### Technical Article

## Interference-Colored Finishes for Automotive Aluminum Alloys

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The purpose of this research was to develop and understand interference-coloring technology for anodized aluminum alloys. The deposited metal salt in the porous anodic coating can cause optical interference effects and produce colors ranging from blue, green, yellow, red and various other shades. The processes for producing these colors are still mainly in the R&D stage because they are complicated and can only be consistently produced through a sophisticated programmable rectifier and under well-controlled experimental conditions. In this paper, the interference colors as function of metal deposition height are clearly demonstrated through Transmission Electron Microscopy (TEM) study.

Aluminum and its alloys are widely used in many engineering applications due to their high strength-to-weight ratio and good formability. One of the best ways to protect the aluminum surface is anodization, which is an electrochemical process where the surface of the aluminum metal is converted to aluminum oxide at the anode during application of electrical current in an acidic solution. As the current is applied to the parts, two coating layers are produced on the aluminum surfaces, an inner barrier layer and an outer porous layer. The compact barrier layer is very thin (~ 20 nm) with protective dielectric properties. The porous layer is much thicker (as much as 50  $\mu$ m), which forms an excellent corrosion-protective coating. These films are nearly transparent and therefore the aluminum retains its metallic appearance.

#### Nuts & Bolts: What This Paper Means to You

This work takes color anodizing in a new direction, toward colored aluminum automotive body panels. Instead of immersion in dyes and sealing the color into the finish, the principles of light interference are used to impart color. By varying and controlling the height (or depth, if you will) of the nanoscopic pores in the anodized layer, this group has developed color finishes from blue thru red and everything in between. There are many ways to color the aluminum oxide surface. The most important coloring method for exterior applications of aluminum parts is the electrolytic coloring of the anodic oxide by electrodeposition of metal inside the pores. The colored anodic film not only has a rich metallic luster but also has better colorfast properties. It is also very hard, with excellent abrasion, wear and corrosion resistance. Although it has the manufacturing advantage of producing multiple colors with a single electrolytic tank, it only offers limited colors, from light bronze to medium bronze to black. However, due to its environmental friendliness and simplicity, color anodizing has been widely used for architectural applications.

The concept of interference coloring, first introduced in the late 1970s, is similar to electrolytic coloring, but it can produce many colors ranging from blue, green or yellow to red. In recent years, tremendous progress has been made to make interference coloring the most technically advanced coloring method.<sup>1-3</sup> In general, after anodization, interference coloring is achieved by modifying the pore structure at the base of the pores in a conditioning tank. The metal salt is then deposited into the pores to produce various interference colors. Interference coloring usually requires sophisticated and precise programming of applied current and voltage. In this report, the interference colors as function of metal deposition heights are demonstrated through transmission electron microscopy (TEM).

Anodizing is an electrochemical process in which the aluminum part is made the positive electrode (anode) in a suitable electrolyte (*e.g.*, sulfuric acid). A sufficiently high voltage is applied to establish sufficient polarization to evolve oxygen at the surface.<sup>4-6</sup> Oxide formation takes place by the migration of  $AI^{+3}$  ions from the metal towards the electrolyte interface, and  $O^{-2}$  ions in the opposite direction. The anodic half-cell reaction for oxide formation is shown as follows:

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

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 film growth and dissolution.<sup>7,8</sup>



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

The characteristics of the anodic film are highly dependent upon 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. A 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. The method is similar in principle to the electroplating process because metal is deposited into the pores of the anodic oxide film. The bath voltage necessary for metal deposition in electroplating is on the order of a few volts. During electrolytic coloring, however, a higher voltage, about 10 to 20V, is used. This is because of the existence of the barrier layer. It is difficult to pass current through the barrier layer, and high voltages are necessary for depositing metal. When the size of the pores in the anodic film is properly controlled for electrolytic coloring, the resulting film can be colored through an interference coloring effect.

The objective of this paper is to document the effect of the height of metal deposition in the aluminum oxide layers during interference coloring, which in turn has a profound impact on the development of a viable coloring technology for engineering applications with very stringent requirements.

#### Concept of interference coloring

The interference coloring method is different from the conventional two-step electrolytic coloring process. The color effect

Table 1 Alloy Composition (wt%)

Alloy	Mg	Mn	Si	Cu	Fe	Zn	Cr	Ti	Al
5083	4.50	0.60	<0.40	<0.10	<0.40	<0.25	0.10	<0.15	94.80
5657	0.59	<0.01	<0.10	0.03	0.03	<0.01	<0.01	0.02	99.20
6063	0.45	<0.10	0.40	<0.10	<0.35	<0.10	<0.10	<0.1	98.90
6111	0.80	0.20	0.60	0.70	0.25	<0.10	0.05	0.06	97.30

arises from the interference of visible wavelengths rather than from light scattering. An intermediate conditioning (pore modification) stage is added prior to conventional electrolytic coloring. When this process is carefully controlled, it gives a greater color range than traditional electrolytic coloring method. Colors of red, orange, yellow, bronze, brown, green, blue and violet can be produced, depending on the time of the intermediate stage, and coloring voltage and time.

Ultramicrotomy, coupled with the transmission electron microscopy study,<sup>9</sup> shows that the intermediate conditioning stage results in the growth of new enlarged pores at the base of the pre-existing film. The metal deposited during coloring is at the base of these enlarged pores. Both Alcan<sup>10,11</sup> and Sheasby, *et al.*<sup>3</sup> suggested that the interference effect arises from light reflecting from deposit surfaces and the underlying aluminum substrate. In order to accomplish a good interference effect, the deposit surface area at the bottom of the pore must be larger than that formed after conventional anodizing. This pore widening treatment not only provides a large reflecting surface but also ensures more uniform metal deposits to establish a good separation between two reflection surfaces to set up an interference color.

#### Experimental

The general interference coloring process consists of two steps:12

1. Conditioning process: This step alters the pore size and determines the final color. It involves an application of combined AC and DC currents in a conditioning bath consisting of 20% sulfuric acid with 0.5 g/L (0.07 oz./gal) aluminum at 21°C (70°F). An infinite combination of AC/DC steps can be used to obtain various colors. Typically, four sequential steps were successfully applied during conditioning, *i.e.*, (1) DC current, (2) AC current, (3) DC current and (4) DC current.

2. Coloring process: This step deposits tin into the pores to set up interference colors. It involves immersing the sample in a coloring bath with 20 g/L (2.7 oz./gal) sulfuric acid, 8 g/L (1.1 oz./gal) tin at 21°C (70°F) and then applying AC current with a ramp time of 10 sec to a target voltage of 12.5V and holding it for 60 sec.

The samples are then sealed for 15 min in a cold seal solution<sup>\*\*</sup> and 15 min in a hot water seal bath for corrosion and color protection.

GMR&D has designed and built a comprehensive lab capable of interference-color anodizing, which involves modification of the pore structure at the base of the pores in a conditioning tank after anodization. The tin metal is then deposited into these pores to produce various interference colors. We have consistently produced interference-colored test panels using various aluminum alloys (*i.e.*, AA5657, AA5083, AA6111 and AA6063; see Table 1 for compositions). Typical AA5657 interference-colored samples for TEM studies were prepared by alkaline cleaning and anodizing in

160 g/L (21.4 oz./gal) sulfuric acid electrolyte at 20°C (68°F) with an applied current density of 1.6 A/dm<sup>2</sup> (15 A/ft<sup>2</sup>) for 35 min. This would produce an anodic film thickness of about 15  $\mu$ m (0.6 mil). After anodizing, the interference coloring was produced according to our coloring procedures. One batch of specimens remained

<sup>\*\*</sup> Anodal CS-2, Clariant Pigments & Additives Div., Clariant Corp., Basel, Switzerland.

unsealed, and the second batch of specimens was sealed by first dipping the sample in the cold-seal solution for 15 min, followed by dipping in boiling water for 15 min. Another series of AA6063 panels was color-anodized by a supplier and used for the TEM study below. Sample preparation procedures for the TEM study are described elsewhere.<sup>4</sup>

#### **Results and discussion**

The TEM micrographs of the AA6063 panels reveal a porous film tied to the aluminum substrate by a barrier layer. Tin deposits are located mainly at the bottom of the pores and

are usually at a uniform height. Interference coloring is produced by the constructive or destructive interference of the light reflected from two reflective surfaces (upper surface of the tin deposits and the aluminum/aluminum oxide interface).<sup>5</sup> The distance between the two reflective surfaces (*i.e.*, thickness t) determines the color and is given by the thin-film interference equation:

 $t = k\lambda/(2n),$ 

where  $\lambda$  is the wavelength in air,

n is the index of refraction  $(1.7 \text{ for Al}_2\text{O}_3)$ ,

k is the number of waves contained in the path length 2t.

Table 2 shows excellent agreement between the measured and calculated thickness using the aforementioned equation. As the thickness of the tin deposit increased, the wavelength increased and the color changed progressively from purple to red. Figure 2 shows the comparison of tin deposit thickness versus observed color. Although pore enlargement was not evident in this case, it is remarkable that the observed colors corresponded to the calculated colors rather nicely.

#### Conclusions

Transmission electron micrographs confirmed that the measured heights of the tin deposition of the interference-colored panels match very well with the theoretical values calculated from the thin-film interference equation. The TEM technique could be a very useful quality control tool for the interference coloring process. The pore widening modification at the bottom of the film claimed in the literature was not evident from TEM pictures. High resolution TEM needs to be used to resolve this issue.

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Figure 2-Interference color specimens: comparison of tin deposit thickness vs. observed color.

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#### Table 2

Wavelength of Various Colors Versus Measured and Calculated Tin Deposit Height of Interference-Colored AA6063 Alloy

Color	Wavelength (nm)	Calculated Height (nm)	Measured Height (nm)	Color Observed	
Red	760-630				
Orange	630-590	180	210	Orange	
Yellow	590-560	164	153	Yellow-green	
Green	560-490	144	125	Green	
Blue	490-440	129	100	Light blue	
Indigo	440-420				
Violet	420-380	110	95	Purple	

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