Anodized Aluminum Alloys
Insulator or Not

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Abstract: The Automated Handling Equipment (AHE) Industry presently uses expensive, exotic and environmental unfriendly conductive or dissipative finishes such as Silver Impregnated Anodize, Black Electroless Nickel, Black Chrome, and Black Copper to control ESD. The purpose of this study was to determine if Anodized Aluminum would provide a sufficient range of dissipation. This paper describes the result of controlled experiments of several plating suppliers and types of plating. When implemented, Dissipative Anodized Aluminum will provide a conservative annual savings of at least $1,000,000 to Universal Instruments Corporation.

Introduction
In the manufacturing of Automated Handling Equipment (AHE), ESD control has to be designed into the product. It is very difficult and expensive to add ESD control solutions to the finished design. When designing ESD controls in AHEs, material selection is very important. If the surface is very conductive, charges may be dissipated too quickly producing high current that can damage components through various methods. If the surface is too dissipative or insulative, charges may be produced or induced by various methods that can also damage product. Assemblies that either guide, handle, or are in close proximity (6 inches) to the path of customer’s product have to be made of materials and coatings that will wear well and provide a path to ground within 1 ohm [1]. Anodized aluminum has always been thought of as insulative in nature and if an inspector wanted to make sure the aluminum was anodized, the inspector would use an ohm meter and point probes that would read infinity (over range) if the coating was indeed anodic. Also, from an electrical perspective, relative to ground, anodic finishes are insulative.

Anodized aluminum has always been thought of as an insulator and therefore detrimental to components and other product when used as a guide or path in some way, or in handling the product. In assemblies, additional ground straps have been used to provide additional ground paths for anodized aluminum. Engineers and designers in order to provide conductive surfaces use a number of finishes with resistance in the conductive range (< 10^5 ohms) [2]. Some of the finishes are expensive, some are environmentally unfriendly, and some do not wear as well as anodic finishes or coatings. Black Chrome, Black Copper, Silver Impregnated Anodize, and Black Electroless Nickel are all more expensive than anodized aluminum finishes (50% to 200% more) while black chrome is environmentally unfriendly and black copper does not wear as well as anodize. Silver impregnated anodic surfaces have been used in assemblies to reduce the resistance to a low dissipative range (<10^7 ohms). In assisting to stabilize a silver impregnated anodizing process, it was observed that typical anodized plating was within the dissipative range (< 10^12 ohms) [2]. If anodized aluminum could be used as a dissipative surface in AHE, the annual savings would be 1 to 1.5 million dollars, which is considered a conservative estimate. It was decided to conduct this experiment to define the electrical characteristics of anodized aluminum.
1 The Anodizing Process
Anodized aluminum is a multi-step process. The object to be anodized is immersed in an acid bath. The bath is an electrolyte and the object to be anodized is the electrically positive part or anode. Direct current is then applied and hydrolysis takes place releasing a high concentration of oxygen in a uniform manner. The oxygen reacts with the aluminum anode to form a greatly thickened, hard, and porous film of aluminum oxide.

The object is then immersed in a bath of dye or other pigments or special electrolytes to obtain the specific color and then sealed by immersion into a bath of boiling water and other chemicals, closing or filling the pores in the aluminum oxide. Depending on the provider’s process and the application, there may be other steps involved such as cleaning or etching prior to anodizing, rinsing, and drying in between the main steps.

Typically, there are 3 types of anodize with modifications available in each type. Chromic acid and sulfuric acid produces films typically from .0002 to .0007 of an inch. Hard Anodize or Hard Coat consists of a modified sulfuric bath, which produces a harder, more dense, and thicker coating. Hard Coating is usually opaque and will vary from gold to bronze or gray to black. Its thickness is usually .0005 to .0015 inches thick. Silver Impregnated Anodize is a process in which the anodized aluminum prior to drying and sealing is placed in a chemical or electrolytic bath and silver is impregnated in the pores with the intent of providing a path through the anodic layer to dissipate electrical charge.

2 Experiment

2.1 Test Design
All 63 samples had to be clearly identified so that correlations in resistance could be made between suppliers and the supplier’s process steps at 12 % and 50 % relative humidity. Supplier 1 supplied 45 samples, Supplier 2 supplied 6 samples and supplier 3 supplied 12 samples. The samples consisted of 6”X6”X .030” thick coupons of 6061 T 6 Aluminum.

Cleaning of Samples and Probes:
All measurement surfaces of the samples and electrodes were cleaned with 70% isopropyl alcohol and water as needed.

2.2 Material Tested
Supplier 1 Samples
- 6 samples anodized, no dye, and no seal
- 6 samples anodized, dyed (black), and no seal
- 6 samples anodized, dyed, and sealed
- 6 samples hard coat, no dye, and no seal
- 6 samples hard coat, dyed (black), and no seal
- 6 samples hard coat, dyed, and sealed
- 3 samples anodized, dyed red and sealed
- 3 samples anodized, dyed yellow and sealed
- 3 samples anodized, dyed blue and sealed

Chemistries Used:
- Clariant’s H3LW Black Dye
- Clariant’s Anodal MS-1 Nickel Acetate Seal
- Clariant’s MF Blue A Dye
- Clariant’s Bordeaux RL Red Dye
- Clariant’s Gold L Dye

Supplier 2 Samples
- 2 samples hardcoat aluminum, no dye, and no seal
- 2 samples hardcoat aluminum, dyed, and no seal
- 2 samples hardcoat aluminum, dyed, and sealed

Chemistries Used:
- Clariant’s H3LW Black Dye
- Clariant’s Anodal MS-1 Nickel Acetate Seal

Supplier 3 Samples
- 2 samples anodized no dye, no seal,
- 2 samples anodized baked, dyed (black) no seal
- 2 samples anodized baked, dyed, sealed
- 2 samples of hard coat, no dye, and no seal
- 2 samples of hard coat, dyed (black), and no seal
- 2 samples of hard coat, dyed, and sealed

Chemistries Used:
- Clear Nickel Cobalt Seal
- Black Dye–Sanadol H3LW
- Sulfuric Anodize
- Hardcoat Anodize

2.3 Equipment Used
Probes: 2.5 inch diameter conductive rubber electrodes weighing 5 lbs. each.
Power supply: Sorensen DRC600.75B
2.4 Test Set Up

Resistance measurements were made in environments of 25 degrees C at 12 % and 50 % RH using an Environmental Chamber. A voltmeter measured the voltage output of a power supply and a meter was used to measure the current. See Illustration 1 for diagram of set up instrumentation. The resistance was calculated. The voltage was always increased from zero to a level that produced a significant current. Both voltage and current were recorded. All samples and probes were placed in the chamber as seen in Figures 1 and 2 at the prescribed environment and soaked for 24 hours prior to making measurements. Since there were many measurements to be made, all of the samples were placed in the chamber for the duration of the test. Three measurements were set up at a time and after they were made the chamber was opened and the next set of measurements set up. One hour after the humidity level stabilized to the set level, the next sets of measurements were made. Two sets of measurements, A and B were made per sample as illustrated in Figure 3. The samples were scanned using a Scanning Electron Microscope (SEM) to determine the degree of porosity and pitting. Since the SEM has a size limitation, the samples were cut along the dashed lines indicated by Illustration 3. By making the recommended cuts the scanned areas would be the same areas contacted by the measurement probes. The measurement set and sample number were randomized to minimize any inherent variation of the measurement process. After the SEM scans were complete the samples were then placed into a salt spray and fog environment for a period of 336 hours to determine the quality of the anodized surface.

3. Results

3.1 Resistance Measurements

The following tables describe the anodize process and graphs indicate the average resistances of multiple measurements made under the stated conditions.

<table>
<thead>
<tr>
<th>Category</th>
<th>Samples</th>
<th>Treatment</th>
<th>Dyed</th>
<th>Sealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>Anodized</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>Anodized</td>
<td>Black</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>Anodized</td>
<td>Black</td>
<td>Yes</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>Hard Coat</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>Hard Coat</td>
<td>Black</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>Hard Coat</td>
<td>Black</td>
<td>Yes</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
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<td>Red</td>
<td>Yes</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>Anodized</td>
<td>Yellow</td>
<td>Yes</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>Anodized</td>
<td>Blue</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 1 lists the samples and treatment from Supplier 1. Note that Supplier 1 was the only supplier of multiple colors.

![Graph 1](image)

Graph 1 is the average resistance of 2 measurements of each of the six samples of each process from Supplier 1 at 12 % and 50% R.H. Note that samples
6, 7, and 9, which matches the treatment listed in Table 1, were higher than the other samples while still well within the dissipative range.

Table 2 lists the samples and treatment from Supplier 2, which was only Hard Coated, some samples were dyed and some were sealed.

Graph 2 that follows indicates the average resistance of multiple measurements of the number of samples and treatments listed in Table 2 at the two levels of Relative Humidity. Note that the resistances were the highest of all the suppliers. While the resistances were the highest of all suppliers samples tested, they were still well within the dissipative range of surface resistance even at 12% R.H.

Table 3 lists the treatment of the samples provided by Supplier 3, which was both Anodized and Hard Coated. There were two samples of each treatment.

Graph 3 indicates the average resistance of multiple measurements of the number of samples and treatments listed in Table 3 at the two levels of Relative Humidity. While at the 12% R.H. the resistances tended to be higher, they are still well within the dissipative range.

3.2 Salt Spray

Table 4, the following table, indicates the number of defects in the finish after subjecting the samples to a salt spray/fog environment up to 336 hours with only minor defects seen. While the Automated Handling Equipment (AHE) is not typically specified for use in a harsh environment, the salt spray is a good accelerated test to determine if there are any defects in the finish that may have had a direct impact on the resistance measurements. After 72 hours, there were no defects realized.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Dyed</th>
<th>72 Hrs.</th>
<th>336 Hrs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>31a</td>
<td>Anodized</td>
<td>Black</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>15a</td>
<td>Anodized</td>
<td>Black</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>17a</td>
<td>Anodized</td>
<td>Black</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>18a</td>
<td>Anodized</td>
<td>Black</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>38a</td>
<td>Anodized</td>
<td>Red</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>41a</td>
<td>Anodized</td>
<td>Yellow</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>44a</td>
<td>Anodized</td>
<td>Blue</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5t</td>
<td>Anodized</td>
<td>Black</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>6t</td>
<td>Anodized</td>
<td>Black</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>31a</td>
<td>Hard Coat</td>
<td>Black</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>32a</td>
<td>Hard Coat</td>
<td>Black</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>33a</td>
<td>Hard Coat</td>
<td>Black</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>34a</td>
<td>Hard Coat</td>
<td>Black</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>50m</td>
<td>Hard Coat</td>
<td>Black</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>51m</td>
<td>Hard Coat</td>
<td>Black</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>11t</td>
<td>Hard Coat</td>
<td>Black</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>12t</td>
<td>Hard Coat</td>
<td>Black</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>
3.3 Statistical Significance of Resistances

Statistical Significance testing was completed using Statgraphics and is available but not included in this report except for graphs 4 – 7.

Graph 4 displays the difference in resistance between the different process treatments of Supplier 1.

Graph 5 displays the difference in resistance of the samples supplied by Supplier 1 at the two levels of humidity. The difference in resistance is minimal.

Graph 6 displays the difference between the 3 suppliers at 12 % Relative Humidity. Note that the difference between Supplier 1 and Suppliers 2 and 3 are significant while the difference between Suppliers 2 and 3 are not significant.

Graph 7 displays the difference between the 3 suppliers at 50 % Relative Humidity. Note that the difference between Supplier 1 and Suppliers 2 and 3 are significant while the difference between Suppliers 2 and 3 are not significant.

3.4 Scanning Electron Microscope

The pictures in this section were taken with a Scanning Electron Microscope or SEM. The reason for this analysis was to rule out the possibility of porosity or defects influencing the resistance measurements. Photo 1 is a 35 X magnified image of a untypical sample submitted by Supplier 1. As indicated by the arrow, a small defect, a small bright spot, was observed. Is the defect a hole and is it sufficient to cause a decrease in the platting resistance? In Photo2, the defect is magnified to 350 X and as seen in the photo, may be a hole in the anodic layer which may provide a short circuit path through the anodize. Does the
hole penetrate to the aluminum surface? As seen in Photo 3, a 1000 X magnified image, the hole is a shallow hole and does not penetrate the anodic layer. As stated earlier, this sample was not typical of Supplier 1 since there were very few defects observed in the samples under similar analysis. Compared to other Suppliers, these samples are smoother looking with fewer pits and porosity. Suppliers 2 and 3 as seen in the following photos appear to be speckled with dark black spots. The appearance of the samples caused quite a concern about the resistance measurements. However, the resistance of the surfaces was typically higher with Suppliers 2 and 3 than Supplier 1 with the relative smooth surface. Photo 4 is a typical example of the 35 Xs magnified images of Hard Anodized samples from Supplier number 2. As seen in Photo 4, there appears to be a speckled or gritty surface finish. A higher (1000 X) magnified image can be seen in Photo 5, which displays pits and porosity in the anodic layer. There is also evidence of microcracking that is exhibited as bright streaks. The reason for the bright streaks and surfaces around some of the pitting is the surface edge retaining a charge from the electron beam. Cross sectioning of the samples from Supplier 2 as seen in Photo 12 revealed the pits and porosity was limited to the anodic surface and did penetrate to the substrate. Photos 6 and 7 are typical of the images taken from Hard Anodized samples from Supplier 3. As seen in these photos, the anodic surface is much like Supplier 2 in that the same level of pitting and porosity is present. And as seen in Photo 7, there is the same level of microcracks as seen in the samples from supplier 2. There does appear to be other particles of material on the surface in addition to the pitting and porosity, which is visible in the some of the cross-sectioned samples. Spectral Analysis of these particles indicated that many of the particles were iron inclusions, which is normal for this type of aluminum alloy and the plating process. Photo 8 and 9 are 35 X and 1000 Xs magnified images of Hard Anodized samples from Supplier 1. Note that compared to Suppliers 2 and 3, it appears smoother or less gritty and as seen in Photo 9, the porosity and pitting is much less than the other supplier samples. Also note in Photo 9 that there does not appear to be as many microcracks as in previous samples.
The following photos are a number of cross-sectioned samples magnified approximately 1000 Xs. Some of the images were taken from a SEM, Photos 10 and 11 while Photos 12 and 13, were taken from the microscope. In Photos 10 and 11, the top or darker area is the mounting medium, the middle area is the anodic layer and the bottom layer is the aluminum substrate. As seen in Photo 11, there is evidence that some cracking takes place in the anodic surface. It does not appear to be sufficient to create a short or reduction in the resistance of the surface. Also seen in the cross-sectioned photos are voids (dark spots) and inclusions of iron. Iron particulate (bright spots) is prevalent with 6061 T6 aluminum alloy. Also note that Iron particles when on the surface, prevents anodize from forming on the such as in Photo 10. The Anodize will grow around contaminates until it encompass the contaminate causing a void. Obviously, that can only take place if the contaminates are smaller than the thickness of the coating. As seen in Photos 12 and 13, most contaminates were quite small and did not pose a problem. Photo 12 is a cross-section of a Hard Coat or Hard Anodize surface and is about .0015 inch thick.

Photo 13 is a cross-section of an Anodized surface and is about .0007 inches thick. Both the Thicknesses are typical for the coatings. Photo 14 is a magnified image of a corner of the cross-sectioned sample. Note some voids are apparent. The crack in the corner is also typical of anodized corners. There are no apparent through holes to the aluminum. Iron inclusions can be seen in the aluminum.

4. Conclusions

The following conclusions are based on the data and the results of this experiment.

Type II and Hard Coat Anodize can be used as an effective and inexpensive surface treatment for aluminum alloys when used in the Automated Handling Equipment applications requiring dissipative ESD Control Surfaces such as slides, guides, and rails. ESD Control applications should be reviewed to identify the proper control characteristics for the application. With each application being properly reviewed, anodized aluminum should be used in place of the more expensive and exotic finishes. In addition to controlling ESD, for cosmetic applications, Black Anodize can be used in place of Black Electroless Nickel.

The resistance of Supplier 1’s anodized aluminum samples appears to be less affected by humidity than the other 2 supplier samples and therefore more consistent in typical manufacturing environments. However, while more dependent on humidity than Supplier 1, both Supplier 2 and 3 anodized aluminum samples are still well within the dissipative range of greater than $10^5$ to less than $10^{12}$ ohms. Platting process and applications should not be taken for granted and should be tested for proper or expected responses.

The samples tested does not appear to contain any significant defects that would explain a reduced resistance measurement in any of the samples provided and therefore the resistance would appear to be typical of anodized aluminum.
All three of the suppliers’ products would provide adequate dissipation of ESD charges in the typical environments associated with Universal Instrument Corporation’s products. However, there are some inconsistencies between the different supplier’s processes, which prove the requirement for qualifying the suppliers. While the each of the suppliers tested are satisfactory, Supplier 1 would be the preferred supplier for this application due to the overall quality.

Anodized aluminum if not used properly can cause severe and expensive problems in the EMC area. If anodized aluminum is being used in applications such as chassis or mounting plates where typically a low impedance mechanical ground is required, additional grounding devices or conductive assembly surfaces will be required.

The correlation between micro-cracking of the anodic layer and wear characteristics, the combined effects of micro-cracking and porosity at high humidity levels was not in the scope of this work and should be considered in future works.

5. Acknowledgements

I would like to Acknowledge Rodger Congdon who provided excellent Technician support and conducted the test and express gratitude to William Rabey and Danielle Lapidus for their continued technical and editorial support. I would also like to thank Megan Pellenz of Anoplate Corporation and Dave Christie, Ed Brothers, Rick Contento, and Jeff Zerilli of Ithaca Material Research for their technical assistance and analysis.

6. References

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