Conversion Coatings for Aluminum and Magnesium

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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 process parameters are important to obtaining best results. Corrosion protection, self-healing, dying, electrical conductivity, bonding, hardness and heat resistance characteristics of conversion coatings containing chromium are discussed. MIL specifications and testing are included. Mechanism of film formation and chemistry is discussed.

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Introduction

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 roll in the metal finishing industry because of their enhanced corrosion protecting and decorative appeal. Conversion coatings have been around for many years. Coatings for iron and iron alloys such as black, and bluing; 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 conversions coatings were developed for zinc, and cadmium, from, 1924 to 1936.[1] Chromates for copper, silver, magnesium and aluminum followed.[2,3,4] The first true chromate conversion coating for aluminum was introduced by Strickland, Mater and Meth in 1952[5] Later improved chromate conversion coatings for aluminum were introduced.[6] Chromate conversion coatings for aluminum became very important due to the corrosion protection, low electrical resistance, improved paint and adhesive bonding, and self-healing properties that protect scratches by migrating into the scratch thus maintaining the protection.[5] Chromate conversion coatings also have low emissivity coefficient, less than that of anodize 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.[7]

Recently, non-chromium containing conversion coatings were introduced that are improvements over the early non-chrome processes and may rival chromate coatings in some characteristics.

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 to metal interface. The result is precipitation of complex hydrous 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 that precipitates. Hexavalent chromium provides the greatest corrosion protection, but the trivalent chromium is necessary to form the proper coating. Activators play an important part in forming the best coating. Materials that act as activators are chlorides, sulfate, formate, acetate, fluoride nitrate, phosphate sulfamate ions. These are used in small quantities. Most used in 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 was due to use as a low cost substitute for anodizing, and to the 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, good spot-welding and arc welding made the use of chromate conversion coatings expand rapidly. The chromate coating protects aluminum from oxidizing and the chromate film acts as a flux to enhance welding characteristics. Bare aluminum oxidizes quickly and continues to build oxide thickness in most environments. For some applications it is important to prevent excess heating of a surface or device. Low emissivity of infrared (heat) is important to prevent excessive heating. Below is a comparison of chromated aluminum with other surfaces. The scale is from 0 to1, where the most desirable is close to 0.

Infrared radiation of aluminum and related protective coatings:[8]

Surface Finish	Emissivity
Bare Aluminum	0.03
Yellow Chromate	0.20
Anodize	0.7
Most Painted surfaces	0.8-0.9

Changing the bath concentration, and treatment time can vary thickness or the chromate coating. The 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 the soluble hexavalent chromium. Leaving the insoluble reaction products in tact. These coatings can be dyed various colors for identification or decorative purposes. It is difficult to maintain exact color matches for decorative applications, but it 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 may indicate over active processing solution or a very active surface, such as an alloy high in copper alloying constituent. Copper in the aluminum alloy accelerates the chemical reaction causing a less satisfactory coating in terms of adhesion and corrosion protection.

Chromate conversion coatings protect aluminum from oxidizing, thus these surfaces will have lower electrical resistance than un-protected aluminum. Thinner coatings have lower the contact resistance. Clear coatings have the least resistance. Rougher surfaces will have lower contact resistance due to the ease of breaking through the coating by contact.

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 168 house of 5% neutral salt spray (ASTM B-119. In fact the protection can often exceed that requirement to over 500 hours. 1000 hours salt spray has been reported.[5] The added protection is dependent on several factors. Most important is the condition of the aluminum surface. By condition I mean that the surface is smooth, free from pits or scratches, and the alloy is not too high in copper and/or other alloying constituents. Heat-treating copper containing alloys, such as 2024 and 6061 causes copper to migrate to the surface. The heat-treat process has fairly loose parameters specifications for heat-treating 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. Or, there can be no coating at all caused by dissolving the coating as fast as it forms. A pre-treatment in nitric/fluoride containing acid dip can make the surface better for chromating. However the corrosion protection is often lessened. It is important to clean the aluminum surface leaving no soils. Careful selection of alkaline of mild acid cleaners is important. Highly silicated alkaline cleaners can leave a silicate film that is not removed by rinses or acid dips. Low silicate cleaners that remove the natural oxide and do not etch significantly are best. Mild phosphoric acid cleaners work well also.

Etching of the aluminum prior to chromate treating will always result in poor corrosion protection. Especially bad is the use of caustic etches (sodium hydroxide also *called caustic soda*). The alkaline etch removes aluminum and not the alloying constituents. Many of the alloying constituents create corrosion cells dissolving away the aluminum, leaving the alloying constituent that can result in capillary holes around them that entrap the etch solution and or subsequent chemicals that cannot be rinsed out of the capillary voids. Etching also leaves pits. This results in poor corrosion protection of the chromate conversion coating. (figure 1-6) Acid etching is somewhat less destructive, but can also lead to lessened corrosion protection. Pure aluminum is not subject the problems associated with etching. Low alloying constituents in the alloy allow for some slight
etching without loss of corrosion protection. The film is soft at first, after treating, but after 24 hours 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 resulting in a reduction in corrosion protection.

Do not sand aluminum prior to conversion coating. (Figure 3) Sanding leaves scratched that entrap the natural oxide. The natural oxide is loosely adherent, and if not removed will result in poor paint adhesion and less protection Sanding leaves loose aluminum particles and burrs. All of these contribute to loss of corrosion resistance and loss of adhesion of paint and adhesive. (Sanding with 600 or higher grit will produce acceptable results.)

Figure 1. Etched aluminum panel showing pits and capillaries.
The etching is over done to illustrate the problem more clearly

Figure 2 After 168 hours 5% salt spray. The non-etched (left) panel shows no corrosion. Others failed

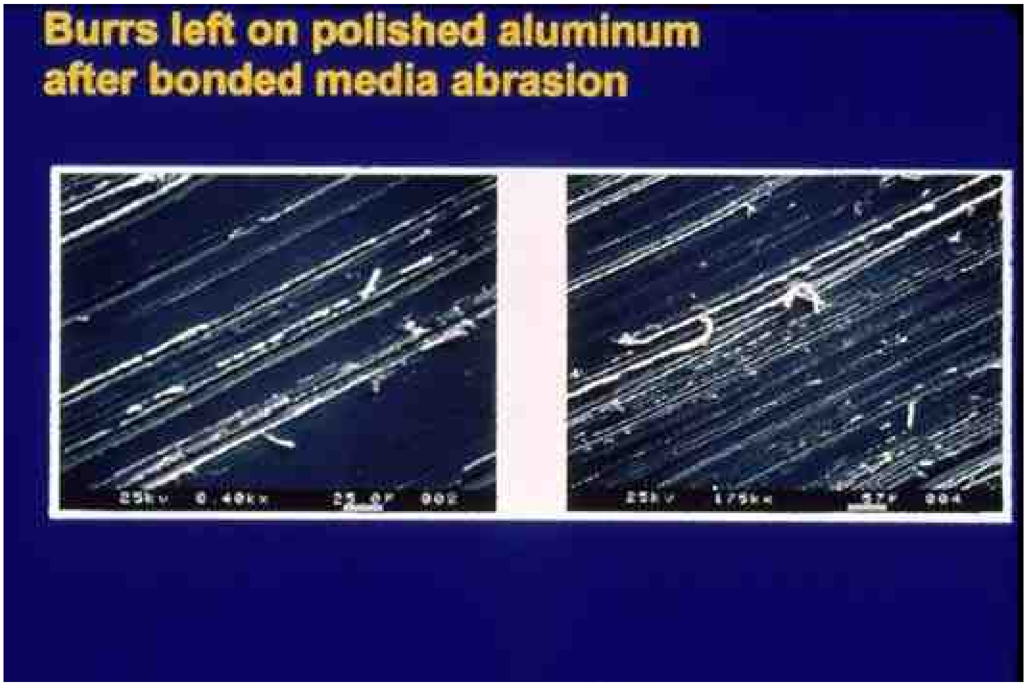
Burrs left on polished aluminum
after bonded media abrasion

Figure 3 Shows burrs and small scratches

Proper preparation of the metal before apply conversion coatings is necessary for good results. After cleaning it is best to deoxidize the aluminum. Solutions containing chromic acid and sulfuric acid, or ferric salts, or sulfuric acid-hydrogen peroxide are used. Thorough rinsing is necessary. For aluminum castings that contain silicon should be treated in nitric-hydrofluoric acid mixture (3: 1) or nitric ammonium bifluoride.

There are also chromium-phosphate conversion coatings. These are used primarily for continuous strip line coating prior to painting. Phosphate conversion coatings are used on aluminum for extruding, functioning as a lubricant.[10]

Chemistry of Chromates

The processing solution contains hexavalent chromium, 1to7 grams/liter, and nitric acid to pH 1.2 to 2.2, activators and a ferric complex. It is useful to add 10 ppm of chloride to a new make up for best results. (6.25 grams non-iodized salt per 100 gallons or solution, if DI water or low chloride tap water is used for make up) The reaction that takes place at the aluminum surface is dissolving of aluminum oxide and some aluminum causing partial reduction of hexavalent chromium to trivalent chromium, a rise in pH resulting in precipitation of hydrous oxides of chromium and basis aluminum and the formation of hydrated basic chromium chromate. The film contains both hexavalent chromium and trivalent chromium. The residual hexavalent chromium provides the best corrosion protection. Hexavalent chromium is yellow in color. Trivalent chromium is light green or clear.[12]

Impurities in the chromate solution and their effect

The following impurities have a negative effect on chromate conversions 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 and thus depletion of ferricyanide, a main ingredient and important to proper performance. Loss of corrosion resistance increases activity and as concentration increases it will stop coating.
Zinc	Precipitates out with ferricyanide similar to copper.
Lead	becomes insoluble and precipitates out leaving no effect/
Chlorides	10 ppm is beneficial, 30 ppm or more there is a loss of corrosion resistance. At higher levels the color lightens 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 that of chlorides.

The effect of operating parameters

pH	The pH of the chromating solution should be maintained at the recommended range. Low pH results in faster coating, but lower then the recommended range results in thin coatings, etching, or no coating. High pH slows the coating rate.
Temperature	Operating temperature is often left at ambient. However, higher temperature produces thicker coatings, and visa versa. Ambient (room) temperature can vary greatly. To keep consistent coatings a controlled temperature slightly above room temperature is useful. Suggest select about 23 to 26°C (75 to 80°F)

Application methods

Racked parts, in tanks are the most used of 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. Time is 1 to 4 minutes with 3 minutes average time of exposure. After applying the chromate, the parts should be thoroughly rinsed then dried.[8] Careful containment of the spent solution for waste treatment to remove the chromium from the effluent is required.

Repair of damaged coatings can be made in the field without loss of corrosion protection.

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. Rinse or swab water onto the surface, and then apply the conversion coating.

Chromates may also be applied by steam application, as from a steam cleaner.

Heat resistant conversion coatings were investigated by Pearlstein and D'Ambrosio. It is well known that chromate conversion coatings dehydrate when heated over 160 degrees F (71°C) for a prolonged time, loosing some of its corrosion protection properties. The experiments showed that a post dip in of freshly chromated aluminum and zinc in sodium silicate, barium nitrate or glycerin solutions at 25°C (77°F) provide resistance to the adverse effects of heating. The glycerin treatment is particularly effective for chromated aluminum, no loss in corrosion resistance resulted after heating 2 hours at 200°C[10] (382°F)

Non-chromium conversion coatings for Aluminum

There are a variety of non-chrome conversion coatings in use, such as Polycrystalline hydrated aluminum oxide coatings, Thin structured oxide coatings, molybdenum based coatings, and 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 chromate coatings by 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. Sanding lowers the adhesion. The thickened material is applied by flooding onto the aluminum surface. The coating is allowed to stand for about 10 minutes and removed by water spray. The composition contains safety solvents, and detergents and a mild acid that cleans and deoxidizes the aluminum prior to forming the thin oxide final coating. The surface is allowed to dry, or can be heated to dry. Since the surface is wetable, paint or adhesive spreads quickly and adheres tightly to the conversion coating. The adhesion is superior to the surface preparation that involves sanding the aluminum. The adhesion exceeds that of chromate conversion coatings. It is not necessary to pre-clean, solvent wipe, sand or deoxidize. The coating can be produced in tank processing, if desired, followed by rinsing and drying. The corrosion protection on bare aluminum is inferior to chromate conversion coatings. But, the adhesion of paint and adhesives, the lower cost and no need to waste treat chromium makes it attractive. The corrosion protection is equal to chromate coatings when chromated primers are used or the newer non-chromated primers. Painted surfaces using this process perform better than chromate treated aluminum in adhesion and equal in salt spray resistance.

The product is effective for titanium and stainless steel where adhesive bonding or painting is required. The oxide coating is durable without painting. Treated aluminum can be stored for long periods of time and retain its wet ability and adhesive characteristics. This process is well suited for large objects. It is in use on commercial aircraft*.

*Chemidize 727 ND, MacDermid, Inc.

The potassium permanganate oxide system is another proprietary pre-coat process that is non-chromated. It can produce a yellow or clear coating on aluminum castings and nearly pure wrought aluminum alloys. Aluminum is processed in a potassium permanganate solution at 60 to 66°C (140 150°F) for 60 to 90 seconds. Alloys containing copper, magnesium, zinc or other alloying constituents require a thicker coating. The first step is to treat the aluminum in boiling DI water for approximately 5 minutes. This imparts a bluish gray color to the surface. The second step is to treat the aluminum in an aluminum salt solution for at least 1 minute at 96°C (205°F) or higher temperature. This results in a metallic color. The third step is a seal involving a permanganate solution at 57 to 63°C (135- 145°F). The oxide coating is thickened and deposits of various manganese oxides are trapped in the coating. The coating will have a metallic or light pink color. The fourth step is an optional seal used for maximum corrosion protection. It involves a treatment in a silicate solution at 157°C (250°F) for not more than1.5 minutes.[12,16]

Buchheit, et al introduced alkaline oxide coatings formed by immersion in an alkaline lithium carbonate solution. This polycrystalline hydrated aluminum oxide conversion coating reports high corrosion resistance. The process is done in two stages. Stage one is immersion in a solution containing 0.5M Lithium carbonate at a pH of 11.5, with 20 to 400 ppm Aluminum oxide (AlO_2). It is operated at 55 to 92°C (131-198 °F) for 5-30 minutes. This produces a hydrotalcite coating. The second stage is immersion in boiling DI water 10 to 30 minutes to convert the hydrotalcite to hydrated aluminum oxide. This process is called “reversion”. The reversion coatings have produced corrosion protection equal to that of anodize and chromate conversion coatings. For 1100 series aluminum alloys, the first stage will protect similar to that of chromates. For alloys containing copper and/or magnesium zinc the two stage system is required. Salt spray test results (ASTM B-117) have shown 1500 hours without evidence of corrosion.[13,14,15]

*A non-chromated metal preparation product** that meets EPA requirements,* that significantly improves adhesion and reduces corrosion is used currently on military aircraft. The corrosion resistance is superior when used prior to a chromated primer. New non-chromated primers are being tested for corrosion resistance with promising results. The pretreatment can be used on aluminum, composite materials, steel, titanium, CRES, galvanized surfaces and plastic. The product can be applied by manually, spray, power wash or dip process. The product is non-toxic, non-corrosive, CFC free, ODS free, and odor free. For waste disposal, it is biodegradable. The product has a complete list of National Stock Numbers, and is approved on six USAF Technical Orders.

The low surface energy allows penetration into pores, removing soils such as oils and particles attached to oxide layers.

**Prekote (™) Pantheon Chemical Co.

Molybdenum based conversion coatings have been studied a great deal as alternatives for chromate conversion coatings. Molybdates, Tungstates, vanadates, and permanganates were all considered. Molybdates were given the most attention, likely because of its non-toxic nature, and because molybdates show corrosion inhibiting properties. Wiggle et al[12] have shown that metaborate is present with molybdates significant corrosion inhibition of aluminum alloys can be achieved. The role of molybdates in corrosion has been reviewed by Wilcox and Gabe.[12] However, the corrosion protection for aluminum alloys falls short of that of chromate conversion coatings.

No-rinse conversion coatings are sometimes used for Reel-to-Reel mil processing prior to painting. The coating solution contains chromium, hexavalent and/or trivalent chromium, mineral acids and organic or inorganic binding agents. Non-chromium no-rinse solutions contain transition metals other than chromium. A limited reaction occurs in the coating solution, but the reaction continues during drying. Coating weight is typically 5 to 30 mg/sq ft the coating weight is adjusted by varying the concentration in the process solution. Application is by spray or immersion.[16]

Specifications for conversion coatings on aluminum[17]

ASM 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 1920's with progressive new treatments over the years. Dow Chemical Co. published treatments for magnesium that include cleaning, pretreatments for chromate conversion coating, and various pickles and etches for the many different alloys, and a method for anodizing magnesium, Dow 17. The HAE process is another method for anodizing magnesium. Anodizing is widely used but it is beyond the scope of this paper. Another process (not discussed in this paper) involves 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 no scale, preparation for protective treatments such as conversion coatings. The Electroplating Engineering Handbook[19] describes various pickle treatments. For example to remove "burned on" graphite, for cleaning prior to arc or gas welding and for removal of mil scale the following formula is suggested: Chromic acid, 24 oz/gal and sodium nitrate 4 oz/gal. Immerse for 1 to 3 minutes, or longer if required using a solution temperature of 15-38°C (60-100°F).

Ferric nitrate (Treatment no. 21) is replacing the chrome nitrate pickle for many of the same applications. This treatment gives a polishing effect. The composition is as follows: chromic acid 24 oz/gal. (180 g/L) iron nitrate 5.3 oz/gal. (3.59 g/L) And potassium fluoride, 0.5 oz/gal. (3.74 g/L) This "chrome pickle" imparts a chromate film that is protective and suitable for painting.

Treatment No.1 is widely used for touch up repair for military applications. (MIL-M-3121A, Type I) The composition is: Sodium dichromate 1.5 lbs/gal. (180g/L) and concentrated nitric acid (70%) 1.5 pt/gal. (710 ml/gal.) It is use for 20 sec. To 2 minutes at 21 to 32°C (70 to 90°F)

The Dow dichromate treatment (Dow No.7) imparts a conversion coating suitable for painting and adhesive bonding. The composition is: Sodium dichromate 20 oz/gal (150 g/L) and calcium or magnesium fluoride 0.33 oz/gal. (2.45 g/L) Operating temperature is near *boiling*. (98-100°C); pH 4.1 to 5.6; for 30 minutes. A pre-dip in hydrofluoric acid for 5 minutes is recommended. (For AZ31B the time in the HF is limited to 30 seconds.)

MIL-M-3171C, Type VIII is widely used chromate conversion coating for magnesium. It is a proprietary chemical composition** that provides a protective coating and is suitable for paint base and adhesive bonding. The immersion time is 15 to 30 seconds. The operating temperature is ambient in most areas, but for consistent results at a temperature just above room temperature is suggested, i.e. 21 to 34°C (70-95°F). There is no post treatment is required except for drying. Temperatures up to 71°C (160°F) can be used for drying without changing the protective value.

The solution composition is: 5 fl oz/gal. (150 ml) of the proprietary solution and 7.5 fl oz. (225 ml) of hydrochloric acid, (20 degree Baume$^{/}$) and 1 ml/gal, of a suitable surfactant. Like chromate 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, trivalent chromium and magnesium in a hydrated oxide gel. The amount of metal removed is about 0.00015" (38X 10^{-8} micrometers) per l minute immersion time. The usual time is 1 to 30 minutes. 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. Casting are lighter in color and may be somewhat uneven. This does not adversely influence the corrosion protection. Excellent paint bonding is an important property of this process. Over 2000 hours salt spry testing has been reported for painted panels protected by the proprietary product. It has been shown that the chromate coating of this process equals or exceeds the requirements of type II, III and IV in addition to type VIII of Mil-M-3171.

**Iridite 15, MacDermid, Inc.

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