Batch and Spot Repairs for Color-Anodized Panels

by Hong-Hsiang (Harry) Kuo & Yar-Ming Wang*

The purpose of this report is to document repair methods for damaged electrolytic-colored anodized panels. For surface damage (i.e., scratches and chipped oxide) with no dents, there are two approaches to repair the surfaces. The first is a full panel repair, by first stripping off the oxide coating then re-growing and re-coloring the anodic oxide using a regular batch color anodization process to match the original coating thickness and color. This method has been successfully demonstrated in our laboratory and is good for repairing damaged panels in a large anodizing facility. The second approach is a spot repair method to restore the damaged panel. The advantage of this approach is that potentially, it can repair the damaged panels without disassembly. After numerous attempts, some very challenging technical issues were identified: (1) a noticeable borderline between the original and repaired anodized surfaces and (2) no electrolytic method available in the market for spot coloring the repaired (i.e., re-anodized) area.

Aluminum is one of the most abundant elements on earth and its alloys are widely used in many engineering applications due to its high strength-to-weight ratio and good formability. Currently, automotive manufacturers are considering higher aluminum content to reduce weight for better fuel economy. Traditionally, the aluminum parts are painted to match other surfaces on the vehicle. The paint operation involves many complicated process steps and environmental safeguards, and it is expensive to build and operate. Alternatively, color anodizing has been proposed to finish aluminum automotive parts since it is already widely used for architectural applications and is a simple, more environmentally friendly process.

Anodizing is an electrochemical process in which the aluminum part is the positive electrode (anode) in a suitable electrolyte (*e.g.*, sulfuric acid). A sufficiently high voltage is applied to establish the desired polarization to generate oxygen at the surface.[1-3] The formation of oxide takes place by the migration of Al^{+3} ions from the metal towards the electrolyte interface, and the O^{-2} ions migrate in the opposite direction. The anodic half-cell reaction for the oxide formation is as follows:

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$$

In the sulfuric acid anodizing process, the oxide formed is slowly dissolved by the electrolyte. Thus, a porous oxide coating is produced (Fig. 1). The net coating growth rate and its porosity depend on the equilibrium set up between the film growth and dissolution.[4]

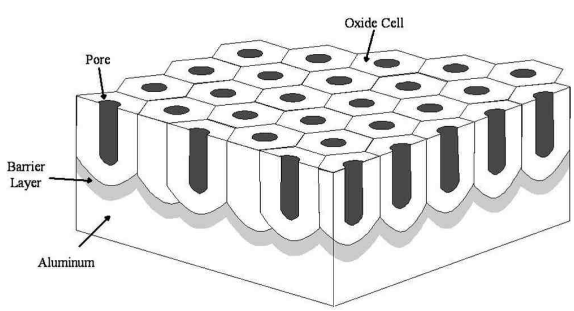

Figure 1—Schematic illustration of anodic oxide structure; typical oxide thickness, 10 to 30 µm; pore diameter, 20 nm.

Nuts & Bolts: What This Paper Means to You

Electrolytic-colored anodized aluminum panels are being proposed as light-weight paint-free automotive body panels. The big question is: If damaged in an auto mishap, how do you fix them? This paper address the question of repairing scratches and chipped oxides, and describes approaches to both a spot repair and a full-panel repair.

* *Corresponding Author:*
Dr. Hong-Hsiang (Harry) Kuo
Materials and Processes Laboratory
GM R&D and Planning
30500 Mound Rd.
Warren, MI 48090-9055
E-mail: harry.kuo@gm.com

The properties of the anodic film are highly dependent on factors such as electrolyte type, concentration and temperature as well as anodizing voltage, current density and time. Anodizing starts with the formation of a barrier (*i.e.*, non-porous) film. Although this film is barely soluble in the electrolyte, with increasing anodizing time the oxide film will grow inward and the outer surface will be slowly dissolved in the electrolyte at the same time. The precise balance of these two actions is needed during anodization in order to produce the desired porous film. This porous film can be electrolytically colored by depositing metal in the pores of the anodic oxide film.

Generally, the oxide film is hard and durable and it can be colored for automotive use. However, a good repair technology needs to be developed before color anodizing becomes a viable alternative method for finishing automotive exteriors. It is preferable that this technology can do the color-anodized repair without disassembly, which includes stripping the damaged anodic coat, re-anodizing and re-coloring to match the original substrate texture, coating thickness and color. Extensive work has been conducted to develop this technology but we have not yet found a comprehensive and viable solution.

Experimental

Batch color-anodized panel repair

This method is targeted to repair the entire damaged color anodized panel with noticeable dents. The following method has been successfully developed to carry out this type of panel repair.

1. Stripping the old anodic coating
The entire anodic coating on the aluminum parts, including both good and damaged surfaces, was removed by a strong sodium hydroxide solution containing additives.

2. Rinsing between chemical steps
There was either a single rinsing step or multiple rinses after each process step. The rinse water was normally flowing from the tank with the cleanest water to the tank with the dirtiest water (counterflow rinse). Tap water was normally used, but the last rinsing step before sealing used deionized water. The temperature of the water should be the same as in the process tanks, and the rinsing time was usually a few minutes. Good agitation of the water is very important to achieve clean surfaces.

3. Mechanical surface modification
The bare aluminum surfaces were sanded to reproduce original surface textures.

4. Degreasing
In the degreasing tank, oil, grease and other surface contaminants were removed from the surface. In this stage, alkaline cleaning was primarily used. Since aluminum is readily attacked by strong alkaline solutions, solutions at relatively low alkalinity were used to prevent attack of the metal during cleaning. Degreasing or acid cleaning by solutions containing sulfuric acid was also used. Temperatures from 20 to 70°C (68 to 158°F) were typical. The cleaning time was between 5 and 15 min.

5. Etching
Aluminum has a thin natural oxide coating on the surface, which has to be removed before anodizing. This oxide coating was removed by a sodium hydroxide solution containing additives. The purpose of this step was not only to remove the thin natural oxide coating on the surface but also to produce a matte appearance.

6. Brightening
The parts were brightened by either an electropolishing or a chemical brightening process, whichever was more suitable to convert the surface back to the original part surface appearance.

Electropolishing is a process by which metal is removed from a work piece by the passage of electric current while the work is submerged in a specially formulated solution. It literally dissects the metal crystal structure atom-by-atom, with rapid attack on the high current density areas and lesser attack on the low current density areas. The result is an overall reduction of the surface profile with simultaneous smoothing and brightening of the metal surface.

Chemical brightening is a process to brighten the aluminum surface by immersing the part in various acids (*e.g.*, a phosphoric and nitric acid mixture) to chemically smooth the surface, creating a brighter, more reflective appearance.

7. Desmutting
During the etching operation, a black smut layer may be left on the aluminum surface. This smut tends to be heavier with more highly alloyed aluminum, and is particularly heavy on copper-based aluminum alloys. It may consist of particles of oxide, secondary metals and the like, which are insoluble in the alkaline solution, and in general are quite loosely bonded to the surface. Smut was usually removed by immersion in an acid solution, most commonly 25 to 50 vol% nitric acid, at ambient temperature. This desmutting step is also called a deoxidization or neutralization step because of the neutralization of the caustic soda by the nitric or sulfuric acid. Such a step did not attack the aluminum substrate.

8. Re-anodizing
During re-anodizing, the aluminum parts were electrically connected as the anode. The cathode was made of a flat bar of stainless steel. The electrolyte and processing conditions used were similar to the original production settings. The electrolyte used for anodizing contained 160 to 200 g/L (21.4 to 26.7 oz/gal) sulfuric acid, at 18 to 22°C (64 to 72°F), at a current density of 1.4 and 1.8 A/dm^2 (13.0 and 16.7 A/ft^2). The anodic oxide typically grew at a rate of about 0.3 to 0.5 μm/min (11.8 to 19.7 μ-in.). It took approximately 30 min to build up an anodizing layer of 15 μm (590 μ-in.).

9. Electrolytic coloring
After anodizing, the metal was immersed in a bath containing an inorganic metal salt. Current was applied to deposit the metal in the base of the pores. The resulting color, ranging from light bronze to black, was dependent on the metal salt used and the specific processing conditions. Commonly used metals included tin, cobalt, nickel and copper. This process offered color versatility and was the most technically advanced coloring method for architectural applications.

10. Sealing
Sealing is one of the most important steps in the anodizing process. It closes the pores in the anodic film, which in turn will influence color stability, abrasion and corrosion resistance. The sealing operation was usually carried out in boiling hot water. During the sealing process, the aluminum oxide is converted to aluminum hydrate (boehmite, $Al_2O_3 \cdot H_2O$). The conversion is accompanied by an increase in volume, which bridges over and closes up the porous structure. It was important that the water in the sealing tank be very clean. Deionized water had to be used since impurities in the sealing bath could have serious effect on the sealing quality of the anodic oxide layer.

Spot anodizing repair

This repair approach was designed to repair the damaged color-anodized parts without disassembling them. The repair steps were:

1. Masking the area to be repaired
2. Stripping the damaged anodic coating
3. Sanding to reproduce the original texture
4. Re-anodizing to rebuild oxide thickness to be even with the undamaged area
5. Re-coloring the damaged portion of the part to match with the undamaged area
6. Sealing
7. Removing the mask

Color measurement

The quality of color produced on the aluminum alloy was determined by measuring color values using a spectrophotometer.** The color was evaluated in terms of L*, a* and b* values of a colorimetric system, where,

- L* (lightness) value - 0 is black, 100 is white
- a* (red-green) value — positive values are red, negative values are green and 0 is neutral
- b* (yellow-blue) value — positive values are yellow, negative values are blue and 0 is neutral
- Gloss at 85° - gloss units returned when measured at 85° from the perpendicular to the surface

SEM analyses

Specimens for SEM examination were prepared by a cryo-fracture technique. Approximately 3.2 × 25.4 mm (0.126 × 1.0 in.) in size, a sample was cryogenically frozen and fractured by dipping in a bottle of liquid nitrogen. The edge of the fractured specimen was then scanned and recorded by SEM. All specimens for SEM analysis were gold-palladium coated to highlight the surface profiles.

Results & discussion

Batch color-anodized repair

Several experiments were conducted and we were able to repair the damaged electrolytic colored anodized panel and reproduce the original appearance. A typical example of batch repaired AA5657 colored anodized aluminum is shown in Fig. 2. The coating thickness comparison is shown in Table 1. For all practical purposes, both optical properties and coating thicknesses of these two panels matched very well.

Spot anodizing repair

This technology is designed to repair the damaged color anodized parts without disassembly, and includes stripping the damaged anodic coating, sanding the aluminum surface to the original texture, re-anodizing and re-coloring the damaged portion of the part. Naturally, the repair area has to match the rest of the original coating in terms of thickness, texture and color.

Currently, we have found that the spot re-anodizing repair has a major borderline problem, which is quite visible to the eye. The following SEM micrographs illustrate reasons for the borderline problem. Figures 3 and 4 show the cross-sectional micrographs of the original and the repaired oxide structures, respectively. The repaired pore sizes appear to be larger than the original ones. Figures 5 and 6 show the surface micrographs of the original and the repaired surfaces, respectively. The surface morphology looks similar. Figure 7 shows the surface micrograph of the spot-repaired region. The borderline, seen as a trench, is clearly visible. Figure 8 shows the cross-sectional view of the borderline (*i.e.*, shattered surfaces). The repaired surface appears to be a bit rougher than the original surface.

Figures 9 and 10 show the polished cross-section of the borderline at two magnifications. These pictures clearly show that, during re-anodizing, the aluminum substrate surface was consumed and recessed to grow oxide. The oxide thickness versus substrate surface dissolution depth was about 2 to 1. If one of the repair objectives is to rebuild the oxide thickness to be flush with the original coating surface, the substrate surface being repaired has to recess to the depth of the original coating thickness (*e.g.*, 10 μm (394 μ-in.) recess for a 10 μm original coating thickness). For spot repair, the substrate underneath the repaired area will be lower than the original substrate, and the coating will be twice as thick as the original. These step changes between the original and repaired surfaces are clearly visible as borderline problem.

In addition, a portable electrolytic coloring method to re-color the re-anodized area has yet to be developed. However, the color anodic coat is translucent, and applying electrolytic coloring cannot solve the borderline problem.

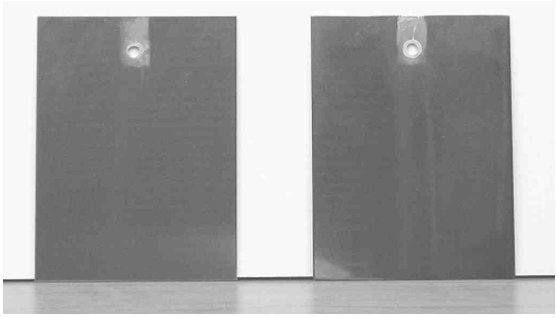

Figure 2—Photos of original (left) and batch repaired (right) panels.

Table 1
Optical properties and coating thickness for the original and repaired panels

AA5657	L*	a*	b*	85°	Thickness (μm)
Original	69.36	1.82	22.25	109.3	10.5
Repaired	68.63	1.90	22.53	110.0	9.3

Summary

For surface damages (*i.e.*, scratches and chipped oxide) with no dents, there are two approaches to repair the surfaces. The first one is a full panel repair which can be performed in some large anodizing repair facilities. This method repairs the panel by first stripping the oxide coating, reproducing the original surface texture and then re-growing and re-coloring the anodic oxide using the following

** *Konica Minolta CM 3700d Spectrophotometer, Konica Minolta Instrument System Div., Ramsey, NJ.*

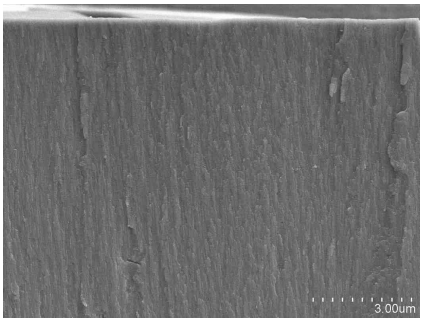

Figure 3—Cryo-fractured cross-sectional micrograph of the original anodized coating.

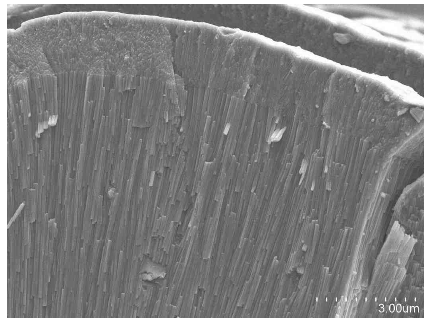

Figure 4—Cryo-fractured cross-sectional micrograph of the repaired anodized coating.

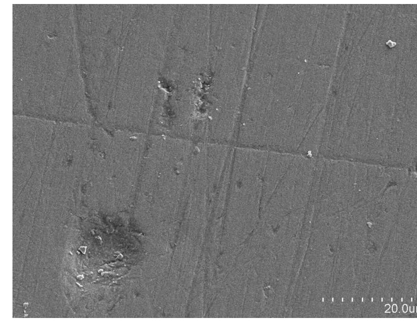

Figure 5—Surface micrograph of the original anodized coating.

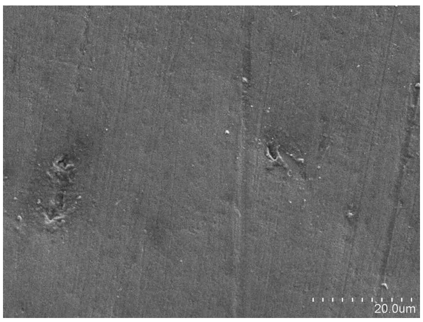

Figure 6—Surface micrograph of the repaired anodized coating.

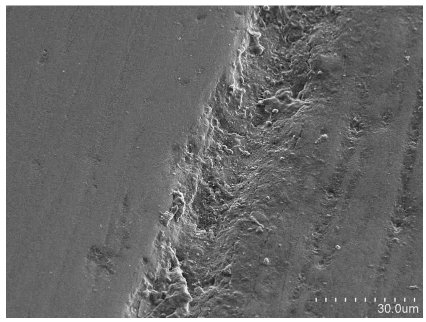

Figure 7—Micrograph of the borderline between original (left) and repaired (right) surfaces.

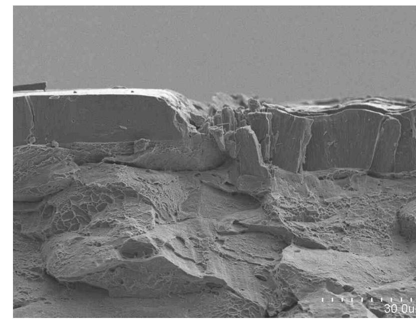

Figure 8—Micrograph of the cryo-fractured cross section of the borderline (i.e. shattered surfaces) between the original (left) and repaired (right) anodized coating.

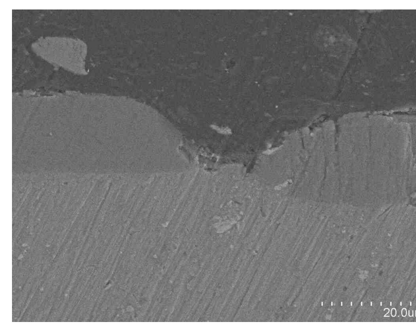

Figure 9—Micrograph of a polished cross-section of a borderline between original (left) and repaired (right) anodized coating.

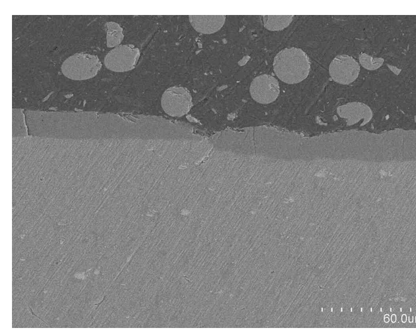

Figure 10—Micrograph of a polished cross-section of a borderline between original (left) and repaired (right) anodized coating.

batch color anodization process to match the original coating thickness and color:

1. Cleaning in alkaline and/or acid cleaners to remove surface grease and dirt
2. Surface pretreatment including etching and/or bright dip
3. Anodizing to the desired coating thickness and specific characteristics
4. Coloring the aluminum oxide coating electrolytically
5. Sealing and closing the pores in the anodic film to provide a surface resistant to staining, abrasion and crazing.

This method for repairing color-anodized oxide has been successfully demonstrated in our laboratory and proves to be a good method to repair the entire damaged panel.

The second approach is a spot repair method to restore the damaged panel. The advantage of this approach is that it has the potential to repair the damaged panels on the spot without disassembly. After numerous attempts, some very challenging technical issues were identified: (1) a noticeable borderline between the original and repaired anodized surfaces and (2) the unavailability of any electrolytic method in the market for spot coloring the repaired (*i.e.*, re-anodized) area.

Acknowledgements

We would like to thank Joseph Simmer and Paul Kozlowski for preparing the test samples, Curt Wong for the SEM micrographs, and Hsai Lee for many helpful discussions.

References

1. Y-M. Wang, H.H. Kuo & S.F. Kia, *Plating & Surface Finishing*, **91**, 34 (February 2004).
2. Y-M. Wang, H.H. Kuo, L. Iglesia-Rubianes, H-Y. Lee & S.F. Kia, "Characterization of Anodic Films on AA5657 Aluminum Alloy," in *Proc. AAC 2003 Anodizing Conference*, Aluminum Anodizers Council, Wauconda, IL, 2003.
3. G.E. Thompson, *Thin Solid Films*, **297**, 192 (1997).
4. S. Wernick, R. Pinner and P.G. Sheasby, *The Surface Treatment and Finishing of Aluminum and Its Alloys, 5th Edition, Volumes 1 & 2*, ASM International, Materials Park, OH and Finishing Publications Ltd., Teddington, UK, 1987.

About the Authors

Dr. Hong-Hsiang (Harry) Kuo is a Principal Research Engineer working in the area of automotive surface finishes at the General Motors R & D Center. He has a B.S. degree in Chemical Engineering from U.C. Berkeley and a Ph.D. in Chemical Engineering and Polymer Material Science from Princeton University.

Dr. Yar-Ming Wang is a Staff Research Engineer at the Materials and Processes Lab, General Motors R & D Center, Warren, Michigan. He received his B.S. degree in Material Science and Metallurgical Engineering from the National Cheng-Kung University, Tainan, Taiwan, and his Ph.D. in Metallurgical Engineering from the University of Missouri-Rolla. Dr. Wang's research interests include battery science, corrosion, surface coatings and anodization.