The term conversion coating, as used in the metal-finishing industry, refers to the conversion of a metal's surface into a surface that will more easily accept applied coatings and/or provide for a more corrosion-resistant surface. Conversion coatings are rather thin (not over 600 nm thick on aluminum), quickly and easily formed, easily scratched, and, if used to enhance paint adhesion, are coated shortly after being formed to prevent degradation of the conversion coating. Conversion coatings for aluminum have been in use since the early 1920s and there are a number of different products on the market. The four main types of conversion coatings in common use are based upon (1) the production of a film of chromium hydroxides and/or oxides; (2) the production of a film of precipitated heavy metal phosphates or oxides; (3) the use of various synthetic polymers, with or without heavy metal phosphates or oxides; and (4) the formation of a manganese oxide/aluminum oxide film by use of permanganates.

CLEANING AND DEOXIDATION

In any metal processing procedure (painting, conversion coating, anodizing, etc.) the most important part of the processing is the proper cleaning of the metal surfaces prior to processing. Cleaning is the removal of surface oils and loose dirt. In general, alkaline cleaners do the best job. When used on aluminum they should be non-etching, as etching will leave difficult-to-remove alloyed elements, such as heavy metals or elemental silicon, and may pit the metal surface (see Fig. 1). To prevent excessive etching, silicates are usually added to alkaline cleaners. If added they should be present in small amounts (generally less than 500 ppm) as excessive amounts will hinder cleaning and leave difficult-to-remove silicate deposits.

Deoxidation is the removal of oxides and other inorganics that would otherwise interfere with further processing of the aluminum without significant attack upon the aluminum surface. To prevent excessive attack (see Fig. 2), deoxidizers generally contain an oxidizing agent designed to maintain a thin film of oxide on the metal's surface. This allows for the oxide to be removed rather than having a direct attack on the metal by the deoxidizer.
Many of the deoxidizers now in use will run an iron (III) salt, such as ferric sulfate coupled with hydrogen peroxide, or any one of a number of different oxidizers (chlorates, nitrates, persulfates, etc.). Iron-based de-oxidizers leave deposits of iron on the surface of the aluminum, which encourage galvanic corrosion, as you now have two dissimilar metals in direct contact with each other. The other oxidizers mentioned are, in general, not strong enough oxidizing agents to maintain a good oxide film on the metal or have toxicity problems associated with them. The best oxidizers for aluminum are those based on nitric acid coupled with another oxidizer, such as hydrogen peroxide or sodium bromate, as bromates are strong enough oxidizing agents (when used with nitric acid) and quite environmentally friendly. Unlike other acids, nitric acid will dissolve aluminum oxide but has very little effect upon aluminum (see Figs. 3-6).
With high-silicon-content alloys it is very difficult to avoid the use of fluoride in spite of their toxicity. If you must use fluorides keep the fluoride level low (generally not more than 200 ppm) as excessive amounts of fluorides will leave a white deposit of insoluble aluminum fluoride on the metal’s surface and will pit the metal, as will the use of acids other than nitric and/or the use of heavy metals such as iron. For years, chromic acid and/or chromates were used in deoxidizers in conjunction with nitric acid, and were generally considered the best deoxidizers on the market. In addition to the toxicity issue associated with the use of hexavalent chromium these deoxidizers always leave a thin deposit of chromium oxides on the metal's surface, which will not allow for the subsequent use of a non-hexavalent chromium conversion coating system.

HEXAVALENT-CHROMIUM-BASED CONVERSION COATINGS

All conversion coating processes use the hexavalent chromium process of producing a film of mixed aluminum oxides, chromium oxides, and chromium hydroxides as a "yardstick" against which all other conversion coatings are measured. Were it not for the issue of toxicity, they would still be in wide use today. The conversion coating film is generated by the reduction of the hexavalent chromium to form a jell-like mixture that, when dry, initially has an open porous structure that allows for the application of organic coatings. After 8 hours, these coatings become quite hydrophobic in nature and much more difficult to coat due to the formation of an inorganic polymer consisting of various chromium plus three compounds and aluminum oxides. For this reason it is generally recommended that they be painted shortly after being conversion coated. It is this polymer that is primarily responsible for the extremely good corrosion resistance shown by these conversion coating systems. It is assumed that traces of hexavalent chromium left in the coating will "self-seal" any breaks that may occur in the coating. These traces of hexavalent chromium compounds are also responsible for the various shades of a yellow to gold color that occur in the coatings. This color is a very useful feature in that it provides for a very quick and easy way to determine if, in fact, the coating has formed properly and of the relative thickness and corrosion resistance of the conversion coating in question.

A clear chrome conversion coating is used when a bare minimum of corrosion resistance is necessary and a conductive surface is required. These coatings are about 100 to 120 nm thick and about 20 mg/ft² in mass. An iridescent to light-yellow coating is used as a paint base and is about 300 nm thick with a mass of 50 to 60 mg/ft². A yellow to gold coating is necessary
for maximum corrosion resistance and has a thickness of about 500 to 600 nm with a mass of about 80 to 100 mg/ft².

The coating compositions must be maintained at a pH of 1.2 to 1.9 and are known as simple chrome fluoride or accelerated chrome fluoride compositions. The chrome fluoride baths contain about 3 to 4 g/L of chromic acid, 3 to 5 g/L of sodium dichromate, and about 1 g/L sodium fluoride. The accelerated baths will contain about 2 to 5 g/L of potassium ferricyanide. One major drawback to the use of these coatings is the fact that they decompose when heated above 160°F due to the loss of water of hydration, which holds their polymeric network together. This feature limits their use to non-powder coating applications. Non-chrome systems attempt to model themselves, in one aspect or another, after the features of the hexavalent chrome systems due to the extreme corrosion resistance shown by this system. Over the years many attempts have been made to duplicate the coating formed by hexavalent chromium conversion coatings using trivalent chromium compounds in place of the hexavalent chromium compounds.

None of them has been successful without first producing hexavalent chromium by oxidizing the trivalent chromium during the course of the reaction; as a result, traces of hexavalent chromium compounds are always found on trivalent-chromium-treated aluminum surfaces.

HEAVY METAL PHOSPHATES

The use of various heavy metal phosphates (iron, zinc, manganese, chromium, etc.) is the oldest of the conversion coating methods in use, and provides the best possible surface for paint adhesion. The corrosion resistance of these coatings is quite poor, with the exception of the hexavalent chromium-based phosphate. Even this is poor relative to a non-phosphate-based hexavalent chromium composition. The use of iron or zinc phosphates on aluminum will leave deposits of iron or zinc on the surface of the aluminum and give rise to galvanic corrosion. In addition these systems will pit the surface of the aluminum. Pits act to trap and hold unwanted heavy metal deposits, water, salt, etc., and give rise to a very corrosion-susceptible surface. In many shops iron or zinc phosphating solutions will be used on iron, zinc, and aluminum surfaces in order to avoid using more than one bath. Aluminum is a negative catalyst to phosphating on iron or zinc surfaces. Aluminium contents as low as 0.76 g/L will greatly retard the process, and concentrations of 1.13 g/L will completely inhibit coating formation. The only phosphate system designed to work well with aluminum is a chrome phosphate system.
There are a very large number of phosphate conversion systems on the market and still larger numbers of formulations that are available in the literature. With the exception of the heavy metal being used; all of the formulations are rather similar. They require constant monitoring to keep the pH and/or concentration of the chemicals in certain narrow ranges and, in general, have a high rate of chemical usage.

A typical zinc phosphate system would contain in percent by weight:

- Zinc oxide, 10.2
- Nickel oxide, 1.85
- Phosphoric acid (75%), 44.3
- Nitric acid, 4.5
- Hydrofluoric acid (70%), 0.97
- Fluosilicic acid (35%), 4.2
- Water, 33.0
- Sodium nitrate, 1-2

The coatings produced consist primarily of porous heavy metal aluminum phosphates. Thin gray coatings are produced in about 1 to 2 minutes at 140 to 150°F with a coating mass of about 100 to 500 mg/ft² and a thickness of about 240 to 480 nm.

**SYNTHETIC POLYMERS**

Synthetic organic polymers were developed in the early 1970s in an effort to improve the adhesion characteristics of water-based painting systems. In this application they work well and will also provide a degree of corrosion protection due to high-humidity conditions. Unless mixed with hexavalent chromium compounds, they provide no salt spray protection. They are very effective wetting agents, which allows for a "water break-free" surface to form over soiled areas. This often results in paint adhesion failures requiring expensive stripping and repainting.

They have a chemical structure quite similar to that of tannic acid, which was used to improve corrosion resistance and paint adhesion on steel and zinc in the late 19th and early 20th centuries. Tannic acid is a polyphenolic compound with a backbone consisting of various simple sugars. Like tannic acid these polymers will only work effectively at certain precise concentration and pH levels. As such, they require constant monitoring. As a general rule, they will decompose at about 330°F leaving a brown stain; and as a result they do not work well in many powder coating applications. Synthetic organic polymers are quite often used in conjunction with zirconium, titanium, or hafnium compounds to increase paint adhesion and prevent water staining of aluminum (to prevent staining, phosphates must be present) due to conditions of high humidity.
The organic polymers used in these applications are attempting to duplicate the inorganic polymers formed in hexavalent chromium conversion coatings with much less success as these polymers are not being formed while in intimate contact with the aluminum. As a result, the attachment of the polymer to the metal's surface (due to the presence of hydroxyl and/or amine groups on the polymer) is not good enough to prevent water and/or salt from getting to the metal’s surface and causing paint adhesion or corrosion problems unless the surface is cleaned to an extent only possible in a laboratory. Even then the corrosion resistance will not come close to that obtained by the use of hexavalent chromium compounds. On average the coatings are about 10 nm thick\textsuperscript{11} with a mass of about 10 to 12 mg/ft\textsuperscript{2} when used with one of the heavy metals mentioned above. Due to the small amount of material present, it is difficult to determine the uniformity or the actual amount of material without the use of expensive laboratory equipment.

Since the late 19th century various polymeric networks of metal oxides and silicon oxides have been used to prepare ceramic or glass surfaces to accept paints.\textsuperscript{13} This process has been studied extensively for the preparation of metal surfaces to accept paint since the 1970s when a low temperature process was developed to produce inorganic gels of various transition metal alkoxides and silicon alkoxides. This is referred to as the "sol-gel" process as a colloidal suspension ("sol") is first formed and then caused to undergo gelation ("gel") to form a unique inorganic network of transition metal oxides and silicon oxides.\textsuperscript{14}

If prepared properly a particular sol-gel is able to provide excellent paint adhesion and in some cases excellent corrosion resistance to a particular aluminum alloy.\textsuperscript{14} As in the case of the polymers modeled after tannic acid, the surface conditions required of the aluminum being processed and the conditions necessary for the proper formation of the sol-gel in question are extreme relative to what may be done in the average industrial metalworking facility. The films are quite thin (50-100 nm), clear, and very difficult to detect without the use of sophisticated laboratory equipment not generally available to the average metal-finishing facility. If not applied properly you will have paint adhesion and/or corrosion problems. Various attempts have been made to attach silanes directly to the surface of aluminum alloys,\textsuperscript{15} but once again the processing is quite involved, the films (50-100 nm) are quite thin, and detecting them is a very difficult process for the average metal-finishing facility. If not attached properly to the metal's surface you run the risk of expensive repainting procedures or corrosion failures.

The exposure of aluminum or its alloys to solutions of cerium, lanthanum, or yttrium chlorides will produce a film of the corresponding rare earth metal oxide and/or hydroxide on the metal's surface, in the form of an inorganic polymer.\textsuperscript{16} As in the case of hexavalent-chromium-generated films this type of inorganic polymer will not stand up to the temperatures used in powder coating and will decompose due to the loss of water of hydration. As in the case of hexavalent-chromium-generated films this is a barrier-type film but is not nearly as good of a barrier. The rare earth salts used are, indeed, quite rare, and as a result rather expensive. Used by themselves these films will not pass the standard MIL-C-5541E salt spray corrosion tests but do show significant improvement in corrosion resistance. The coatings may be clear (about 30 mg/ft\textsuperscript{2} and 100 nm) or have a characteristic yellow color to them (about 60 mg/ft\textsuperscript{2} and 300 nm) that allows for a visual determination of the presence of an acceptable coating. These coatings may be sealed with various organic polymers to improve their corrosion resistance and/or paint adhesion characteristics.

Cobalt compounds, which have been complexed with ammonia, will generate a barrier film of various cobalt oxides and/or hydroxides on a clean aluminum surface.\textsuperscript{17} This film is a polymeric barrier-type of coating, held together by water of hydration, which will also
decompose when heated to the temperatures experienced in powder coating applications. Thin films (25 mg/ft² and about 120 nm) are clear, and thicker films (up to 250 mg/ft² and 600 nm) are yellow in color. The aluminum requires an extensive series of cleaning steps in order to be properly activated to accept the coating; the solutions used are quite concentrated with cobalt, which is expensive; and a heavy metal subject to being removed from the workplace due to environmental considerations. By themselves these conversion coatings will not pass the standard salt spray requirements of MIL-C-5541E and are sealed with one or more organic polymers to improve their corrosion resistance.

**PERMANGANATES**

Going across the third row of transition metals, from left to right, there is a great deal of similarity between the elements in terms of their chemical and physical characteristics, until you reach iron. Thus, the conversion coatings produced by hexavalent chromium compounds are, as expected, quite similar to the one's produced by the heptavalent manganese found in permanganate compounds, as shown by studies at Oxford University. As in the case of hexavalent chromium compounds, the heptavalent-manganese-produced conversion coating contains a mix of various manganese (in place of chromium) and aluminum oxides of various oxidation states. The higher-oxidation-state manganese oxides are reduced to a lower oxidation state, as necessary, in order to prevent oxidation of the aluminum, just as higher-oxidation-state chromium oxides are reduced in the hexavalent conversion coating system. The hexavalent-chromium-based system will produce a protective inorganic polymer, while the heptavalent manganese system will not. This reduces the protective properties of the heptavalent-manganese-based system, but allows the manganese-based system to be used in powder coating applications, as heat will have no effect upon the heptavalent-manganese-generated conversion coating. The paint adhesion characteristics of the heptavalent-manganese-based system are as good as, or better than, the hexavalent-chromium-based system.

With the exception of high copper and/or high zinc alloys (2024, 7075 aircraft alloys, etc.), the corrosion characteristics are the same. In order to compensate for this deficiency, the heptavalent-manganese-based system may be used with a unique organic seal that chemically bonds to the conversion coating to allow for electrical contact resistance. This has shown corrosion resistance that exceeds all the requirements of MIL-C-5541E. The heptavalent-manganese-based system gives a yellow-gold color (about 0.5 mg/ft² and about 20 nm), which is almost equivalent to that of the hexavalent-chromium-based system, assuming that the conversion coating has properly formed and that the aluminum has been properly cleaned. It is very easy to strip and apply another conversion coating if the coating has not properly formed. A cold-applied version (non-dip tank) of the conversion coating, which reacts in a few seconds, is available for doing large structures, assuming the surface has been properly cleaned, to give a uniform and even yellow-gold color. A clear (about 0.1 mg/ft² and 10 nm) version is available with an easy-to-use test solution to confirm that the conversion has properly and uniformly formed.

Permanganates have been used for over 80 years to treat potable water systems, and they are on the list of materials allowed in drinking water. Elemental manganese and/or soluble manganese divalent compounds, starting with heptavalent manganese, are very difficult to generate and, as such, are not produced when permanganate is introduced to a potable water system under normal conditions (absence of any strong reducing agents). Insoluble and very
stable reduced manganese oxides are all that are normally produced when permanganates enter a potable water system, which is why they are used in potable water systems.

**COIL COATING PROCESSES**

All of the above processes may be modified to allow for the application of the conversion coating on a continuous strip of metal, although not all of them are used in this fashion. The strip to be coated is alkali cleaned; rinsed in DI water; rinsed in a mild acid solution to remove traces of alkali; rinsed again in DI water; and then the excess water is removed by the use of a squeegee roll to prevent dilution of the applied conversion coating. In many cases fumed silica is added to enhance paint adhesion, giving a wet film thickness of about 12,000 nm and a dry coating mass of about 19 mg/ft². In another approach, various organic polymers are added to provide for increased paint adhesion giving a wet film thickness of about 4,000 nm and a dry film mass of about 14 mg/ft². The strip is usually heated to about 120°F before application of the coating to enhance drying of the film, and the film is finally dried at between 100 and 500°F depending upon the type of conversion coating being applied and the speed of the strip. In some cases the strip is actually etched by the applied coating to generate metal ions, which then mix with an applied organic polymer to provide for better paint adhesion. All coil coating processes are primarily designed to enhance the paint adhesion characteristics of the aluminum surface being coated.

**RESULTS AND DISCUSSION**

The primary function of any conversion coating is to provide for a corrosion-resistant surface as insurance against any breaks in the secondary coating. By far, the greatest degree of success, in this regard, has been the hexavalent-chromium-based conversion coating systems. Any attempt to duplicate this degree of success must, of necessity, be based upon a process that matches, as closely as possible, to the hexavalent-chromium-based system. Of the approaches taken, only the permanganate-based conversion coating system approaches the results shown by hexavalent chromium in actual test results and in theory. The permanganate-based system allows for the use of powder-coating- and non-powder-coating-based coating systems and is the only heavy-metal-based system that may be disposed of with no environmental concerns.

**CONCLUSION**

Hexavalent-chromium-based conversion coating systems have been used for over 60 years because they have provided such excellent corrosion resistance and paint adhesion characteristics when used with aluminum and its alloys. Any replacement that expects function as well must be designed to duplicate its characteristics as closely as possible. The manganese oxides produced by the heptavalent-manganese-based system are by far the most closely related to the chromium oxides and hydroxides in terms of their respective chemistries. Thus, the aluminum oxide/manganese oxide film, as produced by the heptavalent-manganese conversion coating system, is the most closely matched in terms of performance and actual chemistry.

**BIOGRAPHY**

John Bibber is Research and Laboratory Director at Sanchem, Chicago. He holds a BS and MS in chemistry from Shippensburg University, Shippensburg, Pa., and a Ph.D in organic chemistry from the University of Georgia, Athens, Ga. A holder of U.S. and international patents on surface treatment chemicals of aluminum and other metals, he is a member of the ASTM, AESF, and ACS.
REFERENCES
1. Definitions Committee, Federation of Societies for Coating Technology, Philadelphia; p. 177; 1978
5. U.S. Patent 4,883,541
6. British Military Specification DBF STAN 03-18/1; 2000
16. Mansfeld, F. et al., Corrosion 45(8):615; 1989
25. British Patent 1,349,826, Amchem Products Inc.; 1972