

Insights Regarding the Adhesion Mechanism for Supplementary Organic Coatings on Porous Anodic Films

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Abstract: A novel anodic coating process for aluminum and aluminum alloy substrates has been developed that enables the formation of composite polymer-metal oxide films. An extensive study comparing the adhesion of various inks and adhesives to the new finish and to Types I, II and III anodic films elucidates the reaction and bonding mechanism of the supplementary coatings. By understanding this mechanism, a basis for organic-inorganic reactions within anodic films can be realized, resulting in higher reliability attachments and offering new areas for finish application.

1. Introduction

The use of dual phase transition layers to facilitate ceramic to metal bonding is a well-developed, reliable technology that has a long history of application in any industry that employs seals.^{1, 2} In the realm of polymer – metal sealing, there is currently no known true transition layer. Mechanical and/or chemical roughening and chemical adhesion promoters such as primers are often utilized to enable adhesion of a polymer layer to a metal substrate, be it an ink, paint, lacquer or adhesive. On aluminum, the surface is often anodized.

Anodizing can be viewed as the deliberate, electrochemically controlled corrosion of the aluminum surface in aqueous solutions of sulfuric, chromic or oxalic acid.³ The resultant finishes are typically uniform, continuous and, depending upon the electrolyte, exhibit a unique porous, columnar structure. See Figure no. 1.

Organic dyes and other polymer layers and finishes are often applied to anodic oxide finishes to impart decoration in the form of

color, print, and/or other graphic designs. Thin chromic acid (Type I) and sulfuric acid (Type II) anodic finishes are often dyed, laminated, and/or used as a primer layer for paint. Thin polymer dispersion layers of colloidal PTFE are applied to the surface of hard anodized (Type III) films to reduce friction and increase surface smoothness as an enhancement to the inherent hardness of a Type III anodic finish, often utilized in wear and abrasion applications.

Similarities between the aluminum anodization process and the oxidative polymerization reactions for certain conjugated polymers, as well as the electroactive characteristics of these polymers with protonic acid doping indicated anodizing and electrodeposition of the polymer could be carried out simultaneously, producing composite polymer-metal oxide films. Uniform, continuous films have been electrochemically formed which exhibit structural modification and polymer phase inclusion.

To date, engineering testing of the composite finish has shown increased dyeability, UV stability and adhesion of subsequent polymer layers. Testing has been performed in the laboratory and in various field applications. In an effort to understand the performance improvements, comparative scientific characterization of the composite finish has been performed to standard anodic finishes. This paper presents these analyses and findings.

2. Engineering Characterization

A. Color Fastness

The South Florida Test Service performed accelerated weathering tests according to MIL A 8625 F modifications to ASTM G 23. Aluminum alloy 6061 T6 panels were anodized both conventionally (Type II) and with the composite finish, both dyed black and sealed. Specific panel color, quantifying both the hue and brightness, was determined with a Hunterlab Ultrascan spectrophotometer. The panels were then exposed to 200 hours of radiation using an Atlas FDA-R Single Enclosed Carbon Arc Fade-Ometer. Differences in color were then quantified by the spectrophotometer, outlining the color change over time.

The reported summation of all color and brightness changes for the anodized composite finish, the coefficient value E^* , was 0.42, one third of the change exhibited by the 1.45 E^* value for the conventionally anodized (Type II) panel.

B. Adhesion Testing

Two hundred (200) samples each of aluminum alloy 6061 components were finished with a hard version of the composite coating (Type III equivalent), dyed black and sealed two different ways. One set of one hundred (100) components was sealed with hot water and one set of one hundred components was sealed in a duplex fashion, first with nickel acetate and followed by a sodium dichromate seal. The sample sets were subjected to four (4) permutations of cleaning and treatment with a bonding agent: no cleaning with no bonding agent, cleaned with no bonding agent, no cleaning with bonding agent, and cleaned with bonding agent. All were coated with

adhesive and over-molded with a rubber-based form.

Adhesion testing of the samples was based in ASTM B571 "Test Methods for Adhesion of Metallic Coatings", paragraph 11, and "Peel Test". The rubber coating was cut and pulled at an angle of 90° to the surface of the piece with efforts to maintain the rate of pull. Following testing, the delaminated surfaces were evaluated to determine the point of failure. Inadequate adhesion was considered as failure in the coating-substrate interface.

Comparison of the various samples determined that there was little difference in adhesion between the samples processed with the hot water seal and those with the duplex seal. In fact, it was found that the degreasing operation performed prior to treatment with the adhesion promoter could successfully be eliminated without compromising adhesion of the rubber form.

C. Analysis of Screen Printed Finishes

Unsealed 10 cm² panels of aluminum alloy 6061 were finished with the composite coating, a conventional Type II anodic finish and a chromic acid (Type I) anodic finish. The average finish thickness of the samples from each group was 4 to 5 microns. The panels were screen printed with a cellulose-based ink commonly used in the anodizing industry.

Thin-sectioned samples of a conventional Type II anodized and screen-printed panel, a composite finished and screen-printed panel and a chromic acid finished and screen printed panel were prepared for examination by Transmission Electron Microscopy (TEM). Epoxy was used to mount and fix the samples during preparation. It was noted that the conventional Type II samples exhibited extraction of the ink into the epoxy bond line. The composite samples exhibited no evidence of extraction whatsoever. Clearly, more retention of the ink in the presence of an extracting agent, suggests the screen print ink was better bonded to the composite finish or at minimum, the composite finish is more polar than the Type II finish.

Examination within the TEM revealed the ink components (pigments, cellulose-based resin) exhibited segregation. The ink layer on the Type II sample measured approximately 50 nm thick. The ink layer was separate and distinct from the surface of the anodic film. Intrusion of the ink within the pores of the film was limited to one small area, to a depth of approximately 10nm. The pigment particles appeared fairly uniform in size and shape with evidence of agglomeration. The resin appeared amorphous. See figure no. 2.

Examination of the screen-printed composite finish revealed the quality of the ink layer was very different between the samples, suggesting the solvent permanency may have had an effect on the preparation. However, the interface between the ink and composite film surface exhibited what appeared to be interaction with the composite film microstructure for a distance of approximately 10 – 40 nm. EDS analysis of across the interface determined the constituents of ink within this region of the composite coating. See figure no. 3.

3. Scientific Characterization

A. Transmission Electron Microscopy

Detailed TEM analysis of samples prepared for comparative adhesion testing disclosed the presence of fibrils bridging the interface between the composite anodic oxide finish that had been hot water sealed and the organic bonding agent or adhesive. This feature was not present on the samples processed with the dichromate seal, demonstrating the absence of chemical bonding between the bonding agent and the dichromate coating. The darker appearance of the fibrils indicates that they consist of low-atomic number elements; EDS analysis determined carbon as a significant constitutive element, although the constituents of the anodic oxide were also detected. See figure no. 4.

B. High Intensity Infrared (FT-IR) Spectrographic Analysis

TEM sections of a Type II unsealed anodic film and composite films were analyzed by way of high intensity Fourier Transform Infrared Spectrographic analysis. The energy source for the instrument was

hooked up to a synchrotron light source at Brookhaven National Laboratory in Brookhaven, New York. The resolution of the instrument was 4 –5 μ .

Sections of each coating were analyzed using a 4 μ X 30 μ aperture. Data was collected from the aluminum-anodic film interface (bottom), the film center and the top. The films measured 20-25 μ thick.

The trends in the infrared data collected from the bottom of the films to the top strongly suggest a shift in the formation and amount of active hydroxide and sulfate groups. The Al-O feature at approximately 750 cm^{-1} dominates, but shifts upward in the spectra as the sulfate peaks at 1000 to 1100 cm^{-1} become larger and more defined. With the development of the sulfate absorption, hydroxide absorption becomes pronounced. This actually makes sense, as the surface of the anodic film, regardless of type or formulation, should exhibit more hydration.

The composite coating exhibited evidence of inclusion of the electroactive modifier with absorption in the higher IR. The spectral shifts toward the higher IR were noted from the substrate, where the inorganic absorbances were most pronounced to the middle and finally the surface portions where absorption of both OH^{-1} and carbon-based inorganic salts were detected within the composite film. See figure nos. 5 and 6.

In order to identify the molecular species of the oxide as formed during conventional anodization, a hot water sealed Type III coating was processed within argon plasma. With increased exposure time within the plasma, a residue developed on the surface of the coating. Infrared analysis of the residue determined absorption characteristics for hydrated aluminum sulfate and/or aluminite: $\text{Al}_2(\text{SO}_4) \cdot 18\text{H}_2\text{O}$ and/or $\text{Al}_2(\text{SO}_4)(\text{OH})_4 \cdot 7\text{H}_2\text{O}$.

These results indicate the presence of a compositional gradient from the substrate to the finish surface. This shows that the portions of the film that remain in contact with the electrolyte, in addition to hydration, will also adsorb active counter ion species from the electrolyte. Since the central pore is in constant contact with the electrolyte, a

compositional and therefore reactivity gradient across the porous structure will also be formed, creating the ability of the film to be modified through additives to the electrolyte.

C. X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) studies were performed on Type II and on two (2) groups of composite anodized samples. The composite samples were exposed to different anodizing times. One group of samples was representative of the typical exposure time of 60 minutes and the other group was representative of an extended exposure time. The samples were anodized and mechanically removed to sealed containers to prevent surface contamination through handling or by ambient air. This insured the analysis results would reflect the actual anodized surface composition from a depth of 0 to 30 Angstroms.

The Type II and composite samples anodized for the typical exposure time exhibited the presence of sulfur as sulfate. Additional oxygen and aluminum was also detected. The high-level binding energy component for oxygen corresponded to H_2O and OH^- , which supported the infrared data. The aluminum detected in the film surface of these samples was not metallic in nature; the low binding energy component was typical for disordered aluminum oxide. The composite sample did show chemical inclusion of the electroactive modifier. Saturated and π -conjugated carbons were noted with distinct linkages to the disordered (hydr)oxide structure as $HO-C=O$, $O-C=O$ and $C-OH$.

XPS analysis of the extended exposure samples determined strikingly different surface constituents. More of the electroactive additive was detected in the surface of these samples. No sulfur was determined. Evidence of metallic aluminum, and copper, as Cu_2O was also identified. The results were important because they indicated these species were actually deposited from the electrolyte and not a function of the anodization of the substrate.

4. Discussion and Conclusions

Comparative engineering testing by way of light fastness, adhesion and dye permanency testing was performed on samples finished with standard Type I, II, and III anodized finishes and samples finished with a new composite anodic finish for aluminum. Testing determined differences in performance between the two finishes. Comparative scientific characterization of the finishes was also performed.

Improved light fastness of the composite finish by a factor of three over samples with a standard Type II anodic finish was determined. These results are believed to be the result of the modification of the anodic finish microstructure introduced through the addition of the electroactive polymer to the anodizing electrolyte. The more cellular structure would result in scattering of light within the finish, rather than direct reflection as would be the case with the unidirectional columns of the typical Type II microstructure. Direct reflection would tend to degrade the dye molecules through photo initiated oxidation.⁴ Another possibility to consider would be that the retained polymeric ligands might bind with the dye, improving the stability of the color within the finish.

As the consequence of the adhesion testing, use of the composite finish as a stand-alone finish, hot water sealed, was selected. Adhesion of the bonding agent was as good to the composite finish as it was to the dichromate seal. Implementation of the composite finish with the hot water seal eliminated the use of the heavy metal seal, and the degreasing process, therefore promoting a more environmentally friendly finish and process. It also saved time and money through the elimination of the degreasing step and the duplex sealing process all together.

Comparative analysis within the TEM of the screen-printed samples determined the microstructure of the composite anodic oxide finish appeared finer and denser. The ink-finish interface exhibited evidence of interaction between the ink layer and the finish microstructure within the first 40 nm of the composite finish. EDS across the interface revealed the presence of chlorine,

a constituent of the ink, not characteristic for the composite anodizing process. The Type II film exhibited a less dense microstructure with the unidirectional columns typical for anodic structures. The ink-finish interface was clearly delineated with evidence of delamination; no intrusion of the ink within the porous structure was noted. These results strongly indicate the ink and the composite film indeed reacted together, producing a well-bonded interface.

High Intensity FT-IR analysis determined that in addition to the microstructural gradient determined by way of TEM analysis, a compositional gradient existed from the substrate to the composite finish surface. Aluminum oxide and sulfate species were identified throughout the finish thickness while carbon-based inorganic salts were detected within the top 4-5 microns of the composite finish.

The XPS results show conclusively the inclusion of fragments of the electroactive polymer modifier. Saturated and Π -conjugated carbons were noted. Probably the most significant ligands determined, regarding the possibility of functionality and therefore bonding to subsequent polymers, were carbonyl linkages, bound to the disordered (hydr)oxide structure. The C=O and -COOH groups are powerful electron-withdrawing groups, and therefore would be expected to react with subsequent polymer additions through electrophilic addition, forming stable intermediate compounds between the composite finish and the paint, adhesive, or any other polymer layer.⁵⁻⁷

TEM analysis of the hard version of the composite finish that had been hot water sealed at the interface between the finish and the bonding agent disclosed the presence of fibrils bridging the interface. Images of the composite anodic oxide finish that had been dichromate sealed did not exhibit these fibrous "bridges". Upon consideration of the sample orientation during high intensity FT-IR analysis, 4-5 μ on a short transverse section at the surface, and the depth of analysis during XPS, 0 – 30 Angstroms from the surface, the fibrils imaged at the composite finish – bonding agent interface during TEM analysis may be an intermediate compound formed between

the organic linkages identified as present within the composite finish and the bonding agent/adhesive.

The results of the engineering tests and the scientific characterization strongly suggest the composite coating, because of the retention of the organic ligands, is a binding surface for subsequent polymer layers. The composite finish therefore offers the first true transition layer that enables actual chemical polymer-metal bonding.

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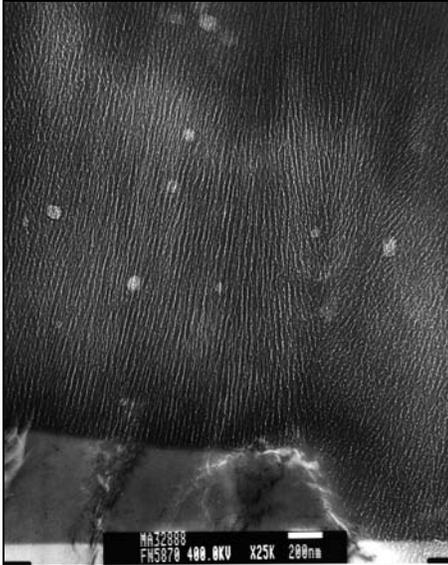


Figure 1a: TEM photomicrograph of a conventional Type II anodic film microstructure.

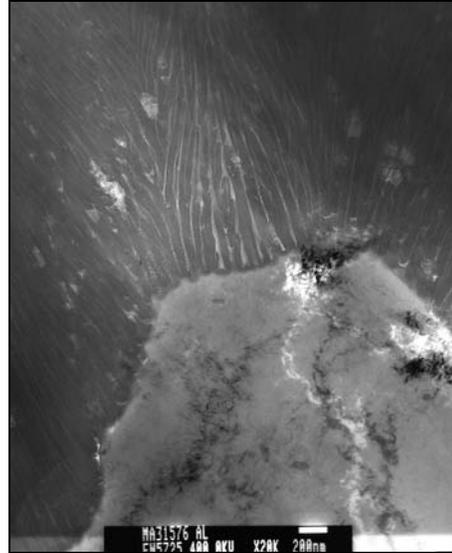


Figure 1b: TEM photomicrograph of a conventional Type III anodic film microstructure.

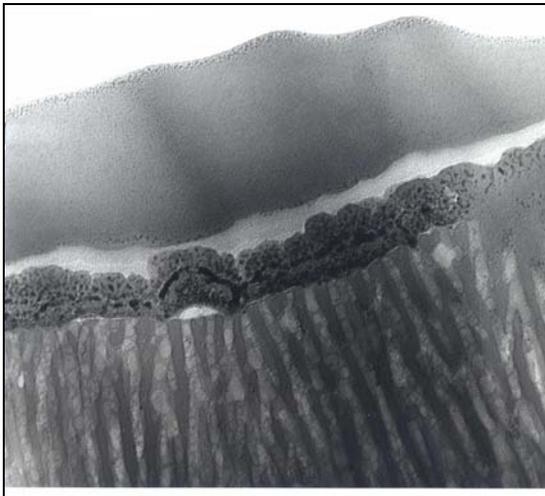


Figure 2: TEM photomicrograph of Type II finish with screen-printed ink layer. Note delamination at ink-finish interface.



Figure 3: TEM photomicrograph of composite finish with screen-printed ink layer. Note apparent interaction at ink-finish interface.

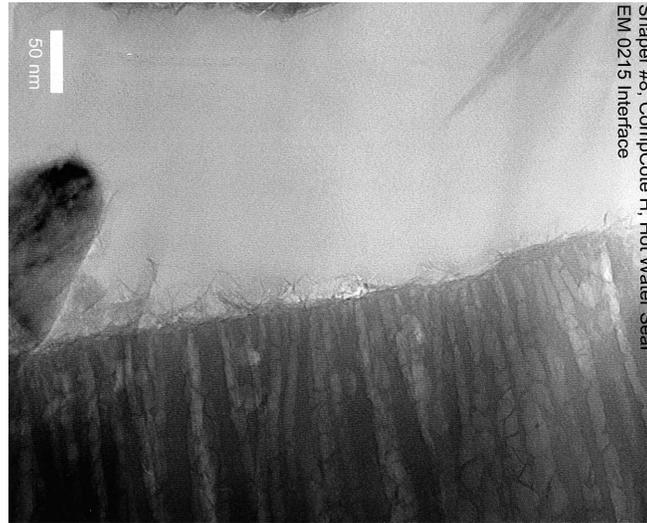


Figure 4: TEM photomicrograph of organic fibrils bridging the interface between the composite anodic oxide finish and the bonding agent/adhesive used to enhance attachment of an over-molded rubber-based form.

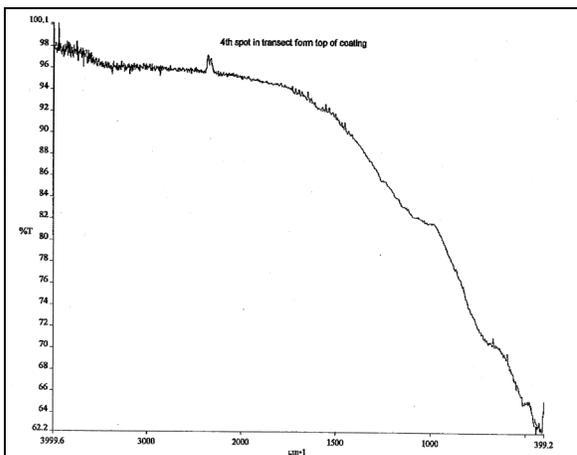


Figure 5: IR spectrum of composite anodic film adjacent to the aluminum substrate is identical to a conventionally anodized Type II film. The low-end absorbance is typical for inorganic species

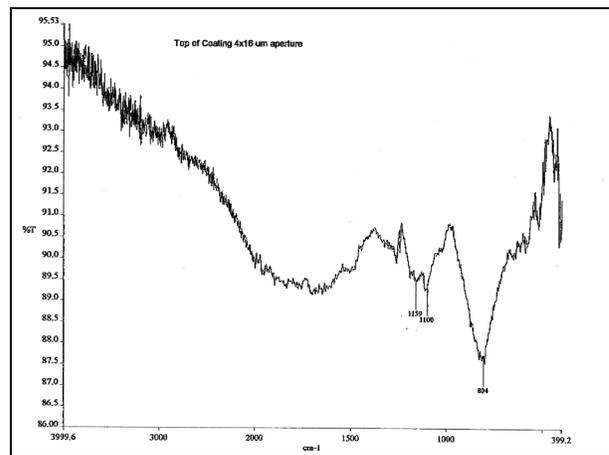


Figure 6: IR spectrum of modified composite film exhibits a shift in the inorganic spectrum toward the more chemically reactive species of sulfate and hydroxide. Some organic absorbances are also present indicative of additive inclusion

