Nuts & Bolts: 
What This Paper Means to You

This paper is a comprehensive tour of conversion coatings on both aluminum and magnesium. It goes beyond chromates to new alternatives, and covers how conversion coatings work, as well as how they perform.

Conversion Coatings for Aluminum and Magnesium

by Don Baudrand, CEF

Conversion coatings can be produced on a variety of metals by chemical treatment or electrolytic processes. This paper will discuss conversion coatings on the light metals aluminum and magnesium. Preparation and operating process parameters are important to obtaining best results. Corrosion protection, self-healing, dyeing, electrical conductivity, bonding, hardness and heat resistance characteristics of conversion coatings containing chromium are discussed. MIL specifications and testing are included. The mechanism of film formation and chemistry are also discussed.

A conversion coating refers to the chemical treatment of a metal surface where the metal is converted into a non-metallic form at the surface, forming a film. Conversion coatings have an important role in the metal finishing industry because of their enhanced corrosion protection and decorative appeal. Conversion coatings have been around for many years. Coatings for iron and iron alloys such as black, and bluing, for copper and brass, such as patina Verdi green and many others are well known. Chromate coating was used for lead from 1872. Chromate solutions were used to treat magnesium as early as 1924. Chromate conversion coatings were developed for zinc and cadmium from 1924 to 1936. Chromates for copper, silver and aluminum followed. The first true chromate for aluminum was introduced by Stricklen in 1952. Later, improved chrome conversion coatings for aluminum were introduced. Chromated aluminum became very important for reasons of corrosion protection, low electrical resistance, improved paint and adhesive bonding. Further, they possess self-healing properties that protect scratches by the inhibiting characteristics of hexavalent and trivalent chromium that migrate into the scratch and maintain the protection. Chromates also have low emissivity coefficients, less than those of anodized or painted surfaces. This is important in preventing parts from heating up during exposure to infrared radiation. However for other applications, emissivity can be increased by applying a thicker film. Recently, non-chromium containing conversion coatings were introduced that are improvements over earlier such processes and may rival chromate coatings in some respects.

Chromate conversion coatings for aluminum

Chromate conversion coatings are formed when the chemicals in the chromating solution react with aluminum, dissolving the aluminum oxide and some metal causing a rise in pH at the solution-metal interface. The result is precipitation of complex hydrated oxides of aluminum, chromium and chromium chromate that form a gel on the surface. A portion of the hexavalent chromium is reduced by the metal surface to trivalent chromium as a precipitate. Hexavalent chromium provides the greatest corrosion protection, but the trivalent chromium is necessary to form the proper coating. Activators play an important role in forming the best coating. Materials that serve as activators are chloride, sulfate, formate, acetate, fluoride, nitrate, phosphate and sulfamate ions. These are used in small quantities. Larger amounts will result in unsatisfactory coatings.

Chromate conversion coatings for aluminum were developed during and following the Korean War. The acceptance of these coatings arose from their use as a low cost substitute for anodizing and their desirable properties. Good corrosion protection, the ability to seal over scratches, low electrical resistance, good grounding of aluminum chassis, good paint adhesion and adhesive bonding characteristics, as well as good spot-welding and arc welding properties expanded the use of chromate conversion coatings rapidly. A chromate coating protects aluminum from oxidization and the film acts as a flux to facilitate good spot and arc welding characteristics. Bare aluminum
oxidizes quickly and continues to build oxide thickness in most environments. Its low infrared emissivity is important in some applications to prevent excessive heating. Table 1 compares the emissivity of chromated aluminum with other surfaces. The scale is from 0 to 1, where the most desirable value approaches zero.

Changing the bath concentration and treatment time can vary the thickness of the chromate coating. Thin coatings are clear. As thickness increases, the color develops as a light iridescent yellow, golden, light brown and finally medium brown. Coatings can be made clear by leaching in hot water. Leaching removes most of the soluble hexavalent chromium, leaving intact the insoluble reaction products that continue to protect, albeit with somewhat less protection. These coatings can be dyed various colors for identification or decorative purposes. It is difficult to maintain exact color matches for decorative applications, but the method is used for special applications.

Thin coatings are used for low contact resistance (good electrical conductivity). Medium and darker (yellow) coatings are best for maximum corrosion resistance. Brown coatings, on the other hand, may indicate an overactive processing solution or a very active surface, such as an alloy high in copper. Copper in an aluminum alloy accelerates the chemical reaction, producing a less satisfactory coating in terms of adhesion and corrosion protection. Chromate conversion coatings protect aluminum from oxidation, and thus these surfaces will have lower electrical resistance than unprotected aluminum. Thinner coatings have lower contact resistance. Clear coatings have the least resistance. Rougher surfaces will have lower contact resistance due to the greater ease of breaking through the coating through contact. However, it remains necessary to break through the coating to assure the lowest contact resistance. The areas around the break do remain protected against corrosion.

**Corrosion protection of aluminum by chromate conversion coatings**

One of the main uses of chromate conversion coatings on aluminum is to protect the aluminum from corrosion. Military specifications require withstanding 168 hr exposure to 5% neutral salt fog (ASTM B-117). In fact the protection can often exceed that requirement to over 500 hr. Salt spray durability of 1000 hr has been reported. The added protection is dependent on several factors. Most important is the condition of the aluminum surface, i.e., the surface must be smooth and free from pits or scratches. Further, the alloy should not be too high in copper and/or other alloying constituents.

**Surface preparation and factors that influence corrosion protection**

In preparing the aluminum for chromate treatment, it is important to clean the aluminum surface, leaving no soils. Careful selection of alkaline or mild acid cleaners is important. Highly silicated alkaline cleaners can leave a silicate film that is not removed by rinses or acid dips. Silicates left on the surface after cleaning will be precipitated by the acid dips. Low silicate cleaners that remove the natural oxide and do not etch significantly are best. Mild phosphoric acid cleaners also work well.

Sometimes etch cleaning is necessary. Etching should be used only in rare cases, such as removing stock for patterning, size reducing or to remove reactive oils that cannot be removed in alkaline cleaners or solvents. Alkaline etched aluminum must be followed by a "deoxidizing" step to remove the smut created in the etching process. Solutions containing chromic acid and sulfuric acid, ferric salts or sulfuric acid-hydrogen peroxide are used.

Thorough rinsing is necessary. Aluminum castings that contain silicon should be treated in nitric-hydrofluoric acid mixture (3:1) or nitric-ammonium bifluoride. If a non-etch or mild alkaline cleaner is used, it is often not necessary or desirable to use a deoxidizer. A mild phosphoric acid or nitric acid may be used. After rinsing, the chromate is applied.

Heat-treating copper-containing alloys, such as 2024 and 6061, causes copper to migrate to the surface. The heat-treat process has fairly loose specifications that can cause more, or less, copper in the surface. Thus batches may vary in the amount of copper in the surface, resulting in varying consequences when chromated. High copper in the surface of the alloy causes an accelerated film formation that adheres loosely. Alternatively, there can be no coating at all actually dissolving the coating as fast as it forms. A treatment in a nitric/fluoride-containing acid dip can only improve the surface of high-copper heat-treated aluminum, such as 2023-T6 or 6061-T6, for chromating. However, the corrosion protection is often reduced.

**Application methods**

Immersing racked parts in tanks is the most common method for applying chromate conversion coatings. However, spray application is a good method for large parts that will not fit into a tank. The chromate can be applied by swab or brush as well. Typical processing time is 1 to 4 min (3 min average) of exposure. After applying the chromate, the parts should be thoroughly rinsed and dried. Careful containment of the spent solution for waste treatment to remove the chromium and ferricyanide from the effluent is required.

Repair of damaged coatings can be made in the field without loss of corrosion protection. As with the case of virgin surfaces, all aluminum surfaces must be clean before applying conversion coatings. A mild phosphoric acid cleaner is ideal. It can be applied in the same way as the chromate. Water is rinsed or swabbed onto the surface, and then the conversion coating is applied.

Chromates may also be applied by steam application, as from a steam cleaner. The moisture from the steam allows exposure to high temperature without dehydrating the coating.

Etching of the aluminum prior to chromate treating will always result in poor corrosion protection. The use of caustic etches (e.g., sodium hydroxide) is particularly bad. The alkaline etch removes aluminum but not the alloying constituents. Many of the alloying constituents create corrosion cells that dissolve away the aluminum, leaving the alloying constituent behind. This can result in capillary holes around the alloy phase “particles” that entrap the etch solution and/or subsequent chemicals that cannot be rinsed out of the capillary voids (Fig. 1). Etching also leaves pits. This results in poor corrosion protection, as shown in Fig. 2. Acid etching is somewhat less destructive, but it can also lead to reduced corrosion

<table>
<thead>
<tr>
<th>Surface Finish</th>
<th>Emissivity</th>
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<tbody>
<tr>
<td>Bare Aluminum</td>
<td>0.03</td>
</tr>
<tr>
<td>Yellow Chromate</td>
<td>0.20</td>
</tr>
<tr>
<td>Anodize</td>
<td>0.7</td>
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<tr>
<td>Most Painted surfaces</td>
<td>0.8-0.9</td>
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**Table 1 Infrared Radiation of Aluminum and Related Protective Coatings**

Plating & Surface Finishing • January 2005
Protection. Pure aluminum is not subject to the problems associated with etching. Low levels of alloying constituents in the alloy will tolerate slight etching without loss of corrosion protection. Immediately after formation, the chromate film is soft, but after 24 hr or after suitable drying, the coating becomes more abrasion-resistant. Drying must be below 66°C (150°F). Higher temperatures cause dehydration of the film and a consequent reduction in corrosion protection.

Do not sand aluminum prior to conversion coating. It has been common practice to sand aluminum in preparation for chromating and painting in the mistaken notion that sanding increases surface area. Sanding leaves scratches that entrap the natural oxide. As shown in Fig. 3, metal splinters and small particles are held tightly by van der Waals forces. It is difficult and in some cases impossible to remove these materials. The natural oxide is loosely adherent, and if not removed will result in poor paint adhesion, adhesive bonding and reduced corrosion protection. Light wet sanding with 600 or higher grit will produce acceptable results only when used on high copper-containing, heat-treated alloys that cannot be chromated by any other preparation procedure.

Chemistry of chromates

The typical processing solution contains hexavalent chromium, 1 to 7 g/L, and nitric acid added to pH 1.2 to 2.2, activators and a ferric complex. It is useful to add 10 ppm of chloride to a new makeup for best results (6.25 g non-iodized salt per 100 gal of solution, if DI water or low-chloride tap water is used for makeup). The reaction that first takes place at the aluminum surface is the dissolution of aluminum oxide and some aluminum, causing partial reduction of hexavalent chromium to trivalent chromium. Then a rise in pH follows, resulting in precipitation of hydrous oxides of chromium and aluminum, and the formation of hydrated basic chromium chromate. The chromate film contains both hexavalent and trivalent chromium. The residual hexavalent chromium provides the best corrosion protection. Hexavalent chromium produces a yellow color. Trivalent chromium produces a light green or clear color.

Effect of impurities in the chromate solution

The following impurities have a negative effect on chromate conversion coatings:

- Phosphates - 200 ppm will stop the coating from forming unless the solution is formulated specifically to include phosphates as a special product.
- Copper - causes precipitation of ferricyanide and thus depletion of ferricyanide, a main ingredient and important to proper performance. Copper reduces corrosion resistance and increases activity. As copper concentration increases it will eventually stop coating formation.
- Zinc - precipitates out with ferricyanide similar to copper.
- Lead - becomes insoluble and precipitates out with no effect.
- Chlorides - 10 ppm is beneficial; 30 ppm or more leads to a loss of corrosion resistance. At higher levels the color lightens, and above 60 ppm, no coating forms.
- Sulfates - 1200-1500 ppm has no effect because it forms an insoluble precipitate with barium. If the conversion coating solution does not contain barium, sulfates behave similarly to chlorides.

Effect of operating parameters

- pH – The pH of the chromating solution should be maintained within the recommended range. Low pH results in faster coating, but also results in thin coatings, etching or no coating. High pH slows the coating rate. The pH range is 1.1 to 1.9, or nominally 1.3 to 1.5.
- Temperature – The operating temperature is often at ambient. However, higher tempera-
Non-chromium conversion coatings for aluminum

There are a variety of non-chromium conversion coatings in use, such as polycrystalline hydrated aluminum oxide coatings, thin structured oxide coatings, molybdenum-based coatings, potassium permanganate induced coatings, sol-gel, no-rinse coatings and sodium silicate films.

A proprietary product that forms a thin structured oxide conversion coating replacement for chrome coatings by cleaning and removing the loosely adherent natural oxide on the aluminum surface and replacing it with a thin structured oxide that is tightly formed is available. The process produces a very wettable surface, ideal for paint and adhesive bonding. Superior adhesion results without sanding or etching the aluminum surface. As with the chromate processes, sanding reduces adhesion. The thickened results without sanding or etching the aluminum surface. As with

The coating can be produced in tank processing, spray or immersion.

Plating & Surface Finishing • January 2005

33
Specifications for conversion coatings on aluminum

The following list contains the most important specifications for the conversion coating of aluminum:

- AMS 2473 - Chemical treatment for Aluminum Base Alloys, General Purpose Coating.
- AMS 2473 - Chemical Treatment for Aluminum Base Alloys, Low Electrical Resistance Coating.
- ASTM D1730 - Preparation of Aluminum and Aluminum Alloy Surfaces for Painting.
- MIL-C-5541 - Chemical Films and Chemical Film Material for Aluminum and Aluminum Alloys.
- MIL-C-81706 - Chemical Conversion Materials for Coating Aluminum and Aluminum Alloys.
- MIL-W-Welding, Resistance: Aluminum, Magnesium, etc.; Spot and Seam.

Conversion coatings for magnesium

Magnesium is a very active metal. Although it forms a natural oxide, the coating is thin and not very protective. Protecting magnesium dates back to the 1920s with progressive new treatments over the years. Dow Chemical Co. published treatments for magnesium that include cleaning, pretreatments for chrome conversion coating and various pickles and etches for the many different alloys, and a method for anodizing magnesium, Dow 17 (MIL-M-45202 Type 1 Class A). The HAE process (MIL-M-45202 Type 1 Class C) is another method for anodizing magnesium. Anodizing is widely used but it is beyond the scope of this paper. Another process (not discussed here) involves the cathodic electrolytic deposition of silicon oxide as a protective coating.18

Magnesium must be cleaned. Strong alkali cleaners are suitable for magnesium. After cleaning, there are numerous pickling and acid treatments from which to select, that are used for scale removal, or if there is no scale, preparation for protective and suitable for painting. For example, to remove “burned on” graphite, for cleaning prior to arc touch up repair for military applications. The composition is:

- chromic acid, 180 g/L (24 oz/gal), ferric nitrate,
- magnesium fluoride, 2.45 g/L (0.33 oz/gal).

The Dow dichromate treatment**** produces a conversion coating for magnesium. It is a proprietary process† that provides a protective coating and is suitable for paint base and adhesive bonding. The immersion time is 15 to 30 sec. The operating temperature is ambient in most areas, but for consistent results, a temperature just above room temperature is suggested, i.e., 21 to 34°C (70 to 95°F). There is no post treatment required except for drying. Temperatures up to 71°C (160°F) can be used for drying without changing the protective value of the coating.

The solution composition is: 39 mL/L (5.0 fl.oz/gal) of the proprietary solution, 58 mL/L (7.5 fl.oz/gal) of hydrochloric acid, (20°Bé) and 0.26 mL/L (260 ppm) of a suitable surfactant. Like chrome conversion coatings for aluminum, the film is a precipitated product of the reaction between the magnesium and an acid chromate solution. The coating contains hexavalent and trivalent chromium and magnesium in a hydrated oxide gel. The amount of metal removed is about 3.8 µm/min (0.15 mil/min). The usual immersion time ranges from 1 to 30 min. The conversion coating does not flake or spall during deformation of the metal. No embrittlement is imparted such as occurs with anodizing. The color is dark to light brown. Chromated castings are lighter in color and the coating may be somewhat uneven. This does not adversely influence the corrosion protection. Excellent paint bonding is an important property of this process. Corrosion-free exposures of over 2000 hr of salt spray testing have been reported for painted panels protected by the proprietary product. It has been shown that this process equals or exceeds the requirements of Type II, III and IV in addition to Type VIII of Mil-M-3171C.

References

1. F. Thomas, U.S. patent 1,480,869 (1924).

**** Dow No. 7, Dow Chemical Co., Midland, MI.
† Iridite 15, MacDermid Inc., Waterbury, CT.

Continued on page 44
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Conversion Coatings for Aluminum and Magnesium

Continued from page 34

18. D. E. Bartak, Electrodeposition and Characteristics of a Silicon-Oxide Coating for Magnesium, Dept. of Chemistry, Univ. of North Dakota, Grand Forks, ND; Technology Applications Group, Inc., Grand Forks, ND.

Additional reading

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