogen. Other  $\text{Cr(III)}$  salts are classified as "questionable human carcinogens."

To quote an earlier researcher in this field, "One of the biggest needs involving the future use of conversion coatings [for aluminum] in aerospace is to find non-toxic substitutes for those chemical processing solutions which are now labeled as pollutants" (Ref 3). Only aerospace was mentioned, because restrictions were expected to be first observed with aluminum fabricators due to the role played by the federal government in setting standards for aircraft manufacture. In the years that have elapsed since this statement was made, very few chromium-base treatments have been replaced by environmentally safer technology, and restrictions continue to be imposed on the levels of chromium in waste water effluent, solid waste, and the air to which workers are exposed.

In the United States, regulations regarding hazardous waste disposal and monitoring proliferated from the mid-1970s through the 1980s. Congress passed several laws empowering the Environmental Protection Agency (EPA) to set regulations for the control of hazardous waste (see Ref 22 for a review up to 1991). Much of this legislation espouses "cradle-to-grave" management of hazardous waste. Some of the principal legislation enacted by Congress includes the Resource Conservation and Recovery Act (RCRA) of 1976, the Safe Drinking Water Act (SDWA) of 1974, the Toxic Substances Control Act (TSCA) of 1976, the Hazardous and Solid Waste Act Amendments (HSWA) of 1984, and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or Superfund) of 1980. Most of these laws have been amended (i.e., reauthorized) at least once since their initial passage. In a number of cases, considerable time passed after enactment of the law before the EPA was able to put the basic regulatory framework together (e.g., 4 years elapsed after passage of RCRA before the basic regulatory structure was in place). HSWA resulted from Congress's dissatisfaction with the EPA's progress with RCRA. All regulations are first published in the *Federal Register*, after which they become part of the Code of Federal Regulations under Title 40, which deals with protection of the environment.

As a result of these laws, chromium and its compounds became specific targets for regulatory control. In 1975 the National Institute for Occupational Safety and Health (NIOSH) recommended a standard for occupational exposure to  $\text{Cr(VI)}$  (Ref 23). The document described a number of studies that detailed medical problems observed by workers exposed to chromium. Included in this report was evidence indicating that certain  $\text{Cr(VI)}$  compounds were carcinogenic. The List of Suspect Carcinogens published by NIOSH now contains a number of chromium-containing compounds.

As a result of regulations enforcing RCRA, all facilities involved in electroplating were forced to comply by 1 July 1984 with the Electroplating Pretreatment Standards that appeared in the 28 January 1981 *Federal Register* (Ref 24-28). These standards were later broadened to include the anodizing and conversion coating industries;

they were also made more stringent in the Metal Finishing Regulations that were printed in the 15 July 1983 *Federal Register* and enacted in 1986 (Ref 24-26, 29). Both sets of regulations were imposed by the EPA through local publicly owned treatment works. These regulations placed discharge limitations on various metals, such as chromium, and on other substances, such as those containing cyanide. Total chromium was limited to 2.77 mg/L/day, with a monthly average of 1.71 mg/L/day, and total cyanide was limited to 1.20 mg/L/day, with a monthly average of 0.65 mg/L/day.

In 1986, chromium and its compounds were put on the Community Right-to-Know List, which resulted from the Superfund Amendments and Reauthorization Act (SARA) of 1986 (Ref 21, 22). SARA established the Community Right-to-Know Program, which requires industry to provide information on the type of chemicals being used at their facility. This was only the beginning; many other regulations governing chromium compounds have been promulgated.

As of the time of this writing, the 1994 session of Congress is expected to pass a second reauthorization of the Clean Water Act (enacted in 1972 and first reauthorized in 1986) that will reflect the "polluter pays" philosophy (Ref 30). The intent of this reauthorization is to provide funding for public water pollution control projects through taxation on discharges. Five groups of taxable pollutants, with tax rates based on toxicity, have been compiled. Chromium falls in Group 4 and cyanide is found in Group 5; these two groups carry by far the highest tax rates. A few milligrams of these substances in the waste stream can warrant a large monetary fine over a year for a high-volume metal finisher.

Agencies such as the Department of Transportation are strengthening restrictions for shipment of treatment chemicals such as hydrofluoric acid, which is found in many chromate conversion coating formulations. Individual state EPAs may also enact their own restrictions, which could further restrict the use of harmful treatment chemicals. For example, on 24 July 1989, both Massachusetts and Oregon enacted sweeping toxic waste reduction bills (Ref 31). These bills require industries to prepare plans to reduce their use of toxic substances and to recover or reuse toxic materials from their effluents. The Massachusetts Toxics Use Reduction Act sets as a goal a 50% reduction of toxic waste in the state by 1997. Although no one can predict whether the use of chromium compounds and accelerators such as potassium ferricyanide will be completely banned, the trend in legislation is obviously making the search for viable alternatives to the current technology a top priority.

Furthermore, the Environmental Protection Agency (EPA) is scheduled to be elevated to the Cabinet level, with the head administrator assuming the post of Secretary of the EPA (Ref 30). This will attach an even greater significance to the role of the government in enacting and enforcing legislation directed at maintaining a safer environment.

## Alternative Technologies

Much research has focused on finding an alternative to chromium-base compounds for use in conversion coating formulations. In fact, the scientific and patent literature show that attempts have been made to incorporate most elements in the periodic chart (except for radioactive elements and the rare gases) into films. This article gives the rationale for various research paths, along with specific examples where appropriate. Three principal subjects are discussed: deposition of organic-based coatings from aqueous solution, deposition of multivalent metals from aqueous solution, and corrosion-resistant surface layers formed from the gas phase, with or without the use of high-energy light or particle beams (e.g., laser and ion beams).

**Organic-Based Coatings.** Given that a large number of water-soluble organic corrosion inhibitors are known to exist (Ref 32, 33), conversion coatings based on organic molecules are logical alternatives to chromium. For example, molecules containing the azole functional group (i.e., those having at least two ring nitrogens in a five-membered ring, such as benzotriazole) are known to be effective corrosion inhibitors for copper (Ref 34) and zinc (Ref 35) and are used commercially in cooling water applications to protect copper piping.

The difficulty in making organic-based conversion coatings of sufficient thickness is that organic species are normally poor oxidizing agents, such as chromic acid. This prevents film thickening because of aluminum oxidation and formation of insoluble oxide and hydroxide species. Typical inhibitor-formed films have thicknesses of only 100 Å or less, making their use in severely corrosive environments impractical. In addition, the time required to form such films can be hours or more (Ref 35) unless it is possible to accelerate their deposition through use of surface activators such as fluoride ion. Aqueous solubility can also be a limitation for some molecules.

Even though these films may be thin, they have application in areas such as the treatment of architectural aluminum (since this material is not usually continuously exposed to corrosive environments). In addition, organic-based conversion coatings have the potential of being excellent undercoats for organic (paint) finishes, for adhesion can be expected to be strong between similar types of molecules. Both sets of molecules contain various active functional groups that can interact (e.g., through hydrogen bonding or possibly formation of cross-linked or intertwined structures). It is likely that organic-based treatments will find some application in replacing chromium-base systems, but great difficulties exist in attempting to produce treatments that can pass the rigors of 168 and 336 h exposure to salt spray, as required by MIL-C-5541 and MIL-C-81706 on active aluminum alloys such as 7075-T6 and 2024-T3.

**Multivalent Metals.** The most logical method for obtaining a chromium replacement is to choose another transition, or even a rare earth metal, that has at least two stable oxidation states, is a good oxidiz-

ing agent, and has high corrosion resistance. To this end, patents and patent applications exist for using most of these metals in some type of formulation to yield a conversion coating. Not all metals are good oxidizing agents, but the ability of certain metals to oxidize can be enhanced through complexation with the appropriate species.

The fluoride-based formulations used in chromate conversion coatings cannot be used with most metals because of the insolubility of many metal fluorides. Other surface activators need to be chosen, and peroxide, nitrate, and chloride are common substitutes for fluoride (see examples below). The initial choices would be molybdenum-based and tungsten-based reagents, because these elements lie under chromium in the same group of the periodic table and both metals are well known for their corrosion resistance. These metals have been extensively researched, but formulations based on them have not been able to match, let alone surpass, the performance shown by chromate coatings (Ref 36). Molybdates and tungstates have found some application as accelerator replacements for the ferricyanides. Three multivalent metal-based systems that have recently received considerable attention in the open literature and/or have reached the trial stage in various aluminum industries are described below.

**Rare Earth Metals.** Treatments based on Ce(III) and other rare earth metals were examined first in Australia (Ref 37-39) and later in the United States (Ref 40-42). Coatings in excess of 1000 Å in thickness and rich in cerium + oxygen species were formed on aluminum alloy 7075 after a 20-day exposure to a 100 ppm CeCl<sub>3</sub> solution at pH 5.8 (Ref 43). X-ray photoelectron spectroscopy (XPS) indicated that the film contained both Ce(IV) and Ce(III) species, which likely existed as CeO<sub>2</sub>, Ce(OH)<sub>4</sub>, and Ce(OH)<sub>3</sub> (Ref 43). X-ray absorption near edge structure (XANES) studies likewise indicated the presence of a mixed cerium valence film (Ref 44). Coating process time was decreased to 10 min by adding hydrogen peroxide, lowering pH, and increasing the solution temperature (Ref 45). Immersion of the film in NaCl solution converted all of the Ce(III) to Ce(IV) (Ref 43). Measured corrosion rates of treated 7075 indicated that a 50% reduction in corrosion rate from that of an untreated substrate can be obtained (Ref 45). No mention of its effect on pitting corrosion was made, but excellent paint adhesion (comparable to that on chromated surfaces) was observed.

A cathodic mechanism has been proposed to account for cerium deposition: pH is increased at the cathodic sites, because of either oxygen reduction or hydrogen evolution, to form excess hydroxyl ions (Ref 37). The hydroxyl ions can attack the metal surface and react with metal ions in solution. The mixed metal oxide/hydroxide then precipitates onto the surface to form the corrosion-resistant film.

The development of "stainless aluminum" has also been claimed for cerium-treated pure aluminum and aluminum alloy 6061-T6 (less satisfactory behavior was obtained for aluminum alloy 2024-T3) (Ref 46). The treatment involves a 2 h

exposure to three separate solutions: boiling 10 mM Ce(NO<sub>3</sub>)<sub>3</sub>, boiling 5 mM CeCl<sub>3</sub>, and anodic polarization in the passive region in deaerated 0.1 M Na<sub>2</sub>MoO<sub>4</sub>. Excellent corrosion resistance was found upon immersion of treated samples in 0.5 N NaCl. Scratched surfaces also showed excellent resistance. No mention of salt spray testing of the cerium-based treatments was made, however.

Ce(III) molybdate has shown some promise as a corrosion inhibitor in an epoxy/polyamide primer but still does not match the performance of strontium chromate pigmented primers (Ref 47).

**Manganese-based treatments for aluminum and aluminum alloys** have recently been patented (Ref 48-50). One of the treatment steps involves exposure of the aluminum alloy surface to permanganate ion, which contains manganese in the +7 oxidation state. Like chromate, the permanganate ion is an excellent oxidizing agent, suggesting that the mechanism of film formation is similar to that of chromate. Although no information on film thickness or composition is given in the patents, one would expect that the manganese found in the film is in some reduced oxidation state (probably either +4 or, more likely, +2). This is a multistep treatment in which many of the steps require elevated temperatures. The last step, which involves a "seal" with alkali metal silicate, is probably necessary to block the pores created in the film during deposition. Good corrosion resistance, as evidenced from salt spray exposure, has been observed for high-copper-containing aluminum alloys.

**Trivalent Cobalt.** The final system is based on the use of basic solutions containing complexes of trivalent cobalt, for example, Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> (Ref 51). CoCl<sub>2</sub> has shown some promise as an inhibitor for aluminum alloy corrosion (Ref 52). It is likely that Co(II) compounds have been examined in the presence of fluoride, for CoF<sub>2</sub> does possess appreciable solubility in water. This new system deposits a corrosion-resistant cobalt-containing film on aluminum alloys. Preliminary examination of this coating with electrochemical impedance spectroscopy (EIS) indicates that the coating has corrosion-resistant properties similar to those of a chromate treatment on aluminum alloy 2024-T3 (Ref 53). Good corrosion and paint adhesion properties are also claimed (Ref 51).

**Gas Phase.** Although gas-phase/high-vacuum techniques will probably not replace chromating of large parts or continuous chromating of high volumes (e.g., aluminum alloy coil stock for beverage cans) in the near future, these processes should not be ignored, for they offer the possibility of forming entirely new corrosion-resistant films. Experiments have already been undertaken in Japan to produce large surface areas of galvanized steel sheet through gas phase deposition of zinc (Ref 54). A partial selection of these techniques as they apply to the formation of corrosion-resistant films on aluminum and magnesium is briefly reviewed below.

Sputter deposition and ion implantation are nonequilibrium alloying techniques that allow

solid solution alloys to be formed, which are unattainable by conventional alloying techniques. Corrosion-resistant aluminum-molybdenum and aluminum-chromium alloys have been formed by cosputter deposition of aluminum with each of the two metals (for details see Ref 55 and 56). Ion implantation of silicon, chromium, zirconium, niobium, and molybdenum into pure aluminum have been found to enhance pitting resistance of the aluminum, whereas implantation of magnesium and zinc had no effect on pitting resistance or lowered pitting resistance, respectively (Ref 57, 58). Beneficial results have been observed for iron and boron implantation into magnesium and magnesium alloys (Ref 59, 60). Ion implantation can easily form layers up to several thousand angstroms thick, depending on the mass of the species being implanted and the ion beam energy. Even thicker layers can be produced by ion beam mixing, which combines ion implantation with a vapor deposition process such as evaporation or sputtering.

Corrosion-resistant oxide mixtures can be formed on aluminum and magnesium by laser irradiation of a surface that contains a thin vapor-deposited metallic film such as chromium or molybdenum (Ref 61-64). Laser irradiation is performed in an air or oxygen atmosphere to enhance the formation of oxides. The rapid heating and cooling rates provided by a laser can produce an amorphous, metastable surface composition that enhances the corrosion resistance of the substrate. Laser-irradiated chromium and molybdenum films on pure aluminum have been found to be very resistant to pitting by chloride ion (Ref 64).

Metal organic chemical vapor deposition (MOCVD) can also be used to deposit corrosion-resistant oxides onto low-melting metal substrates. MOCVD involves the deposition of thin oxide films by thermal decomposition of organometallic compounds. Metal alkoxides are the most commonly used precursors and have been used to deposit metal oxides such as  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  (Ref 65-68). The metal alkoxides generally have high vapor pressure and readily decompose at low temperatures (as low as 150 °C, or 300 °F). For example,  $\text{Al}_2\text{O}_3$  films have been obtained by decomposition of the aluminum alkoxides: tri-tert-butoxide, tri-sec-butoxide, tri-n-butoxide, tri-isopropoxide, and acetyl-acetonate (Ref 69). Interestingly, the introduction of water vapor to aluminum acetyl-acetonate produces an extremely ligand-free, pure  $\text{Al}_2\text{O}_3$  with a smooth surface morphology (Ref 70).

Additional information on alternatives to chromium is available in the article "Chromium Elimination" in this Volume.

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