Trivalent Chromium for Enhanced Corrosion Protection on Aluminum Surfaces

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A chromate conversion coating is a type of conversion coating applied to passivate aluminum in order to slow corrosion. The process uses various toxic chromium compounds, which may include hexavalent chromium. The surface finishing industry is developing less toxic alternatives in order to comply with substance restriction legislation such as RoHS. One alternative is trivalent chromium, which may not be as effective as hexavalent chromium, though it is less environmentally damaging. This paper will describe a new trivalent chromium process for chromate conversion on aluminum with outstanding results. It is QPL (Qualified Product List) approved by the United States Navy - Defense Standardization Program under Governing Spec MIL-DTL-81706B.

Keywords: *Chromate conversion coatings, trivalent chromates, aluminum substrate, corrosion resistance, environmental compatibility, RoHS compliant, MIL-DTL-81706B*

Introduction

This paper will outline various chromate conversion techniques for aluminum. It will address a new environmentally-friendly, cost efficient and performance-oriented chromate conversion coating with a unique and patented trivalent chromium pre- and post-treatment chemistry for aluminum.

Chromate conversion of aluminum

Chromate conversion coatings are applied to passivate aluminum, zinc, cadmium, copper, silver, magnesium, tin and their alloys to slow corrosion. To achieve their full protective properties on aluminum alloys, most organic coatings require the metal surface to be pre-treated. This provides a surface film which becomes an integral part of the metal surface, involving virtually no dimensional change. Chromate coatings, similar to phosphate coatings, are processes of chemical conversion. They are formed by the reaction of aqueous solutions of chromic acid or chromium salts. The coatings can be applied to aluminum, zinc, cadmium and magnesium. The coatings usually have good atmospheric corrosion resistance. These conversion coatings form an ideal substrate for paints and precious metals, providing a clean, essentially inert surface, which gives optimum adhesion. The application of chromated aluminum can cover a wide range of functions.

Conversion coatings can provide mild wear resistance, better drawing or forming characteristics and may be used to serve as a decorative finish. They are also ideal for pre-treatment prior to organic coating.

Most organic coatings applied directly to aluminum surfaces will not adhere well, and if subjected to any deformation, will tend to flake off, exposing the bare aluminum. Scratching off the paint surface would also provide a nucleation site for aluminum corrosion and further undercutting of the coating.

The successful application of this conversion process requires the aluminum to be clean and free from organic soils, oxides and corrosion products. Therefore a pre-treatment is required which can be applied to the aluminum, and provides a suitable basis for subsequent coatings. Conversion coatings have been developed which can be used on aluminum alloys and are compatible with most paint systems. The term "conversion coating" describes a process of chemical reaction that results in a surface film. As a result of this reaction and conversion, the film becomes an integral part of the metal surface and exhibits excellent adhesion properties.

Chromate conversion coatings are thin chemical films, usually less than 0.25 microns in thickness, and are electrically conductive.

Hexavalent chromates

Historically, hexavalent chemistry has been used in the chromate conversion of aluminum parts. There are some benefits with hexavalent chemistry. Chromate passivation systems containing

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hexavalent chromium compounds are an extremely versatile group of aqueous chemistries that are extensively used in a diverse range of electroplating and metal treatment processes. They impart many beneficial and essential characteristics to metallic substrates and to deposits obtained from a number of techniques such as zinc electroplating.

Hexavalent based passivation (Cr^{+6}) exhibits a number of desirable characteristics, as outlined in Table 1. They passivate the surface of zinc and zinc alloy electrodeposits with a thin film that provides end-user benefits such as color, abrasion resistance and increased corrosion protection. When damaged, these hexavalent chromates possess a unique "self healing" property. This means that soluble hexavalent chromium compounds contained within the passivation films will re-passivate any exposed areas. Hexavalent chromate exhibits a wet, gelatinous film, drying at the surface. Subsurface moisture (dehydrating in approximately 48 to 72 hr) provides self-healing and lubricity characteristics. The deposits are harder than conventional trivalent chromate films. It offers torque-tension characteristics which meet fastener finishing requirements.

Hexavalent chromium products however, are carcinogenic substances. They are hazardous to human health and the environment. Hexavalent chromates leach into the ground and cause damage. Because of its toxic nature, environmental guidelines and regulations have been in place to restrict and prohibit its usage.

The industry is developing less toxic alternatives in order to comply with substance restriction legislation and directives from the European Union. The most affecting directive is Restriction of Hazardous Substance (RoHS), 2002/95/EC of the European Parliament and The Council of the European Union, signed on 27 January 2003 and became effective on July 1, 2006. It covers six hazardous substances - lead, mercury, cadmium, hexavalent chromium (Cr^{+6}), PBB (polybrominated biphenyls) and PBDE (polybrominated diphenyl ether). Another European Union directive, the second directive that also contains hexavalent chromium, is the End of Life Vehicle (ELV) directive, 2000/53/EC of the European Union and the Council of European Union, signed on September 18, 2000 and became effective on July 1, 2007. The four heavy metals included in ELV directive are cadmium, lead, mercury and hexavalent chromium (Cr^{+6}), (approximately 70% of total heavy metals is Cr^{+6}).

Trivalent chromates

The surface finishing industry has been actively following any new developments to replace hexavalent chromium. The most common alternative is trivalent chromium, which is environmentally friendly. However, there are still some weaknesses with trivalent chromate coatings. In order to achieve equal or better corrosion resistance, as compared to hexavalent chromate, in most cases a sealer or a topcoat is required. Some chemical manufacturers now offer better salt spray performance without sealers or topcoats.

Trivalent chromates are not self-healing. The process bath life is shorter than that of hexavalent chromate baths and an operating temperature of 60°C (140°F) is required. Nor do the trivalent processes offer identical colors.

In recent years there have been new developments in trivalent chemistries. More colors are now available and coating performance has significantly improved, especially for corrosion resistance. A typical trivalent chromate film has a pale greenish color. Trivalent chromate deposits are electrically non-conductive (unless applied over a zinc alloy or a metallic substrate).

The most significant development for the replacement of hexavalent chromates is the trivalent chromium pretreatment (TCP), developed by the United States Navy, Naval Air Systems Command (NAVAIR). This is a unique chemistry, specially formulated and developed for aluminum.** NAVAIR has spent over two and a half years testing more than 15,000 panels for development of the product. This formulation contains less than 1% trivalent chromium and operates at ambient temperatures [18 to 29°C (65 to 85°F)]. It does not contain any restricted or hazardous substances and as a result, does not require any exhaust systems. Most importantly, it complies with **all** European Union directives including the Restriction of Hazardous Substances (RoHS), End of Life Vehicle (ELV) and Waste Electric and Electronic Equipment (WEEE) Directives.

The trivalent chromium pretreatment has shown outstanding performance compared to other conventional trivalent chromates. This trivalent chromate film is harder than conventional trivalent chromate. It is electrically conductive (low electrical resistance) and it meets or exceeds ASTM D2559-9, MIL-DTL-5541 F and MIL-DTL-81706 standards for electrical resistance. Therefore it is useful in electric and electronic equipment where surface resistivity is critical.

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Table 1

Favorable characteristics of hexavalent chromate passivates

• Prevents oxide formation • Provides color • Slow corrosion in prototype tests (*e.g.*, salt spray, rooftop, etc.) • Provides adhesion for organics (*e.g.*, paints) • Helps prevent corrosion of painted surfaces • Conductive • Thin • Flexible	• Lubricious • Easily applied • Stable for weeks or months • Durable • Resilient (self-healing) • Coats in recesses • Easy to strip • Inexpensive equipment • Single tank • Inexpensive charge up cost

The trivalent chromium pretreatment has excellent adhesion and bonding properties and provides an undercoat for organic coatings such as paints. It meets or exceeds dry tape adhesion requirements for ASTM D3359 - Methods A and B. It is an ideal undercoat for cured coatings and as an overcoat for plated materials that require subsequent hydrogen relief. It can be exposed to temperatures exceeding 427°C (800°F) following a 24-hr cure period. It can be baked for hydrogen relief in excess of 260°C (500°F) for more than 24 hr without loss of performance while hexavalent chromates cannot be baked above 60°C (140°F) without performance loss. In most cases, its corrosion resistance performance is equal to or better than conventional trivalent chromates and also hexavalent chromates. Results of 168 to 500 hr can be achieved in neutral salt spray testing (ASTM B117), depending upon the aluminum alloy tested. In short, this trivalent chemistry from NAVAIR offers an overall superior performance without any sealer or a topcoat.

NAVAIR's TCP has also been used to replace high- and mid-temperature anodize seals. It has proven to be an environmentally friendly and efficient anodize seal with no hazardous chemicals. The TCP is QPL (Qualified Product List) approved from the United States Navy - Defense Standardization Program under Governing Spec MIL-DTL-81706B (1), "Chemical Conversion Materials for Coating Aluminum and Aluminum Alloys."

Process considerations

The pretreatment of aluminum is important to meet the desired specifications. Alloys such as 6061 and 7075 are relatively easy to process and can work with most available detergent and activation agents, acids or deoxidizers. On the other hand, 2024 alloy (with up to 5% copper content) is sensitive and requires specific pretreatment. The nature of this alloy makes it sensitive to some etching cleaners and may require certain acids to activate the part surface. The patented NAVAIR TCP process is simple to operate provided that attention is paid to the pretreatment and the pH of the bath. The normal operating pH range of this bath is 3.6 to 4.0. A lower pH may cause early corrosion in salt spray testing as the bath becomes more aggressive. A combination of lower pH and slightly elevated temperature makes it highly aggressive and supports a shorter time cycle.

Studies were done by a licensee of NAVAIR's TCP process which examined test results of various aluminum alloys treated with different process cycles. Various times, temperatures and concentrations of more than one detergent were examined. Special attention was given to the etching tendencies of some of the detergents. The objective was to achieve a clean surface with no surface modification or powdery film formation. After cleaning, the surface was activated by various chemical methods which were chosen based on the alloy studied. Other important factors included concentration and cycle time in the activation bath. Rinsing was also given special attention. Tap water or deionized water was selected as required. The quality of the rinse water, in terms of the levels of chlorides and total dissolved solids, was observed. The trivalent chromium pretreatment bath was operated at ambient temperature as well as at elevated temperatures for evaluation purposes. Testing of different alloys included different concentrations of trivalent chromate and different time cycles.

The results were based on the performance in neutral salt spray. We evaluated different test matrices and found that certain alloys required a specific overall treatment. Alloys which were relatively easy to process produced excellent results. Neutral salt spray results ranged from 168 to 800 hr. When a specific process cycle was followed, the salt spray performance for 2024 alloy ranged from 168 to more than 1000 hr.

Enhanced performance additive

One of the most daunting aspects of trivalent conversion coatings as a drop-in replacement for hexavalent chromium chemistries is the requirement of rigid pretreatment parameters in order to realize maximum corrosion performance. Across the board, job shops and formulators alike go to great lengths to produce consistent results that pass requirements such as MIL-DTL-5541 and other corrosion specifications. Application facilities not well equipped to perform experiments for pretreatment optimization are finding themselves making small beaker size batches of solutions with the intention of scaling up to their production line. This is good practice when tight controls are met with proper standards, but can be convoluted for some and more work than what a typical job shop is used to when integrating a new product into their line. The standard practice in industry is to purchase a material, follow the operating parameters and - voilá - it works. Trivalent chromium conversion coatings are not, in general, that straightforward. The nature of the technology poses the burden of tailoring the facility's resources and equipment constraints to the product, which requires a slightly more sophisticated level of understanding. This may come as a shock to those transitioning to trivalent chromium chemistry and can often be discouraging.

There have been successful attempts in creating a more robust process to allow leeway in pretreatment parameters. Research institutions and private industry groups are looking for additives to put in trivalent chromium conversion coating baths. Anyone with experience using trivalent conversion coatings knows that the more surface modification done to a substrate, such as etching, the greater the risk for a drastic decrease in corrosion resistance. A study of one particular additive indicates a 50% improvement rate for corrosion resistance on etched substrates and 38% on non-etched substrates when using an enhanced bath (Table 2). The study included 163 different processes that utilized several different cleaners, deoxidizers and etchants at various temperatures, concentrations and cycle times. All panels treated with the enhanced protection additive (EPA) process were tested against a standard, non-enhanced (NAVAIR) TCP bath. Test panels were sent to an outside party, a NADCAP-certified laboratory for neutral salt spray testing (ASTM B117) as well as examined in-house. Panels were examined at intervals of 96, 168, 212, 267, 336 and 407 hr and beyond. For the sake of brevity, only one parameter will is reported in this paper: etched versus non-etched substrates. The total number of test panels was in the hundreds.

Table 2

The effect of the performance additive on the corrosion performance of etched and non-etched aluminum substrates

Conversion Coating	Pretreatment	% Passed	% Failed
Additive enhanced	Etched	81	19
Standard	Etched	31	69
Additive enhanced	Non-Etched	90	10
Standard	Non-Etched	53	47

The data in Fig. 1 indicates that, statistically, out of 100 different process variations, 81 of them passed MIL-DTL-5541 on etched substrates using the enhanced trivalent conversion coating while only 31 process variations passed with a standard, non-enhanced trivalent chromium chemistry.

Though the improvement on non-etched substrates is not quite as dramatic as for etched substrates, using an additive in a trivalent chromium bath is still beneficial. The data in Fig. 2 indicates that statistically, out of 100 different process variations, 90 of them met the specification using an enhanced version and only 53 did so using a standard, non-enhanced bath.

Discussion

The process containing the extended protection additive (EPA) performed much better than the standard trivalent chromate bath (NAVAIR). The addition of the EPA in a standard trivalent chromate pretreatment bath can be varied from 15% to 30%. We used an addition of 25% EPA in a standard trivalent chromate bath for our test evaluation. The objective here was to study the influence of the additive in a standard (NAVAIR) TCP bath and to evaluate the difference in performance with the addition of the EPA. In order to do this, we set up a test plan and selected the appropriate chemistry. We had selected the 2024 aluminum alloy as our baseline standard. Alloy 2024 contains up to 5% copper, which can be an issue for corrosion resistance. We assumed that if superior results could be achieved on 2024 alloy, the other alloys such as 5052, 6061 and 7075 would perform as well or better. We wanted to determine if the additive enhanced the corrosion resistance performance of trivalent chromium pretreatment on aluminum.

The detergents for this trial were selected based on customer suggestions as well as our past history of various testing with trivalent chromium pretreatment applications. The temperature was one of the important factors, controlled in a range from [49 to 52°C (120 to 125°F.)] As much as cleaning of a part surface is important, it is also critical to clean the surface without drying out the surface during transfer. The detergent concentration was based on the chemical manufacturer-suggested operating range at the lower end.

The neutral salt spray results indicated no reasons for any of the detergents being responsible for any failure. We therefore concluded that the process parameters for all of the detergents were acceptable as tested for evaluation of the extended protection additive.

The test panels were etched using a selected etchant used in regular practice. The study was centered around the difference in performance with and without the etchant to assess the performance of the extended protection additive. The results for the etchant were favorable. The process parameters were kept constant for etched and non-etched test panels.

Out of the 164 total test panels, 119, or 73% of the etched panels passed neutral salt spray. There were fewer failures for the etched panels (22%) with the EPA than without it in a standard TCP bath. On the other hand, there were fewer failures of non-etched panels (8%) when used with the EPA than when used in a standard TCP bath. It was concluded that the extended protection additive improved corrosion resistance by 51% on the etched panels. It was also concluded that extended protection additive increased the corrosion resistance by 39% on the non-etched panels. This data shows that the additive enhanced the corrosion resistance with or without the etchant as compared to a standard (NAVAIR) TCP bath.

The results from neutral salt spray testing performed by the NADCAP certified laboratory showed that the standard (NAVAIR) TCP on etched panels performed from 96 to 768 hr. The non-etched panels performed better, ranging from 168 to 2786 hr to failure. The NADCAP lab results for the extended protection additive showed that the etched panels endured 174 to 912 hr, while non-etched panels lasted from 72 to more than 3120 hr.

To activate the part surface, an acid in a combination with a deoxidizer was used. There were different mix ratios of acid and deoxidizer as well as the process cycle time in our test matrix. The results were based on various combinations of cycle time and concentration ratios. Neutral salt spray results indicated that a lower concentration of acid in a deoxidizer performed better than one with the standard TCP (NAVAIR) bath. However, the acid concentration did not substantially influence the trivalent chromium pretreatment with the additive. Test panels processed with a low concentration of acid/deoxidizer in the standard bath failed at 168 hr, while test panels with the EPA treatment passed 267 hr.

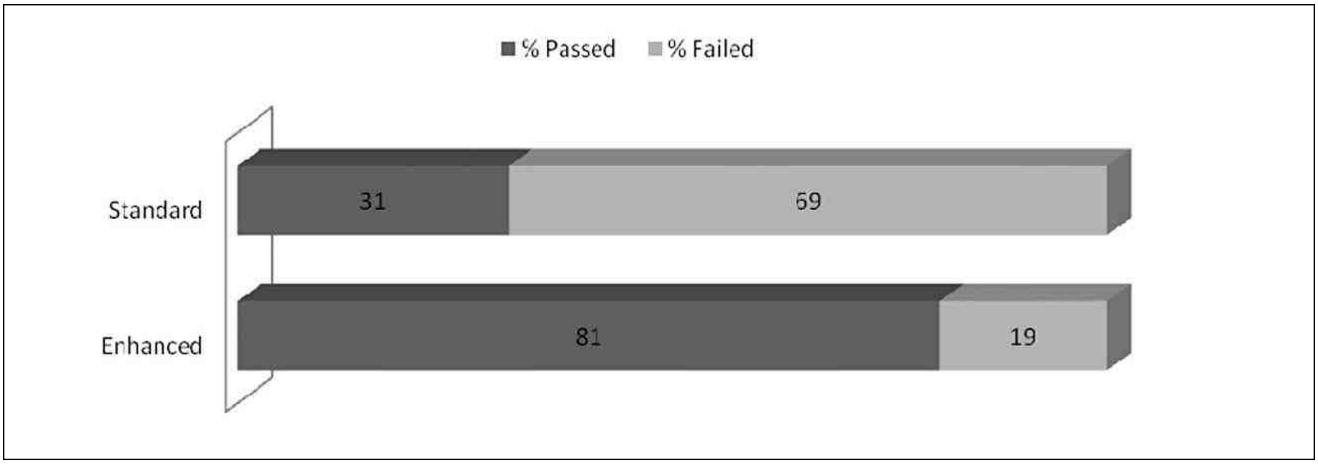

Figure 1—Neutral salt spray performance to MIL-DTL-5541 for etched aluminum substrates.

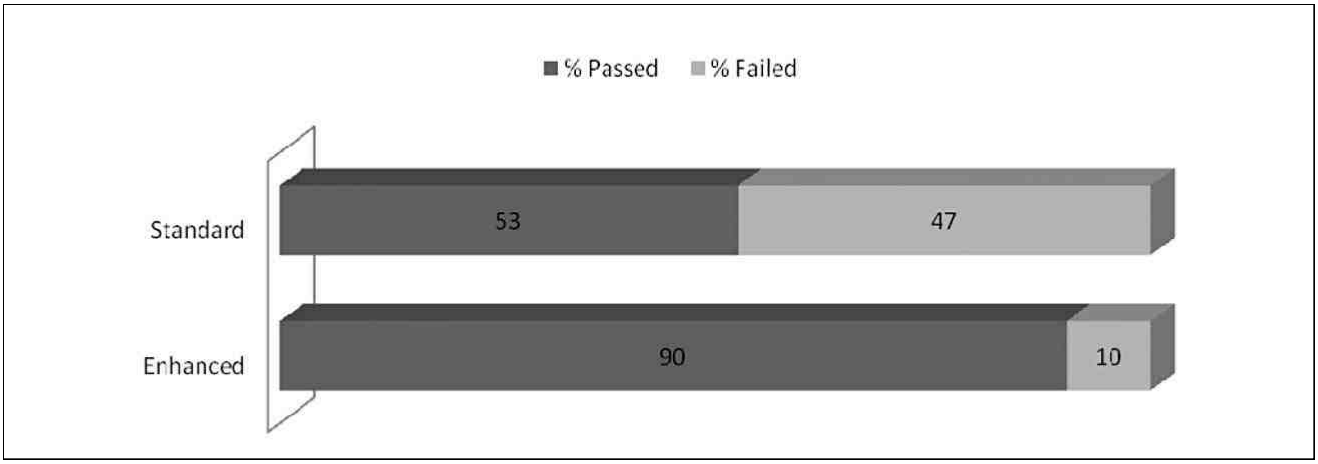

Figure 2—Neutral salt spray performance to MIL-DTL-5541 for non-etched aluminum substrates.

Summary

Trivalent chromium pretreatment (TCP) formulated and invented by NAVAIR performs very well as a replacement for hexavalent chromium on aluminum. Its performance varies depending on the type of detergent, its concentration, temperature and cycle time. Also important is the surface activation and type of the acid and/or deoxidizer that is used for the application. However, the most important factor is the type of aluminum alloy to be chromate conversion coated. It was concluded that 2024 was the most difficult alloy to chromate, due to its metallurgical content. If satisfactory results can be obtained for 2024, the other aluminum alloys would not be as difficult to achieve successful results.

The extended protection additive (EPA), when added to the standard TCP (NAVAIR) bath, has shown outstanding performance in neutral salt spray. The additive is designed to enhance corrosion resistance of aluminum alloy for trivalent chromium pretreatment performance. The EPA offers consistent corrosion performance for difficult alloys such as 2024. It improves the performance of the standard NAVAIR trivalent chromium application on aluminum.

It is sufficient to say that the most important aspect of using this newly developed, patented additive for the trivalent chromium pretreatment is its consistent robust corrosion performance. It is QPL (Qualified Product List) approved from the United States Navy - Defense Standardization Program under Governing Spec MIL-DTL-81706B (1) "Chemical Conversion Materials for Coating Aluminum and Aluminum Alloys."

Additional reading

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Editor's Note: *Extenuating circumstances prevented the references from being enumerated and referenced in the text. However, all of the materials in the above list are germane to the subject of the paper.*

About the author

Harish Bhatt is Vice President, Technical Support & Industry Relations at METALAST International, Minden, Nevada. Internationally respected and former Senior Technical Specialist for Visteon Automotive and Ford Motor Company for 16 years, Harish has over 30 years of experience in the metal finishing industry. He served as an active member of the SOC (Substance of Concern) committee for US CAR (United States Council of Automotive Research), which was founded by Ford, General Motors and Chrysler as the auto industries leading technology and environmental association consisting of 33 of the top automotive companies in the United States. Additionally, for over 15 years, he has been the speaker at various technical conferences around the world including the NASF, SAE (Society for Automotive Engineers) and the AAC (Aluminum Anodizing Council). As Vice President of Technical Support & Industry Relations for METALAST, Harish directs and manages all metal finishing and technical support-related operations, including research and development, training and education, as well as new and existing product/technology validation.