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Non-chromated Conversion Coating for Magnesium Alloys and Zinc-Nickel Plated Steel

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ABSTRACT

A novel hexavalent chromate-free conversion coating was developed to improve anti-corrosion and adhesive-bonding characteristics of the magnesium alloys and zinc-nickel (Zn-Ni) plated steel substrates. The corrosion behavior of the coated and uncoated alloys was investigated by neutral salt fog (NSF) and electrochemical corrosion tests. Surface wettability of the pretreated substrates was investigated by static contact angle measurements. Wet-tape adhesion tests verified that there is strong adhesion between the primer and the chem film-treated substrates. The morphology and composition of the coated surfaces were investigated by optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX) methods. This trivalent chromium-based surface treatment is a potential hexavalent chromate conversion coating replacement for magnesium alloys and Zn-Ni plated steel.

Keywords: hexavalent chromium replacement, conversion coating, magnesium alloy substrate, zinc-nickel plated steel substrate

Introduction

Chromates (Cr^{+6}) are very effective and extensively used as corrosion inhibitors for ferrous and non-ferrous alloys in aerospace, military and general industry applications. Hexavalent chromate compounds are employed in the conversion coating formulations to provide improved adhesive bonding to the subsequent primer/topcoat and to protect the substrate against the environment and corrosion. In addition to the self-healing characteristics, chromated chemical films exhibit both a corrosion-inhibiting effect and a physical barrier layer to the corrosive media.[1,2] Although hexavalent chromate is currently the most effective compound to provide the anti-corrosion properties to the chem films applied on metals, solutions containing Cr^{+6}-based compounds are highly toxic and adversely affect the environment and human health.[3] The Environmental Protection Agency (EPA) regulates chromate usage and emissions mainly through Clean Water Act (CWA) and Toxic Substances Control Act (TSCA).[4] The Occupational Safety & Health Administration (OSHA) has mandated a Permissible Exposure Limit (PEL) of 5 $\mu g/m^3$ (in air) of hexavalent chromium, an unrealistic level for the vast majority of metal finishers and manufacturers to obtain. In addition to the European Union (EU) directives and OSHA requirements, the EPA Executive Order 12856 showed the need to eliminate the release of chromates during aircraft coating applications. The cost of preventive maintenance, improved service life requirements of the fleet of airplanes and strict environmental regulations on the use and handling of hexavalent chromates have motivated U.S. Air Force to invest to find a more suitable method of corrosion control of metals used in aerospace applications. There is, therefore, a need for environmentally-green chem films that can provide high corrosion resistance and increase the adhesive bonding strength characteristics of the metal surface. Although there are other commercially available chem film technologies which do not contain hexavalent chromate, their corrosion performance and paint adhesion characteristics are not as effective as the Cr^{+6}-based chem films.

Magnesium alloys and Zn-Ni plated steels have been used in a variety of aerospace and defense sectors. Both magnesium alloys and Zn-Ni platings require a chem film treatment for maximum corrosion protection and to improve the paint adhesion characteristics of the surface. Chromate conversion coatings have been used on magnesium alloys and Zn-Ni platings mainly for temporary corrosion protection and to improve the adhesive bonding characteristics of the surface.

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In this work, an eco-friendly trivalent chromium (Cr^{+3})-based conversion coating technology is studied on magnesium alloys and Zn-Ni plated steel substrates. Neutral salt fog (NSF), potentiodynamic polarization, and open circuit potential (OCP) methods were used to evaluate the corrosion properties of the chem films. Wet-tape adhesion tests were performed on coated and uncoated magnesium and Zn-Ni plated 4130 steel substrates and rated in accordance with ASTM D3359A.[5] Comparative performance analysis results for the uncoated, trivalent chromium- and hexavalent chromate-processed magnesium alloys and Zn-Ni plated steel is presented.

Experimental

Materials

The magnesium alloys used were AZ31B-H24 and AZ92A-T6. Test specimens were metallurgically polished to 1200P using SiC wafers (unless otherwise specified), rinsed in DI water, and dried for corrosion experiments and paint adhesion studies. Polished samples were subsequently degreased in a proprietary alkaline magnesium cleaner** for 5 min at 140ºF and thoroughly rinsed in deionized water. Rinsed samples were then immediately immersed into the surface activation baths or directly into the conversion coating bath. In addition to surface activation via acid pickling per AMS-M-3171-C specification,[6] two new proprietary surface activation agents were used prior to application of the conversion coatings.

The Zn-Ni plated steel samples were degreased with an acetone wipe and activated in diluted nitric acid solution for 30 sec at room temperature prior to the conversion coating treatment. Commercially available hexavalent-chromium-based conversion coatings were applied on magnesium alloys and Zn-Ni plated steel substrates as the benchmark reference in the present work.

Test methods

Corrosion resistance testing was done on test coupons for each pretreatment process using a neutral salt fog salt spray chamber maintained in accordance with ASTM B117.[7] Potentiodynamic polarization and open circuit potential (OCP) measurements were performed by using a G300 Gamry Potentiostat. The experiments were carried out in an aerated 3.5% NaCl (pH 6.5-7.2) electrolyte.

Test samples were primed with non-chromated epoxy primer (MIL-PRF-23377J, Type I, Class N)[8] and cured for seven days at room temperature prior to the wet-tape adhesion test. The wet-tape adhesion test was performed in accordance with Federal Test Method Standard 141 (FED-STD-141)[9] and rated in accordance with ASTM D3359A.[5] Sealed and plated Zn-Ni plated steel test coupons were exposed to salt spray for one week prior to the wet-tape adhesion test. The adhesion rating per ASTM D3359 - Method A is shown in Table 1.

Contact angle measurements were made by using a Rame-Hart model 250-F1 contact angle goniometer. The surface morphology of deposited films was observed using a Hitachi S-4700 scanning electron microscope (SEM/EDX). All coated panels were cured for 24 hr at ambient temperature prior to the measurement of anti-corrosion and paint adhesion properties.

Table 1 - Wet tape adhesion rating per ASTM D3359 - Method A.[5]

ASTM D3359 - Method A	*Rating description of coating after tape removal*
5	No peeling or removal
4	Trace peeling or removal along scribes.
3	Jagged removal along scribes up to 1/16 in. (1.6 mm) on either side.
2	Jagged removal along most of the scribes up to 1/8 in. (3.2 mm) on either side.
1	Removal from most of the area between the scribes under the tape.
0	Removal beyond the area of the scribes.

**Metalast Magnesium Cleaner, Metalast International, Inc., Minden, NV 89423.

Results and discussion

Magnesium alloys

Figure 1 shows the potentiodynamic polarization curves of AZ92A-T6 magnesium alloy samples processed with trivalent chromium, hexavalent chromate, and an uncoated substrate after immersion in 3.5% NaCl for 20 min. Compared with the untreated AZ92A substrate (E_{corr} = -1.53 V), E_{corr} shifted to more noble potential values after the deposition of trivalent chromium-based conversion coating (E_{corr} = -1.38 V) and hexavalent chromate-based chem film (E_{corr} = -1.49 V). Similarly, the corrosion current density of the bare AZ92A substrate decreased from 4.48 mA to 18.1 µA for trivalent chromium and to 24.6 µA for hexavalent chromate-coated magnesium. The calculated corrosion rate (mils per year [mpy]) was found to be 682 mpy for uncoated AZ92A, 8.26 mpy for the trivalent chromium-based coating and 11.23 mpy for the hexavalent chromate-based commercial chem film. The above results demonstrate that this novel trivalent chromium-based chem film can effectively improve the corrosion resistance of magnesium alloys by blocking the penetration of aggressive ions.

Scanning electron microscopy (SEM) images along with the energy dispersive x-ray spectroscopy (EDX) studies revealed that the surface of the magnesium alloys was homogeneously covered with the trivalent chromium-based deposits with relatively less mud-cracking. The details will be presented elsewhere.

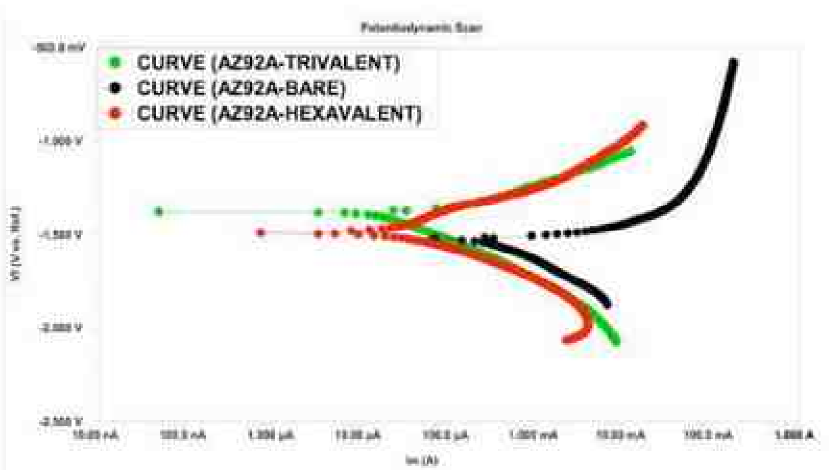

Figure 1 - Polarization curves of uncoated and coated AZ92A-T6 magnesium alloy with trivalent chromium-based and hexavalent chromium-based conversion coatings.

Figure 2 shows the optical microscope images for uncoated and trivalent chromium-based conversion coated AZ31B-H24 magnesium alloy surface after 26 hr of exposure to corrosive aqueous salt solution (5% NaCl, pH 6.5-7.2) at room temperature. These images clearly demonstrate that trivalent chromium conversion coating-processed sample had far less corrosion (dark brown spots) compared to the uncoated magnesium alloy.

Static contact angle measurements revealed that the uncoated AZ31B-H24 magnesium alloy had a contact angle of 70.69 ± 8.25º. On the other hand, processing with the trivalent chromium conversion coating makes the same surface very wettable and reduces the contact angle to 18.49 ± 3.65º.

Trivalent chromium, hexavalent chromate, and uncoated AZ31B-H24 magnesium test coupons were primed with non-chromated epoxy primer (MIL-PRF-23377J, Type I, Class N)[8] before performing the wet-tape adhesion test. Figure 3 shows the wet-tape adhesion results for trivalent chromium-coated and uncoated test samples. A cleaned and primed (no pretreatment) magnesium sample showed separation of the paint from the panel beyond the cuts and had a rating of zero per ASTM D3359 - Method A. On the other hand, trivalent chromium and hexavalent chromate chem films significantly improved the adhesion of the primer to the magnesium substrate with no visible flaking or separation from the chem film. Both coatings had a rating of 5A (highest) per ASTM D3359.

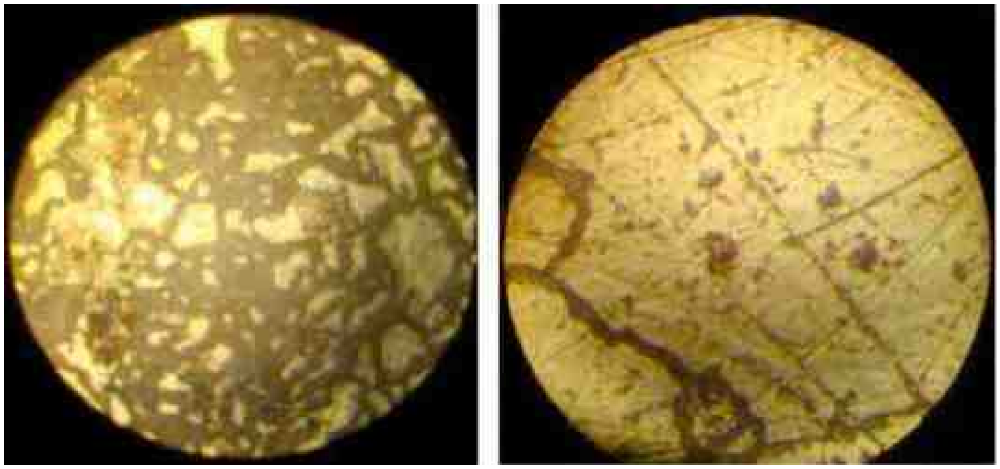

Figure 2 - Optical microscopy images for uncoated (L) and trivalent chromium conversion coated (R) AZ31B-H24 magnesium alloy surface after 26 hr of exposure to 5% NaCl solution (pH 6.5-7.2) at room temperature.

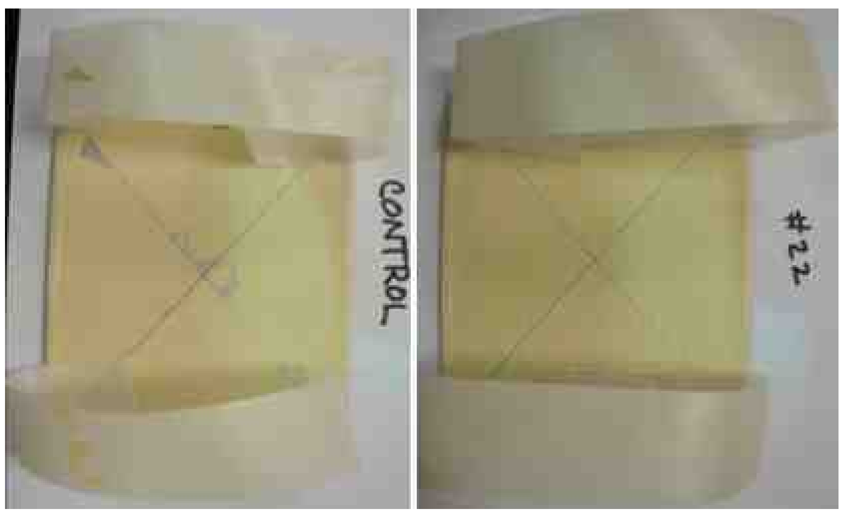

Figure 3 - Wet tape test results for non-chromated epoxy primed and scribed AZ31B-H24 magnesium alloys; bare (L), trivalent chromium-coated (R) magnesium samples. Scale from the surface was removed chemically. Trivalent chromium-based chem film on the magnesium alloy surface provided excellent tape adhesion characteristics with a rating of 5A in accordance with ASTM D3359 - Method A.

Zn-Ni plated steel

Sealed and unsealed Zn-Ni plated 4130 steel substrates were exposed to neutral salt fog (NSF) test per ASTM B117 for testing the 96 hr white corrosion and 500 hr red rust formation resistance. Bare (unsealed) Zn-Ni plated steel developed white corrosion on more than 5% of the exposed surface area within 24 hr of salt spray exposure. On the other hand, the trivalent chromium-sealed Zn-Ni plated steel substrate showed no white corrosion or red rust formation even after 528 hr (Fig. 4). The anti-corrosion properties of the trivalent chromium-based coating against white corrosion and red rust formation on the Zn-Ni plated steel was equivalent to the conventional hexavalent chromate sealed substrates as shown in Fig. 4.

Open circuit potential (OCP) measurements in a naturally-aerated 3.5% NaCl (pH 6.5-7.2) corrosive medium revealed that sealing the Zn-Ni plated steel with the novel trivalent chromium-based coating solution resulted in a positive potential shift from -875 mV (for bare unsealed Zn-Ni-plated steel) to -840 mV (for trivalent chromium-sealed Zn-Ni plated steel) as shown in Fig. 5.

Figure 4 - Zn-Ni plated 4130 steel test panels sealed with the novel trivalent chromium (L) and hexavalent chromate (R) after 528 hr neutral salt fog test per ASTM B117.

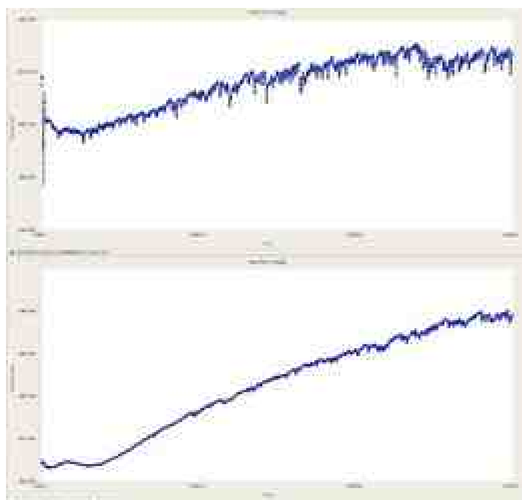

Figure 5 - Open circuit potential (OCP) diagrams for bare Zn-Ni plated 4130 steel (top) and trivalent chromium-sealed Zn-Ni plated 4130 steel (bottom). Sealing with the novel environmentally green trivalent chromium coating solution caused a positive potential shift from -875 mV to -840 mV.

Figure 6 shows the wet-tape adhesion test results on non-chromated epoxy-primed and scribed Zn-Ni plated 4130 steel panels after 168 hr of salt spray exposure. The unsealed Zn-Ni plated substrate showed visible paint removal from the scribed area. On the other hand, trivalent chromium and hexavalent chromate-sealed Zn-Ni plated steel showed excellent tape adhesion characteristics with a rating of 5A in accordance with ASTM D3359 - Method A.

Conclusions

Results obtained in this study revealed that the novel eco-friendly trivalent chromium-based conversion coatings on magnesium alloys and Zn-Ni plated steel performed equally to the conventional hexavalent chromate-based technologies. Neutral salt fog (NSF) and electrochemical corrosion tests showed that the trivalent chromium-based coating technology can meet the anti-corrosion properties of the hexavalent chromate. Trivalent chromium-sealed Zn-Ni plated 4130 steel showed no sign of white corrosion or red rust formation even after 528 hr of salt spray exposure. Similarly, paint adhesion test results revealed that both trivalent chromium and hexavalent chromate-pretreated magnesium alloys and Zn-Ni plated steel substrates had the highest ranking of 5A in accordance with ASTM D3359.

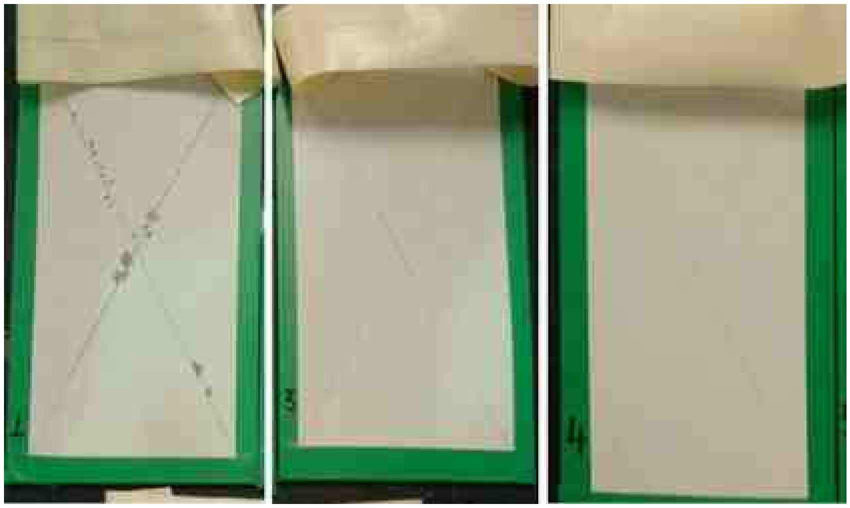

Figure 6 - Wet-tape tests on non-chromated epoxy primed Zn-Ni plated steel after 168 hr of salt spray exposure: Bare Zn-Ni plated steel (left), hexavalent chromated (center) and trivalent chromium-sealed (right).

Acknowledgements

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References

1. M. Kendig, *et al.*, *Surface & Coatings Technology*, 140 (1), 66 (2001).
2. F.W. Eppensteiner & M.R. Jenkins, *Metal Finishing Guidebook*, 109, 417 (2011).
3. H. Bhatt, A. Manavbasi & D. Rosenquist, *Metal Finishing*, 107 (6), 39 (2009).
4. *EPA Federal Register, National Emission Standards for Hazardous Air Pollutants for Source Categories: Aerospace Manufacturing and Rework Facilities*, 60 (170), 45947 (1995); http://www.epa.gov/ttn/atw/aerosp/fr9195.pdf.
5. ASTM Standard D3359, 2002, "Standard Test Methods for Measuring Adhesion by Tape Test," ASTM International, West Conshohocken, PA, DOI: 10.1520/D3359-02.
6. AMS-M-3171-C, "Magnesium Alloy, Processes for Pretreatment and Prevention of Corrosion on," Society of Automotive Engineers, Warrendale, PA: Standardized Document Order Desk).
7. ASTM B117, 2002, "Standard Practice for Operating Salt Spray (Fog) Apparatus," ASTM International, West Conshohocken, PA, DOI: 10.1520/B0117-02.
8. MIL-PRF-23377J, "Performance Specification - Primer Coatings: Epoxy, High Solids," (2006).
9. FED-STD-141, "Federal Test Method Standard Paint, Varnish, Lacquer, and Related Materials: Methods of Inspection, Sampling and Testing," Philadelphia, PA: Standardization Document Order Desk.

About the author

Dr. Alp Manavbasi is Vice President of Technology at Metalast International, in Minden Nevada. He has prior training and professional experience in materials research, mainly focused on the metallurgical analysis of corrosion-resistant alloys, electrochemistry, powder metallurgy, electroceramic synthesis/characterization and experience with design of experiments. As an engineer with interdisciplinary background and research experience, Alp leads the research and development team focused on the development of eco-friendly coatings for metals, surface treatment of alloys, materials testing and characterization, and has a technical role in the continuous improvement activities at Metalast. Dr. Manavbasi holds an M.S. degree in Metallurgical Engineering and a Ph.D. in Materials Science and Engineering from the University of Nevada - Reno.