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New Pretreatments and Non-Chromated Chemfilm for Magnesium Alloys

ABSTRACT

A new environmentally friendly non-chromated chemfilm with different pretreatments was studied as a replacement to conventional hexavalent chromium-based chemfilm technologies for magnesium alloys. Anti-corrosion and paint adhesion properties of conversion-coated sand-cast AZ92A-T6 magnesium alloy were investigated. Open-circuit potential (Eoc), potentiodynamic polarization, neutral salt spray and gravimetric methods were employed to evaluate the corrosion resistance of this novel conversion coating. Surface morphology and the presence of the coating were investigated by scanning electron microscopy (SEM) technique. Tape adhesion and pull-off adhesion studies were performed to characterize the paint adhesion properties. Rework along with the Touch-Up application and turbine-oil immersion studies was performed in order to simulate the depot-level maintenance. The results of corrosion and paint adhesion studies revealed that the new non-chromated conversion coating technology could be a drop-in replacement to the conventional hexavalent chromium-based conversion coatings.

Introduction. There are various physical or chemical surface treatment technologies developed in order to improve the anti-corrosion and/or surface adhesive bonding properties of magnesium alloys. Chemical conversion coating methods have been proven to be very effective and cost-efficient technologies to provide anti-corrosion and paint adhesion properties on magnesium alloys. The type of pretreatment used prior to conversion coating application is very critical for the corrosion protection, adhesion and paint-base properties to the metal. Although magnesium quickly forms a passive oxide film on its surface in air or water, it is porous in nature and non-protective [1]. This natural oxide layer on magnesium, consisting of oxide-hydroxide, has a detrimental effect on the coating deposition and uniformity. Therefore, an appropriate cleaning and pretreatment of the magnesium surface is very crucial to obtain good and consistent chemical conversion coatings. Mechanical, chemical and electrochemical pretreatment methods, including acid pickling, alkaline cleaning, fluoride activation, etc., have been commonly used for the removal of the natural oxide layer to provide a relatively better receptive surface for the subsequent chemical conversion coatings on magnesium alloys [2,3]. Proper pretreatment enables the formation of homogeneous chemfilm on the magnesium surface with good barrier layer properties and higher corrosion resistance.

The conventional chemical surface treatment of magnesium alloys involves the use of hexavalent chromate compounds, which are highly toxic and adversely affect the environment and human health. Although there are other commercially available chemfilm technologies that do not contain hexavalent chromate, their corrosion protection and paint-adhesion properties cannot compete with the hexavalent chromates. Therefore, an environmentally friendly chemical surface treatment method has to be developed to eliminate the usage of chromates and to meet or exceed the protectiveness-to-cost ratio of the conventional chromated coatings.

This work presents the corrosion and paint adhesion properties of a new trivalent chromium-based conversion coating technology along with three different pretreatment methods on AZ92A-T6 cast magnesium alloy. The performance results were compared with the commercial hexavalent chromated magnesium alloy to show that this novel coating technology can replace the conventional chromated conversion coatings.

2. EXPERIMENTAL

2.1 Materials and Sample Preparation. The substrate material used was an AZ92A-T6 sand-cast magnesium alloy. The chemical composition of the alloy is given in Table 1. All samples were mechanically polished with SiC papers of 1200 grit and then acetone wiped before the pretreatment and/or conversion coating application. Alkaline cleaning was done in a METALAST Magnesium Cleaner at 140°F for 5 min. Three novel pretreatment chemicals were used prior to the conversion coating application. Immersion time for the pretreatment solutions and the trivalent chromium coating was five minutes at ambient temperature. Specimens were rinsed for one minute in RO water between each step. All coated samples were cured for 24 hours at ambient temperature prior to the measurement of anti-corrosion and paint adhesion properties.

Al (wt. %)	Zn (wt. %)	Mn (wt. %)	Si (wt. %)	Cu (wt. %)	Ni (wt. %)	Others (wt. %)
8.3-9.7	1.6-2.4	•0.1	•0.3	•0.25	•0.01	•0.3

Table 1. Composition of AZ92A-T6 sand-cast magnesium alloy.

2.2 *Analysis and Test Methods.* The microstructure of AZ92A-T6 alloy was characterized by using an Olympus PMG3 Metallurgical Inverted Optical Microscope with Olympus DP-70 controller camera and software. Surface morphology of deposited films was observed using a Hitachi S-4700 scanning electron microscope (SEM).

Corrosion resistance tests were performed on test coupons for each pretreatment process using a neutral salt fog salt spray chamber maintained in accordance with ASTM B117 [4]. Open circuit potential (Eoc) and potentiodynamic polarization measurements were performed by using a G300 Gamry Potentiostat. Experiments were carried out in an aerated 3.5 wt.% NaCl (pH 6.5-7.2) electrolyte.

Gravimetric study was done on the coated and uncoated samples by measuring the weight loss per surface area per day (g/sq.ft./day) during the neutral salt spray exposure (ASTM B117).

Test samples were primed with a non-chromated epoxy primer (MIL-PRF-23377J, Type I, Class N) [5] and cured for 7 days at room temperature prior to the corrosion and adhesion tests. Cyclic corrosion test was done in accordance with GM9540P [6] and the creepback rating was done in accordance with ASTM D3359A [7].

Oil immersion tests were conducted in MIL-PRF-23699F [8] turbine oil at 250°F for a period of 24 hours.

3. RESULTS AND DISCUSSION

3.1 *Microstructure.* The microstructure of sand-cast AZ92A-T6 magnesium alloy is shown in Figure 1. The alloy was mainly composed of primary α-phase, β-phase ($Mg_{17}Al_{12}$) and the eutectic phase (α + β-$Mg_{17}Al_{12}$) in the form of fine lamellar structure. The -phase can act as a barrier or as a galvanic cathode depending on the volume fraction of β-phase in α-matrix [9]. The β-phase serves as cathode and accelerates the galvanic corrosion of the α-matrix if the volume fraction of β-phase is relatively small. It is expected that AZ92A-T6 will have micro-galvanic activity around the primary α-phase. On the other hand, the corrosion attack will be limited on the grains with fine lamellar structure (eutectic phase) due to the fine distribution of the β-phase and to the formation of a protective corrosion layer with relatively high aluminum concentration [9,10].

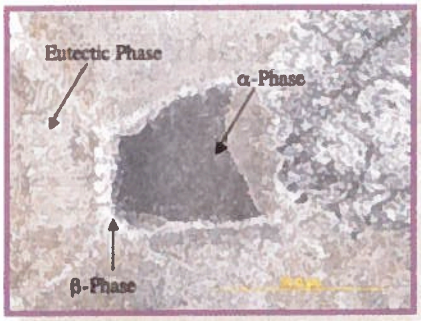

Figure 1. Microstructure of AZ92A-T6 alloy.

3.2 *Coating Formation.* Figure 2 shows the open circuit potential (Eoc) evolution of the AZ92A-T6 alloy immersed in the trivalent chromium conversion coating bath for 1800 seconds. The Eoc shows a sharp increase towards more positive potential values during the first 200 s of immersion. This positive shift in potential from -1.88 V to -1.63 V indicates the surface activation and the formation of the stable protective coating layer. After 360 s the Eoc approached constant values by reaching the stable state and completing the formation of the chem-film on the magnesium alloy.

The surface morphology of AZ92A-T6 magnesium alloy processed with the novel trivalent chromium based conversion coating for 5 min and cured over 24 hours at ambient temperature is shown in Figure 3. The coating covered the surface uniformly with relatively less

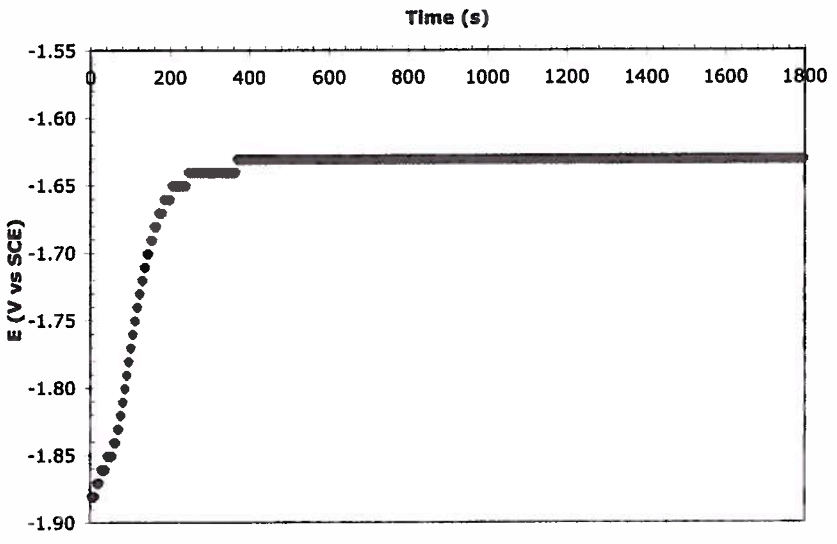

Figure 2. Open Circuit Potential evolution of AZ92A-T6 in trivalent chromium conversion coating solution.

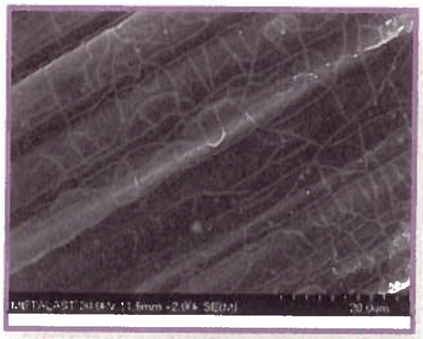

Figure 3. SEM micrograph of trivalent chromium conversion coated AZ92A-T6 magnesium after 24 h curing at ambient temperature.

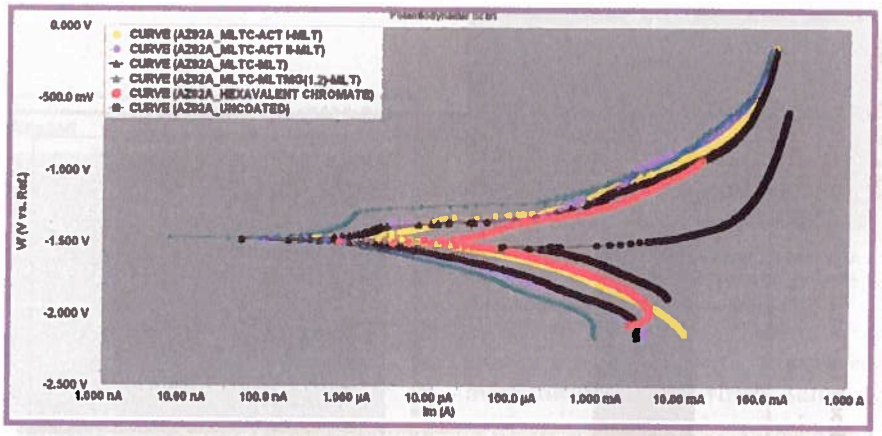

Figure 4. Potentiodynamic polarization curves of coated and uncoated AZ92A-T6 magnesium alloy.

Sample ID	Icorr (µA)	Ecorr (V)	CR (MPY)
UNCOATED	4480	-1.53	6.82E+02
HEX-CR6+	23.7	-1.49	10.84
MLTC-MLT	3.28	-1.47	6.67
MLTC-ACTI-MLT	7.14	-1.45	14.5
MLTC-ACTII-MLT	2.9	-1.48	5.89
MLTC-MLTMG(1,2)-MLT	0.76	-1.46	1.53

Table 2. Calculated corrosion rates for coated and uncoated AZ92A-T6 magnesium alloy.

amount of micro-cracks developed during the curing stage. This type of coating morphology provides good barrier-layer and relatively higher anti-corrosion properties.

3.3 Corrosion Resistance and Paint Adhesion Properties.

Potentiodynamic polarization curves of the coated and uncoated AZ92A-T6 magnesium alloy are shown in Figure 4. METALAST Magnesium Cleaner (MLTC) and three different activators (ACT I, ACT II, MLTMG(1,2)) were used prior to trivalent chromium (MLT) application. Trivalent chromium conversion coating increased the pitting potential and also restrained largely anodic and relatively less degree cathodic reactions. Calculated corrosion rates for uncoated, hexavalent coated and trivalent chromium processed samples were 682 mills per year (MPY), 10.84 MPY, and 6.67 MPY, respectively. Using activators significantly improved the corrosion rates to as low as 1.53 MPY when the surface is treated with MLTMG(1,2) activator prior to the trivalent chromium application as shown in Table 2.

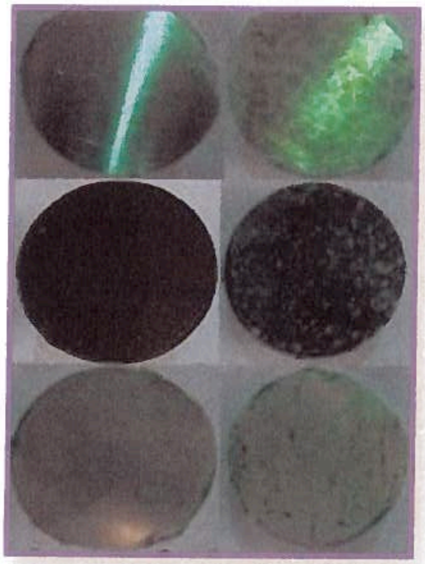

Figure 5. Uncoated (top), hexavalent chromated (middle) and METALAST trivalent chromium (bottom) coated AZ92A-T6 before (left column) and after (right column) 4 h neutral salt spray testing in accordance with ASTM B117.

Figure 5 shows the METALAST trivalent chromium processed, hexavalent chromated, and uncoated AZ92A-T6 magnesium alloys before and after 4 hours of salt spray exposure in accordance with ASTM B117. Uncoated magnesium showed significant corrosion formation throughout the exposed surface and hexavalent chromated magnesium alloy showed some white corrosion along with a few pit formations after 4 hours of neutral salt spray exposure. On the other hand, trivalent chromium processed AZ92A-T6 magnesium developed relatively less amount of corrosion except a few isolated pits on the exposed surface. This shows that this novel trivalent chromium provided relatively better corrosion protection compared to the commercial hexavalent chromate-based conversion coatings.

Gravimetric study was done on the coated and uncoated AZ92A-T6 magnesium alloy by measuring the weight loss per surface area per day (g/sq.ft./day) during the neutral salt spray exposure per ASTM B117 (Figure 6). Trivalent chromium coated samples (MLT) had almost five-fold less mass loss compared to uncoated AZ92A-T6 magnesium alloy and it was at comparable levels to the mass loss observed on hexavalent chromated samples.

Coated and uncoated AZ92A-T6 magnesium samples were primed with non-chromated epoxy primer (MIL-PRF-23377J, Type I, Class N) and then top-coated with MIL-PRF-85285 polyurethane paint before neutral salt spray exposure. Figure 7 details the images of the scribed samples before and after 336 hours of neutral salt spray. METALAST trivalent chromium and hexavalent chromated samples had the same rating of 8 in accordance with ASTM D1654. On the other hand, samples

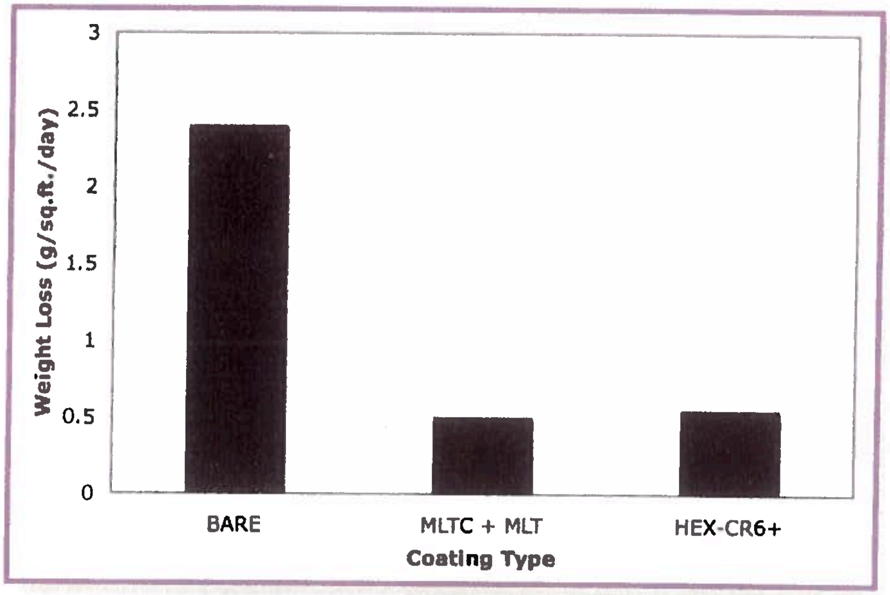

Figure 6. Weight loss per surface area per day (g/sq.ft./day) of bare and conversion coated AZ92A-T6 samples when exposed to neutral salt spray corrosion testing per ASTM B117.

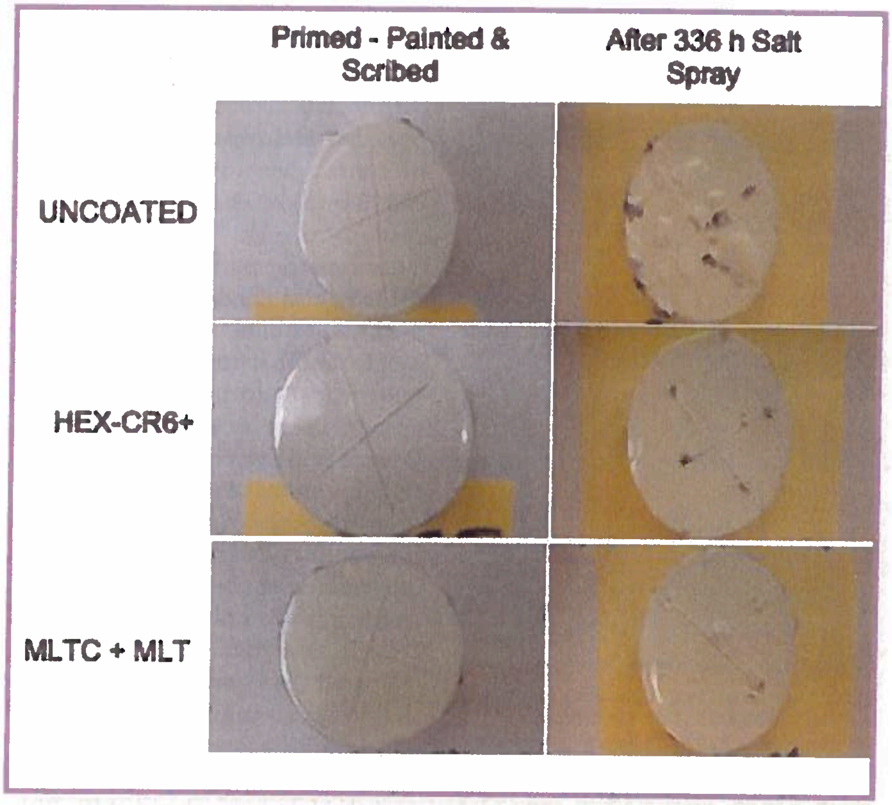

Figure 7. Primed and polyurethane painted AZ92A-T6 samples with no conversion coating, hexavalent chromated and trivalent chromium treated.

with no conversion coating had a corrosion rating of less than 3.

Cyclic corrosion testing of conversion coated and uncoated AZ92A-T6 magnesium alloy conducted in accordance with GM9540P. Table 3 details the ASTM D1654 creepback ratings of trivalent chromium coated, hexavalent chromated and uncoated samples after 60 cycles. Samples with no conversion coating had a rating of 6 after 10 cycles; on the other hand, trivalent chromium- coated samples performed comparably similar to hexavalent chromated samples even after 60 cycles with a corrosion rating of 7 and 8, respectively.

Oil immersion tests were conducted in MIL-PRF-23699F turbine oil at 250°F by immersing the test samples half way through into the bath for a period of 24 hours. Table 4 details the visual rating per ASTM D1654, Pull-Off adhesion test results and failure mechanisms of non-chromated epoxy primer painted bare or conversion coated AZ92A-T6 samples after the oil immersion test. Samples without any conversion coating had a corrosion rating of 9 and the failure mode for the pull-off adhesion was substrate/adhesive with very low adhesion value of 2271 psi. On the other hand, both METALAST trivalent chromium-processed and hexavalent chromated AZ92A-T6 magnesium alloy samples had a corrosion rating of 10, and the failure mode for the pull off adhesion was primer/cohesive. Trivalent chromium coated samples had relatively higher pull-off adhesion value of 3140 psi compared to the hexavalent chromated samples (2542 psi).

3.4 TOUCH-UP AND REPAIR

Depot-level maintenance procedures require stripping and recoat applica-

ASTM D1654 Creepback Ratings for GM9540P Cyclic Corrosion				GM 9540P Cycles					
Sample ID	Surface Finish	Primer	Topcoat	10	20	30	40	50	60
MLT	Mechanical	MIL-PRF-23377J	MIL-PRF-85285D	9	9	9	8	7	7
Hex-CR6+	Mechanical	MIL-PRF-23377J	MIL-PRF-85285D	9	9	9	8	8	8
Bare	Mechanical	MIL-PRF-23377J	MIL-PRF-85285D	6	-	-	-	-	-

Table 3. ASTM D1654 Creepback ratings for GM 9540P cyclic corrosion testing of bare and conversion coated AZ92-T6 magnesium alloy.

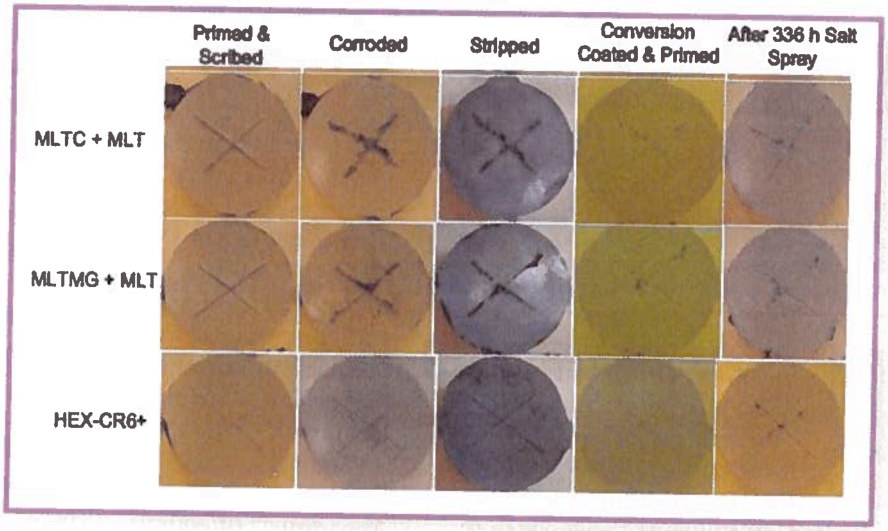

Figure 8. AZ92A-T6 magnesium samples with multiple conversion coatings after rework and 336 hours neutral salt spray. MLTC: METALAST Magnesium Cleaner, MLTMG: METALAST Magnesium Activator, MLT: METALAST Trivalent Chromium, HEX-CR6+: Commercial Hexavalent Chromate.

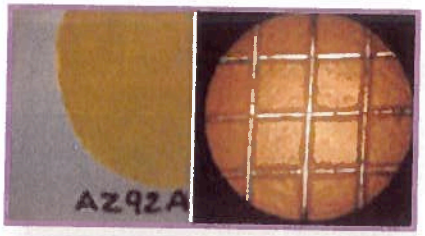

Figure 9. Cross-hatched area after 24 hours oil immersion. Samples were METALAST trivalent chromium processed and then primed.

tion in order to complete the rework on damaged surface. Bare and conversion coated AZ92A-T6 magnesium samples were primed with MIL-PRF-23377J (Type I, Class N) primer and cured. Samples were artificially corroded in sodium chloride solution and then the primer and corrosion products were removed mechanically. After which, samples were re-conversion coated and primed to simulate touchup and repair. Samples were then tested in accordance with ASTM B117 in a neutral salt spray chamber to quantify the corrosion protection offered. Figure 8 shows the images for the samples in this rework process, and Table 5 details the corrosion performance ratings per ASTM D1654. METALAST trivalent chromium coatings provided the best corrosion protection after rework with a rating of 8 and outperformed the hexava-

COATING TYPE	VISUAL RATING (ASTM D1654)	PULL-OFF ADHESION (PSI)	FAILURE MODE
MLTC+MLT	10	3140	PRIMER/COHESIVE
HEX-CR6+	10	2542	PRIMER/COHESIVE
UNCOATED	9	2271	SUBSTRATE/ADHESIVE

Table 4. Visual rating per ASTM D1654, Pull-Off adhesion test results and failure mechanisms of the primed AZ92A-T6 samples (bare and conversion coated).

COATING TYPE	ASTM D1654 RATING AFTER 336 h SALT SPRAY
MLTC + MLT	8
MLTMG + MLT	6
HEX-CR6+	6

Table 5. Neutral salt spray corrosion performance ratings for reworked AZ92A-T6 magnesium samples shown in Figure 8.

lent chromated samples (rating of 6).

Paint adhesion studies in accordance with ASTM D3359 have been conducted on AZ92A-T6 alloy after exposed to hot turbine oil for 24 hours. Samples were initially reworked by removing the corroded areas, then trivalent chromium conversion coated and non-chromated (Type N) MIL-PRF-23377J primer was applied. After oil immersion, cross-hatched area was examined to give the adhesion rating in accordance with ASTM D3359. All samples had an excellent rating of 5 in accordance with ASTM D3359-Method A and Figure 9 shows the cross-hatched surface after oil immersion for 24 hours.

It is also important to note that there was no hexavalent chromium formation in the bath even after processing large amount of surface area. Additionally, these new pretreatments and the trivalent chromium conversion coating did not change the fatigue properties of the magnesium alloys. All these details will be published elsewhere.

CONCLUSIONS

New environmentally green pretreatment chemicals and trivalent chromium based conversion coatings were deposited on AZ92A-T6 magnesium alloy. The coating formed a uniform and compact layer on the magnesium substrate. Comparative performance analysis showed that META-LAST trivalent chromium coated surface provided relatively better corrosion performance compared to the conventional hexavalent chromated magnesium.

Potentiodynamic polarization, neutral salt spray and gravimetric methods revealed that this new trivalent chromium conversion coating outperformed the commercially available hexavalent chromates. Primed and scribed surfaces with and without stripping & rework gave comparable results for both the new trivalent chromium and hexavalent chromium processed magnesium surfaces. Touch-Up and rework studies revealed that the new trivalent chromium combined with the proper surface pretreatment can outperform the corrosion performance of hexavalent chromates commercially available in the market. These results showed that this eco-friendly trivalent chromium-based conversion coating chemical could be a drop-in replacement to the conventional hexavalent chromates for magnesium alloys.

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