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Alkaline Corrosion-Resistant Sealant for Anodized Aluminum Alloys

ABSTRACT
Corrosion resistance of anodized aluminum sealed with conventional and a new sealant was tested against the alkaline, acid and neutral chloride salt solutions. The results show that the conventional water based sealants have good acid and Neutral Salt Fog resistance; however, they do not possess the necessary alkaline corrosion resistance to be used for decorative and automotive exterior applications. A new anodic coating sealant was developed to provide the necessary alkaline corrosion resistance along with the acid and neutral salt attack resistance. Acid Dissolution Test (ADT) Rating, Alkaline Corrosion Resistance, Neutral Salt Fog, Heat Resistance and Alkaline Car Wash Detergent tests were done in accordance with General Motors Spec GMW 14665. Results revealed that this novel sealant is significantly capable of meeting the rigorous GMW 14665 specification and can be used for sealing the anodic coatings used in automotive exterior applications.

Anodizing is an efficient electrochemical conversion coating method to improve the corrosion and wear resistance of aluminum alloys. In general, acid, alkaline and salt attack resistance of the anodic films depends on the integrity, physicochemical properties, thickness, and the sealant type used as a post-treatment for anodic coatings [1,2]. Sealants improve the corrosion resistance of anodized aluminum by closing the micro-pores of anodic films to prevent the corrosive media from reaching the aluminum substrate [2]. Hydrothermal, nickel acetate, and dichromate are the most commonly used commercially available anodized aluminum sealants. Cold nickel fluoride and trivalent chromium-based room temperature anodized aluminum sealants are relatively new technologies.

All of these commercial sealants have the advantage of being water based and exhibit relatively good acid and salt attack resistances. However, they do not have the necessary alkaline corrosion resistance to be used for decorative and automotive exterior applications above beltline per GMW 14665 [3].

In the present study, the alkaline, acid, and neutral salt spray resistance of anodic coatings sealed with the new MLT anodizing sealant was investigated. A comparative performance study between the commercially available seals and this newly developed MLT anodic coating sealant was made.

1 EXPERIMENTAL
6061-T6 wrought aluminum alloys were used for experiments. Test coupons were degreased and cleaned in alkaline cleaner. Cleaned and degreased coupons were rinsed in flowing tap water for 1 min. After alkaline etching and rinsing, coupons were deoxidized in mixed acids at room temperature and rinsed in flowing tap water for 1 min. Thin film sulfuric acid anodizing (12 ASF (1.3 A/dm²), 7.5 mm) was performed in an electrolyte consisting of 190 g/L sulfuric acid and 7 g/L Al₂O₃ ions at 21°C. The processing details of the applied post treatment processes for the anodized aluminum samples are listed in Table 1. The resultant anodic coating thickness was measured in accordance with ASTM B244 [4] using a pre-calibrated eddy current instrument.

High pH alkaline corrosion resistance of the sealed anodized aluminum was measured by immersing the test coupons in a high pH test solution prepared in accordance with GMW 14665 [3]. The measured pH of the test solution was 13.0 and the immersion time was 10 min at room temperature. Alkaline corrosion resistance tests were performed, both without, and after exposure to car wash abrasion testing. The sealed sample was continuously scrubbed with a nylon bristle brush and car wash kit.

<table>
<thead>
<tr>
<th>POST TREATMENT</th>
<th>CHEMICAL SOLUTION</th>
<th>TEMPERATURE (°C)</th>
<th>TIME (MIN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrothermal</td>
<td>DI water + 0.5% v/v METALAST Seal 6000</td>
<td>100</td>
<td>30</td>
</tr>
<tr>
<td>Nickel Acetate</td>
<td>4% v/v METALAST Seal 6100</td>
<td>88</td>
<td>20</td>
</tr>
<tr>
<td>Trivalent Chromium</td>
<td>25% v/v Trivalent chromium (TCP)</td>
<td>21</td>
<td>5</td>
</tr>
<tr>
<td>New MLT Sealant</td>
<td>Water based - No heavy metal</td>
<td>21</td>
<td>3-10</td>
</tr>
</tbody>
</table>

Table 1: Post Treatment Processes for Anodized Aluminum

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wash detergent solution up to 200 motions back and forth prior to the alkaline resistance test. Sealed samples with no surface change after the alkaline immersion test were exposed to Neutral Salt Fog test for 480 hours in a salt spray chamber maintained in accordance with ASTM B117 [5]. Alkaline car wash detergent resistance was measured in a modified car wash detergent solution, described in GMW 14665, with a pH of 11.2. Test coupons were immersed in room temperature detergent solution for 10 min to observe any surface change.

Temperature resistance of the sealed anodic coatings was measured after heating the test coupons at 90°C for 24 hours in air, and the evaluation was done while the test coupons were still hot. Acid Dissolution Test (ADT) rating was calculated per GMW 14665 after measuring the coating weight dissolved in chromic-phosphoric acid solution as per ASTM B680 [6] and the total coating mass in mg as per ASTM B137 [7]. Dye Stain test on sealed anodized aluminum samples was done in accordance with ASTM B136 [8].

Water contact angle measurements were carried out to quantify the degree of hydrophilicity using a Rame-Hart model 250-F1 contact angle goniometer.

Field Emission Scanning Electron Microscopy (FE-SEM) images of the anodized aluminum before and after sealing were acquired with a Hitachi S-4700 FE-SEM.

Wet tape adhesion studies were performed in accordance with FED-STD-141, Method 6301 [9]. Sealed anodic coatings were primed with a non-chromated water based epoxy primer qualified to MIL-PRF-23377J (Type I, Class N) [10].

2 RESULTS AND DISCUSSION
2.1 Alkaline and Neutral Salt Fog Corrosion Resistance. High pH alkaline corrosion performance and dye stain test (ASTM B136) results for the traditional sealants, including hydrothermal, duplex hydrothermal and trivalent Cr, trivalent Cr, and duplex nickel acetate and trivalent chromium seals are shown in Figure 1. All panels were anodized to 7.5 μm, and the operating parameters for the sealants were given in Table 1. The dip line indicates that commercially available traditional sealants were attacked by the high pH alkaline test solution. On the other hand, dye stain test was done above the dip line and conventionally sealed samples passed the test with no stain formation. Samples post-treated with a clear organic coating provided the necessary alkaline corrosion and 480 hours Neutral Salt Fog resistance with no demarcation and/or pit formation. However, additional coatings or topcoats before or after sealing are not a robust and economical way to provide the necessary alkaline corrosion resistance on anodized aluminum. Furthermore, using additional topcoats such as organic or inorganic paints, sol-gel, nanoparticles, physical or chemical vapor deposits, etc. will not meet the requirements of GMW 14665 specification.

Figure 2 shows the MLT sealed test coupons after high pH alkaline immersion test followed by 480 hours salt spray. Anodized test coupons sealed with MLT sealant for 3 min, 5 min, and 10 min at 65°C prevented the alkaline corrosion and neutral salt fog attack. Similarly, two-step electrolytic colored anodized aluminum (20 μm) sealed with new MLT sealant provided the necessary alkaline and neutral salt fog resistance to meet the GMW 14665 requirements. In addition, MLT sealed samples did not.
show any sign of degradation or surface appearance change after the car wash abrasion and alkaline resistance tests. Dye stain test results per ASTM B136 indicated that anodic coatings sealed with the new MLT sealant has the necessary stain resistance to be used in decorative applications.

Longer exposure times (4,000 seconds) to the high pH alkaline test solution revealed that 10 min sealing time in MLT sealant provided the best alkaline corrosion resistance as shown in Figure 3. Anodized samples sealed for 3 min with MLT sealant indicated some local alkaline attack after 4ks, and 5 min MLT sealing showed relatively better alkaline corrosion resistance.

3.2 Alkaline Car Wash Detergent Resistance. Alkaline car wash detergent chemical test solution defined in GMW 14665 was modified to test the detergent resistance of the MLT sealed anodic coatings. Sealed anodized aluminum test samples were immersed in alkaline car wash detergent test solution for 10 min, then rinsed and air-dried. Visual inspection of the tested samples revealed that there was no surface appearance change.

3.3 Acid Dissolution Test (ADT) rating and Temperature Resistance. For clear anodized and sealed aluminum, the Acid Dissolution Test (ADT) Rating was defined as [3]:

\[
\text{ADT Rating} = \frac{((W1-W2)/(W1-W3)) \times 7.8}{T}
\]

- where W1-W2 is the coating weight (mg) measured per ASTM B680 [6], W1-W3 is the total coating weight (mg) of anodic coating measured per ASTM B137 [7], and T is the anodic coating thickness in micrometers.
- The calculated ADT rating has to be less than 6.0 in order to meet the GMW 14665 requirements [3].

- New MLT sealed anodic coatings (7.5 mm) had an ADT rating of 5.4 ± 0.5. This shows that the MLT sealant has the required acid corrosion resistance in addition to the alkaline corrosion resistance per General Motors spec GMW 14665.
- Temperature resistance test was done by heating the sealed anodic coating for 24 hours at 90°C in air. Visual inspection was made when the samples were hot and there was no sign of cracks or scratches induced by the heat treatment.

3.4 Surface Hydrophilicity and Wet-Tape Adhesion Performance. Static water contact angle measurements revealed that the new MLT sealed anodic coatings have an initial contact angle of less than 5 degrees, and after overnight curing the contact angle values reached to 20 degrees. Longer drying/curing at ambient temperature for over four weeks indicated that the contact angle reached to 30 degrees. This indicates that the new MLT sealed surface is highly hydrophilic and can be easily wetted by topcoats.

MLT sealed anodized aluminum samples were primed with a non-chromated water based epoxy primer qualified to MIL-PRF-23377J (Type I, Class N) [10]. Primed samples were cured at room temperature for seven days before being scribed and immersed in RO water. Wet tape application after 24 hours immersion in RO water revealed that there is no peeling or removal from the scribed areas (See Figure 4).

3.5 Surface Morphology. SEM micrographs of the MLT sealed and unsealed anodized aluminum surface are shown in Figure 5. Unsealed anodic coating has the characteristic porous structure of the anodic film. It is homogeneously distributed and the typical pore size is about 10 to 15 nm range. After MLT sealing, the initial porous structure completely disappeared (Fig. 5A). As a result, MLT sealing efficiently blocks the channels through which corrosive media attack the aluminum substrate. Studies to understand the sealing mechanism are currently in progress.

CONCLUSIONS
Commercially available traditional anodic coating sealants do not have the required high pH alkaline corrosion resistance to be used in automotive exterior applications. Alkaline corrosion resistance tests were done in accordance with General Motors
spec GMW 14665 and all the conventional single or duplex sealants including the nickel acetate and hydrothermal seals indicated severe alkaline corrosion attack. On the other hand, a newly developed MLT sealant provided the necessary alkaline corrosion and the neutral salt fog resistance per GMW 14665. There were no surface changes after the alkaline car wash detergent test and the temperature resistance tests. For the new alkaline-resistant MLT sealant, Acid Dissolution Test ratio was found to be 5.4 ± 0.5, exceeding the General Motors spec for the anodic coatings. New MLT sealed anodized aluminum surfaces are very hydrophilic even after four weeks of curing at room temperature and wet tape adhesion studies showed that MLT could be used for paint applications on the anodic coatings.

ACKNOWLEDGEMENT
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REFERENCES
3. GMW 14665, “[Anodic Oxidation Coating on Aluminum]” (General Motors Material Specification Finish - Worldwide Engineering Standards, [January 2009]).


AVAILABLE FOR DOWNLOAD ON METALFINISHING.COM...
“Alternative to Dichromate Sealer in Anodizing Operations.”
This paper describes the requirements for anodizing and sealing operations within Ogden Air Logistics Center (OO-ALC), as well as the sealing technologies that are available and a path forward to demonstrate/validate the most promising alternatives for the specific needs and applications of OO-ALC. To meet this need, the Air Force Research Laboratory tasked Concurrent Technologies Corporation, Largo, Fla., to identify viable alternatives to the sodium dichromate sealer, conduct testing on these alternatives, and recommend the most promising sealer(s) for implementation based on the test results.

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