Interference Coloring of Dual-Anodized Films on Aluminum Containing Electrolytically Deposited Thin Metal Layers

By S. Kawai & M. Yamamuro

This study concerns the properties and structure of oxide films on aluminum, anodized in a sulfuric acid bath, first by DC, and next by AC in the same bath; Sn-Ni metal was then deposited electrolytically into the micropores. Each film showed fine colors that varied from blue, green, and to gold in medium tones as thickness of the AC films increased. EPMA line analyses disclosed that Sn deposited cleanly at the bottom of the micropores, with maximum intensity increasing with the kind of colors. In observations with SEM, the back-scattered electron images proved clearly the difference for AC films; also, the secondary electron images exhibited metal deposition like tree twigs in very fine micropores. The colors obtained indicated good corrosion resistance and light fastness.

Originally, the principle of electrodeposition of anodic films was discovered by Caboni[1] and G. Elssner.[2] Since then, T. Asada[3] invented more practical coloring treatment, and the technology has grown into a large industry because of its superior qualities.

The process consists of two treatments—anodizing of aluminum in sulfuric acid, as usual, to a certain thickness, then Sn or Ni metal deposited electrolytically into the micropores in a conventional plating bath with commercially supplied AC. Finally, dispersed fine metal crystals in the transparent films scatter incident light and produce colors of bronze and black.

One of the authors and a colleague[4] found Sn or Sn-Ni alloy baths that are easy to control for uniform deposits. Also, Keller and Gedde[5] obtained a patent related to the Sn bath. Because of the columnar structure of the deposits, Ni, Co and Fe metals revealed a perpendicular magnetic property.[6]

Durability of Sn colorings was investigated by Gohausen and Schoener,[7] who compared it with Ni and recommended actual applications despite high acid content in the coloring baths. In extensive studies, Baba[8] disclosed that a few H^+ ions penetrate the barrier layer, reach the aluminum base metal, discharge and expand as gas. Moreover, many improved bath compositions and waveforms have been proposed; for example, AC coloring in high-conductivity baths of both Sn and Ni, and DC electrolysis in a Ni bath with extremely low concentration of neutral salts. Unsymmetrical AC, square pulses and anodic DC have been utilized for practical applications.

Recently, composite films anodized in different baths have been of considerable interest. Takahashi *et al.*[9,10] intensively examined pore formations of composite films and pore linking between them.

Optical properties of thin metallic films were studied by Wada *et al.*[11] Meanwhile, Sheasby and Short[12] investigated blue color films generated by optical interference produced by anodizing in sulfuric and phosphoric acids, followed by metal deposition. They noted also that other films produced by anodizing, but beneath metal layers, yielded more light colors. Barba[13] introduced a new process that showed a blue color after anodizing in sulfuric acid, followed by a conditioning treatment in the same bath and by Sn deposition. Recently, many patents related to interference colors have been published, with special interest shown in anodizing by AC.[14]

Preparation of Specimens

1. **Aluminum**

   Specimens were made of sheets of bright mill-finished, 99.9-percent pure aluminum, 100 x 50 x 1 mm.
2. **Pretreatment**

Table 1
Anodizing & Coloring Conditions

Process	**Composition g/L**		**Condition**
Anodizing DC (SCR)	H_2SO_4, 150		13-16 V
	Al^{+3}, 2		1.0 A/dm^2
			20 °C
			30 min
			Carbon
Anodizing AC (50 Hz)	As above		3-8 V
			1.0 A/dm^2
			1-8 min
			Carbon
Coloring AC (50 Hz)	$SnSO_4$	8	10-13 V
	$NiSO_4 \cdot 6H_2O$	25	25 °C
	H_2SO_4	17	2-8 min
	Tartaric acid	10	
	Anti-oxidant	10	
Sealing	$NiSO_4 \cdot 4H_2O$	6	95 °C
	Anhydr. $NaC_2H_3O_2$	2	20 min
	Additive	2	pH 5.8

Table 2
Anodizing Times & Colors

		Specimen Number		
		S-1	**S-2**	**S-3**
DC anodizing (min)		30	30	30
AC anodizing (approx. min)		2	4	6
Color		blue	green	gold
CIE	L	58.9	67.5	63.6
	a	-2.8	-6.0	-0.5
	b	-1.0	9.9	26.9

Specimens were wiped with cotton cloths containing organic solvents, then immersed in a degreasing solution, followed by a slight etch in 5-percent NaOH solution at 45 °C for 5 min. They were then treated in a 5-percent HNO_3 solution at room temperature for 10 min to be neutralized and to remove smudges.

3. DC Anodizing

Anodizing conditions were as described in Table 1.

4. AC Anodizing

AC anodizing was carried out in the same bath, as noted in Table 1, at 50 Hz. The applied voltage was held within the range of 3-8 V and current was slowly increased. The greatest current density was about 1.0 A/dm^2 and was influenced by the initial DC anodizing conditions. The time of anodizing was shifted in one-min intervals, which was critical to formation of the colors.

5. Electrodeposition

The Sn-Ni coloring bath conditions, listed in Table 1, were developed by one of the authors and is considered easy to control for coloring. At first, specimens were merely immersed in the bath for 2 min. The AC voltage was then increased slowly to 10-13 V over 30 sec.

6. Nickel Salt Sealing

Before sealing, specimens were washed in running water for 10 min and in still DI water for 5 additional min. Conditions of Ni salt hot sealing are also contained in Table 1.

Experimental Procedure and Results

1. Anodizing Time and Color

Anodizing by DC formed oxide films approx. 9 μm in thickness; further anodizing by AC produced very thin additive layers beneath the DC films. After Sn-Ni deposition, very fine colors appeared on the films. During AC treating time, colors varied from blue through green to gold (reddish yellow) in medium tones. DC and AC anodizing times and typical colors are listed in Table 2.

2. Chemical Corrosion Properties

Chemical corrosion properties of colored films were measured as in Table 3. Rating Numbers of the CASS Test and the Alkaline Dropping Corrosion Test (ADCT) were obtained in conformity with JIS.

3. Light Fastness

Light fastness was tested by carbon arc lamp. Results (Δ) after 1000 hr are listed in Table 3.

4. Heat Fastness

For an expedient test, specimens were held at 300 °C for 1 hr to estimate heat fastness; resulting color diversity is listed in Table 3.

5. EPMA Line Analysis

Cut profile sections of colored films were investigated by Electron Probe Micro Analysis (EPMA). Line spectra of Sn and Al are shown in Fig. 1, where (S-1), (S-2) and (S-3) represent blue, green and gold, respectively.

6. SEM Observation

Specimens were also observed by SEM; two distinct images were produced by the back-scatter and secondary electron methods. Each specimen was prepared by Os vaporization to 1.5 nm thickness to provide surface conduction. Figure 2 shows an electron back-scattered image of blue film. Figure 3, (1), (2) and (3) shows secondary electron images of blue, green and gold colors.

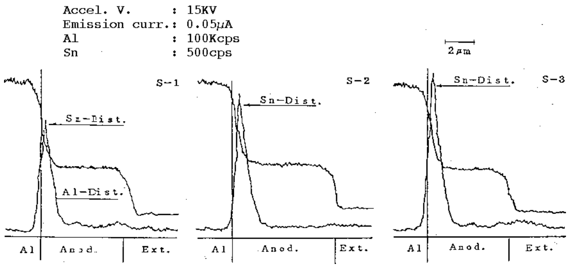

Fig. 1—EPMA line chart of colored films.

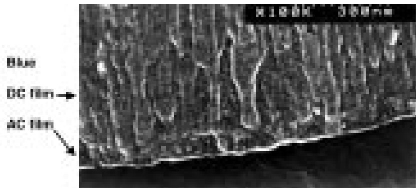

Fig. 2—SEM photomicrograph of back-scattered electron image (blue).

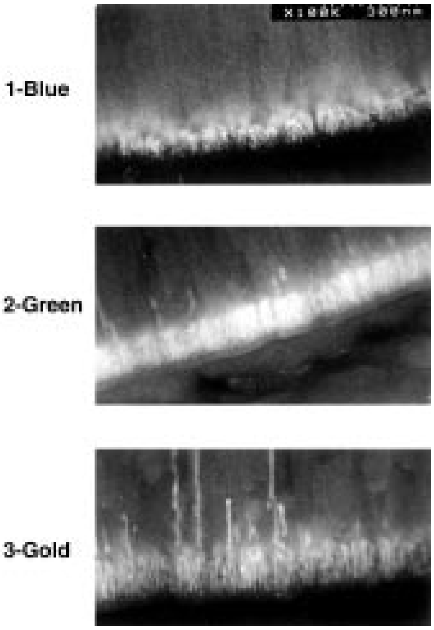

Fig. 3—SEM photomicrograph of secondary electron images: (1) blue; (2) green; (3) gold.

Table 3
Results of Durability Tests

	Specimen Number		
	S-1	S-2	S-3
Chemical Corrosion			
CASS RN (36 hr/18 μm)	9.6	9.6	9.6
ADCT (sec/μm)	20	14	12
Light Fastness ΔE (1000 hr)	1.7	-	0.8
Heat Fastness 300 °C (1 hr)	turned slightly yellow	none	none

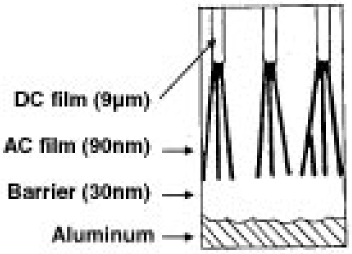

Fig. 4— Schematic model of colored film.

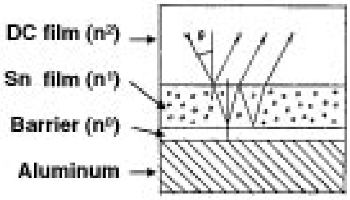

Fig. 5—Interference layer of anodized film.

Discussion

Structures of Anodized Films

It is well known that micropores of films anodized by DC grow in columnar shapes and by AC form in zigzag orientations. In Fig. 2, either DC micropores about 10 nm in diameter apparently stand in parallel, vertically, or AC micropores show vague irregular form.

The microstructure of AC films can be discerned more precisely in Fig. 3, (1), (2) and (3), in which film thickness shifted from approx. 100 nm for blue, 120 nm for green and to 150 nm for gold, respectively.

In each colored film, the thickness of the barrier layer is about 30 nm and can be seen as a faint fringe in each image. The thickness is somewhat greater than with normal DC barriers.

In AC anodizing, 90-120 min were required before full current flow was obtained because DC barriers changed gradually to meet new bath conditions. Although it has been reported that thicker films beneath metal layers produce more lighter colors, in this study only moderate and ordinary tones were generated.

Metal Distribution

Tin-nickel deposits in AC films resembled tree twigs that measured about 100-150 nm in length and 3-6 nm in diameter. The dimensions coincide with pore shapes because the metal is densely stuffed into the pores. The metals were deposited not only within AC pores, but protruded into DC pores as well. This excess deposition may affect the particular colors obtained, but can be controlled by lowering the AC voltage. A schematic view of pores is shown in Fig. 4. In all EPMA profile spectra, it is clearly observed that Sn metal sticks closely to the bottom of the micropores, and that each peak intensity increased slightly as the AC films grew thicker. Maximum values of spectra were about 1/100 lower compared to those of conventional colored films of the same Sn bronze color.

Traces of sulfuric acid can be found in micropores even after thorough rinsing; therefore, it can be accepted that Sn deposits from acidified baths are more readily crystallized than Ni from weakly acidified baths.

Table 4
Colors & Thickness of Films

nd (nm)	150	180	260	320	340
Color	purplish blue	blue	gray	greenish yellow	reddish yellow

Interference Color

In the AC films, each micropore is filled by deposited Sn, so that entire layers appear as spongy films. From the bulk viewpoint, it is as though the metal films are suspended between two transparent oxide films.

Figure 5 shows a sectional model of a colored film, where the DC film, the twig-like metal, and the AC barrier are arranged in order. In the layers, n_0 and n_2 indicate anodized films of 1.6 refractive index, while n_1 represents either Sn or Ni metal, having refractive indices of 1.5 and 1.7, respectively.

Necessary conditions for interference by a C standard light can be expressed by the following equations, where d is AC film thickness and m is an integer:

$$\text{No reflection: } n_0 \text{ x } n_2 = n_1^2 \qquad (1)$$

$$\text{Light pass difference: } 2nd \sin \theta = m\lambda \qquad (2)$$

These kinds of anodized films easily generate optical interference color. From a CIE chromaticity diagram, the relation of nd to the various colors is shown in Table 4.[15]

In the blue color, the calculated film thickness roughly coincided with the 100-nm thickness observed by SEM; the green and gold thicknesses were not so close.

Chemical Properties and Light Fastness

AC films anodized at low voltages produced very fine pores and a noticeably thicker barrier than with normal DC films. This may have produced the observed better corrosion resistance, however.

After thermal and light fastness tests, each specimen showed good endurance for ordinary environments. Under severe conditions, the blue color took on a darker tone (slightly toward black), and it is assumed that some metal diffused into the AC films and that layers became thinner. Overall, the results obtained indicated that this method is at least the equivalent of conventional methods.

Summary

Aluminum was anodized in sulfuric acid by DC in the usual way, then, in the same bath, anodized by AC for a brief period, then coated electrolytically with Sn-Ni. The films produced various shades of blue, green and gold by adjusting the thickness of the layers deposited by AC. The explanation of the colors is that thin Sn films exist between two transparent anodizing films, giving rise to interference colors.

Beautiful and uniform colors can be obtained in a simple electrolytic bath with easy control technology. The colors have not been subjected to long-term outside exposure, but there seems a strong possibility for architectural use.

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