Electrolytic White Coloring of Anodic Oxide Film on Aluminum in Hydrated Titanium Oxide Sol

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Abstract

An attempt was made to develop an electrolytic method to color anodized aluminum white by depositing hydrated titanium oxides in pores in the anodic oxide film by electrophoresis. The objective of this study is to determine the optimum process parameters which give sufficient whiteness to anodized aluminum.

It was found that the whiteness depends significantly on the anodizing process. Sufficient whiteness was not obtained on the aluminum which anodized in sulfuric acid bath, while sufficient whiteness was obtained on the aluminum which is anodized in two acids: first in sulfuric acid bath and then in phosphoric acid bath. It appears that the stronger whiteness in the latter process is due to the formation of the larger pore size in the anodic oxide film which allows sufficient amount of hydrated titanium oxide particles to deposit in the pores.

It was found from the polarization curve that the deposition of titanium oxide on the anodic oxide film takes place at about $-3\text{ V} \sim -3.5\text{ V}$. More homogeneous whiteness was obtained by A.C. electrolysis at about 16 V than by D.C. electrolysis at $-3 \sim -3.5\text{ V}$.

1. Introduction

Although many studies have been pursued to determine a method to color an anodized aluminum white¹⁾, no products of pure white have been obtained to date.

Methods which may improve whiteness include: ① roughen the anodic oxide film surface to cause light scattering, ② change the coating material to another white compound, or ③ depositing an insoluble white compound inside the pores of the anodic oxide film, etc. Of these methods, only ② and ③ are likely to provide a pure white film. Method ② has been introduced by the author²⁾. According to this method, the white anodic oxide film is obtained by changing the original anodic oxide film to aluminum phosphate by hydrothermal treatment in phosphoric acid solution. The use of an autoclave makes this method practical but the resultant white film is appreciably softer than the original. The approach ③ has been tested for a substantial number of experimental examples^{1), 3)}. All of the experiments were carried out by electrolysis in a solution of salts of alkaline-earth metals such as Ca or Ba. In these methods, the coloring components are the insoluble compounds of that salts formed in the solutions. However, none of them showed sufficient whiteness.

For obtaining a white anodic oxide film by method ③, the best method should be to deposit a white pigment such as titanium oxide (which has a large refractive index) in the pores of the anodic oxide

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film by electrophoresis. Little work has been performed in this area, probably because the pore diameters (100~300 Å) of the anodic oxide film are usually smaller than the particle diameter of a white pigment such as titanium oxide. However, if an ultrafine titanium oxide particle of colloidal dimension is prepared, it may be feasible to utilize this method.

From this standpoint, the writers attempted to prepare a hydrosol containing ultrafine particles of hydrated titanium oxide and to deposit it by electrolysis.

2. Experimental

2.1 Anodic oxide film

A 15 μm thick anodic oxide film with unsealed pores was obtained by anodizing aluminum plate*¹ (5 cm $\times$ 10 cm $\times$ 0.08 cm or 2 cm $\times$ 4 cm $\times$ 0.08 cm*²) of 99.5% aluminum by the following pretreatments: Expose to 5% sodium hydroxide (for 40 sec at 60°C)-water rinsing-cleaning with 30% nitric acid (for 20 sec at 60°C)-water rinsing, followed by anode oxidation performed in a 17% sulfuric acid bath with a lead plate as the cathode electrode (for 25 min with 2 A/dm² D.C. at 20°C). This film thus formed will be referred to as the sulfuric acid bath film.

Another experiment was carried out with a double layered film. The double layered film with its pores unsealed was prepared by anodic oxidizing the sulfuric bath film prepared by above method in a phosphoric acid bath 1 mol/l with carbon as the opposite electrode (for 10 min with 16 V D.C. at 20°C).

2.2 Electrolytic coloring

2.2.1 Electrolytic solutions

The electrolytic solutions used were of two types: 1) a titanium(V) oxide sulfate solution and 2) a hydrosol of hydrated titanium oxide prepared from titanium(V) oxide sulfate.

The hydrosol was prepared by the gradual addition of 0.2 mol/l ammonia water (at a rate of 6~7 ml/min) to 0.1 mol/l of titanium(V) oxide sulfate solution maintained at 20 $\pm$ 1°C and constantly stirred.

2.2.2 Electrolyzing method

- 1 : Carbon electrode (0.54 dm²)
- 2 : Sample (1 dm²)
(Cathode in the case of DC)
- 3 : Electrolytic solution (20°C)
- 4 : Electrolytic bath
- 5 : Thermostat
- 6 : Power source (A.C. or D.C.)
- 7 : Stirrer

Fig. 1. Electrolytic coloring equipment

The electrolysis was performed at a constant voltage using the device illustrated in Fig. 1. In order to suppress the rupture of the anodic oxide film the voltage stepping up method, as shown in Fig. 2, was employed to apply the voltage.

More details about the electrolytic conditions were examined by the following experiments:

(1) Examination of the D.C. electrolytic coloring method

(a) Potential scanning method

Fig. 3 provides a schematic view of the apparatus of D.C. electrolysis. The potentials on the anodic

Fig. 2. Voltage stepping-up method

*¹ JIS Designation A 1050 P-H 24

*² To be used only when examining the energizing method.

1: Carbon electrode (0.2 dm^2)	2: Control electrode (Saturated calomel electrode)
3: Sample (0.16 dm^2)	
4: Electrolytic bath	5: Electrolytic solution
6: Thermostat	7: Stirrer
8: Potentiostat	9: Linear sweep power
10: X-Y recorder	

Fig. 3. Direct current electrolytic equipment

oxide film were scanned^{*3} from 0 V to -20 V with the use of a linear sweep power supply and the potential-current curve obtained was recorded on an X-Y recorder. The scanning was stopped when more than 1 A of current flowed in view of the line capacity.

Fig. 4. Potential-time Curve

(b) Constant potential method

Constant potential electrolysis was conducted for 5 and 10 minutes using the apparatus shown in Fig. 3 when the potential is raised to V_c at a rate of 0.1 V/sec as shown in Fig. 4. V_c represents 4 V, 6 V, 8 V or 10 V.

(2) A.C. electrolytic coloring methods

(a) Voltage scanning method

Fig. 5 shows a schematic view of the apparatus of A.C. electrolysis. The voltages were scanned from 2.5 V to 30 V at a speed of 0.1 V/sec and the current-voltage curve converted into D.C. voltage

1: Carbon electrode (0.2 dm^2)	2: Sample (0.16 dm^2)
3: Electrolytic bath	4: Electrolytic solution
5: Thermostat	6: Stirrer
7: Transducer	8: AC power source
9: X-Y recorder	

Fig. 5. Alternating current electrolytic equipment

*3 The scanning speeds are 0.01 V/sec and 0.1 V/sec .

by means of a transducer was recorded on an X-Y recorder.

(b) Constant voltage method

The constant voltage electrolysis was carried out using the apparatus shown in Fig. 5 when the voltage was raised to the predetermined voltage V_N at a specified stepping up rate (V_S), similar to that of Fig. 4. The electrolyzing time was always set for 5 min. V_S represents 1.25 V/sec, 0.63 V/sec and 0.1 V/sec and V_N stands for 15 V, 18 V, 20 V and 25 V.

2.3 Coloring state of anodic oxide film

The coloring state of the anodic oxide film was examined visually and by measuring color difference. The color difference was measured using a colorimetric color-difference meter type ND-1001 DP manufactured by Nippon Denshoku Kogyo (K. K.).

2.4 Analysis of anodic oxide film for Ti

With the anodic oxide film dissolved in a phosphoric acid-chromic acid solution^{*4}, the amount of Ti in the solution was measured by spectroscopic atomic absorption.

3. Results and Discussion

3.1 When the sulfuric acid bath film was used

3.1.1 Electrolytic coloring in titanium(IV) oxide sulfate solution

The sulfuric acid bath film was electrolyzed by the voltage stepping up method in 0.2 mol/l and 0.5 mol/l titanium(IV) oxide sulfate solution. The conditions for voltage stepping up were as follows: In the A.C. case, $V_1=4$ V, $V_2=6$ V and $V_3=8$ V, and $T_1=30$ sec, $T_2=3$ min and $T_3=6$ min. In D.C. case, $V_1=2$ V, $V_2=4$ V and $V_3=6$ V, and $T_1=T_2=T_3=1$ min.

The result showed that only air bubbles were produced in the film surface and no coloring was recognized by visual observation. When this film was dipped for 5 min in 0.05 mol/l ammonia water (heated to 70°C) in order to ascertain whether any titanium oxide (hydrated titanium oxide) had been deposited in the anodic oxide film, the film surface turned white, which indicated deposition of TiO_2 . However, this product was not sufficient in whiteness and homogeneity; thus it was concluded that it is impossible to obtain satisfactory products which were satisfactory in performance by electrolysis in the unmodified solution of titanium(IV) oxide sulfate.

3.1.2 Electrolytic coloring in hydrosol of hydrated titanium oxide

Since it was impossible to obtain a satisfactory white anodic oxide film by using an unmodified titanium (IV) oxide sulfate solution, as described in 3.1.1, electrolysis was attempted in a hydrosol of hydrated titanium oxide. The hydrosol was prepared by the gradual addition of ammonia water into a titanium (IV) oxide sulfate solution. Four types of hydrosol were prepared with pH of 1.2, 1.4, 1.6 and 1.8^{*5}. The electrolyzing conditions adopted were as follows: In the D.C. case, the voltages were 1.8 V and 2.7 V, and the electrolysis time 10 min. In the A.C. case, the voltages were applied by the voltage step method as follows: $V_1=4$ V, $V_2=8$ V and $V_3=16$ V, and $T_1=30$ sec, $T_2=3$ min and $T_3=6$ min, respectively.

The results showed that the anodic oxide film was slightly colored white, regardless of the electrolysis condition. This suggests that by this method titanium oxide is more readily deposited than by using as the electrolyte the solution of titanium(IV) oxide sulfate described in 3.1.1. But, this method lacked in homogeneity.

3.2 When the double layered film is used

3.2.1 Electrolytic coloring in titanium(IV) oxide sulfate solution

When electrolytic coloring was attempted under the same conditions as in 3.1.1, using the double layered

^{*4} Twenty grams of chromium(IV) oxide is added to 35 ml of 80% phosphoric acid and the mixture is diluted to 1 l with water.

^{*5} The present writers have, heretofore, prepared large numbers of ultrafine particles of metal oxides having around 100 Å or smaller particle diameters by making use of the colloid chemical approach⁴⁾; the particle diameters of hydrated titanium oxide in the hydrosol prepared under such conditions are smaller than 100 Å.

film, the film was not colored at all although 3.5 mg/dm^2 of Ti was deposited.

3.2.2 Electrolytic coloring in hydrosol of hydrated titanium oxide

The coloring effects were not observed when titanium(IV) oxide sulfate solution was used as the electrolyte, even through the double layered film was used in place of the sulfuric acid bath film. Electrolysis was attempted using the hydrosol of hydrated titanium oxide as the electrolytic solution next. The electrolysis was carried out by applying the voltage by the voltage stepping up method. The voltage stepping up conditions were: $V_1=8 \text{ V}$, $V_2=12 \text{ V}$ and $V_3=16 \text{ V}$, and $T_1=T_2=T_3=3 \text{ min}$ in the A.C. case, $V_1=4 \text{ V}$, $V_2=6 \text{ V}$ and $V_3=8 \text{ V}$, and $T_1=T_2=T_3=3 \text{ min}$ in the D.C. case.

The results are shown in **Table 1**. This table shows that a homogeneous white anodic oxide film is produced by performing A.C. electrolysis using the hydrosol at pH 1.6 as the electrolytic solution.

As described above, even when the same hydrosol was used as the electrolytic solution, the white film obtained when the double layered film was used was superior both in whiteness and homogeneous to that obtained when the sulfuric acid bath film was employed (3.1.2). This seems to be due to the fact that the pores in the anodic oxide film are expanded by the anodic oxidation in the presence of phosphoric acid, thereby facilitating the electrophoresis and deposition of titanium oxide into the pores in the film.

3.3 Examination of the electrolyzing method

The results obtained to date show that the preferred white colored film is produced by electrolysis of the double layered film in a hydrosol of hydrated titanium oxide at pH 1.6.

3.3.1 D.C. Electrolytic coloring method

(1) Potential scanning method

A current-potential curve (cathodic polarization curve) determined by potential scanning is given in **Fig. 6**.

Regardless of scanning speed, the current begins flowing at approx. -1.6 V and at approx. -2 V , a first peak current appears. With the scanning speed at 0.01 V/sec , and at 0.1 V/sec , a second peak current appears at approx. -3 V and -3.5 V respectively, and from about -8 V , an abrupt current increase is observed.

This seems to suggest that at approx. -2 V , hydrogen gas is produced and that at around $-3 \text{ V} \sim -3.5 \text{ V}$, deposition of titanium oxide into the film's pores takes place. The abrupt current increase over -8 V seems to be attributable to the electrolysis of water.

Accordingly, it is proper to conduct the electrolytic coloring at the voltage level of $-3 \text{ V} \sim -3.5 \text{ V}$.

(2) Constant potential electrolytic coloring method

Constant potential electrolytic coloring was performed. The conditions of electrolysis and the coloring state of the film and the results of the potential scanning of (1) (Nos. 1 and 2) are shown in **Table 2**.

Table 1. Electrolysis condition and coloring state

pH of Hydrosol	Power Source	Peak current density [A/dm^2]	Coloring state
1.4	{ A. C.	0.48	B
	{ D. C.	0.12	B
1.6	{ A. C.	0.48	A
	{ D. C.	0.11	B
1.8	{ A. C.	0.38	C
	{ D. C.	0.10	C

A : White with perfect homogeneity

B : White with partial inhomogeneity

C : White with inhomogeneity

Fig. 6. Potential-Current Curves

Table 2. Electrolysis condition and coloring state in the case of constant potential electrolytic coloring method

No.	V_s [V/sec]	V_c [V]	T [min]	Coloring state	L	a	b	Peak current density [A/dm ²]
1	0.1	12	2	C	54.2	1.6	-9.0	—
2	0.01	12.5	20	D	50.2	-1.9	-2.9	—
3	0.1	4	5	C	54.6	1.4	-9.7	0.22
4	0.1	6	5	C	54.1	1.9	-9.1	0.20
5	0.1	8	5	C	50.6	-1.8	-3.0	0.20
6	0.1	10	5	C	50.8	-1.8	-2.5	0.23
7	0.1	8	10	C	50.4	-2.0	-2.4	—
8	0.1	10	10	C	49.6	-1.7	-2.8	—

C : White with inhomogeneity

D : Not colored

Fig. 7. Relation between V_c and L value (D.C. Electrolytic coloring) **Fig. 8.** Current-Voltage curve

The coloring, as visually observed, was slightly whitened, with inhomogeneity.

As the L value determined by a color difference meter is plotted against the potential V_c (Fig. 7), the higher the voltage of V_c , the lower the value of L . At lower V_c , the highest whiteness was obtained.

The peak current density changes with V_c (approx. 0.2 A/dm²). This may be considered a reasonable result in view of the current-potential curve.

3.3.2 A.C. Electrolytic coloring method

(1) Voltage scanning method

The current-voltage curve obtained by the voltage scanning method is shown in Fig. 8. Because of the characteristics of the power supply, the scanning could not be made from 0 V and, therefore, it was impossible to measure the value of voltage at which the current began to flow. The current abruptly rises in the neighborhood of 10 V, with peak current observed in the neighborhood of 16 V and 24 V.

The results indicate that deposition of titanium oxide takes place at about 16 V and that electrolysis of water occurs at about 24 V.

Accordingly, approx. 16 V is the optimum voltage for the coloring.

(2) Constant voltage electrolytic coloring method

The results of constant voltage coloring are shown in Table 3. In this table, the result (No. 1) of voltage scanning is also presented. Whiteness and homogeneity of the film depend on the condition of electrolysis as shown in Nos. 5, 6 and 12.

L values plotted against V_N are shown in Fig. 9. When the voltage step rate is set at 0.1 V/sec and

Table 3. Electrolysis condition and coloring state in the case of A.C. Electrolytic coloring method

No.	V_s [V/sec]	V_N [V]	T [min]	Coloring state	L	a	b	Peak current density [A/dm ²]
1	0.1	30	5	D	53.9	-1.5	-2.5	—
2	0.1	18	5	C	57.6	-1.6	-2.2	1.05
3	0.63	18	5	D	54.4	-2.0	-2.8	1.45
4	1.25	18	5	B	58.7	-1.5	-3.0	1.56
5	0.1	15	5	A	63.9	-1.7	-2.0	0.92
6	0.1	20	5	A	61.2	-1.6	-2.7	1.13
7	0.1	25	5	B	54.5	-1.6	-3.1	1.41
8	0.63	15	5	C	56.6	-1.6	-1.8	1.02
9	0.63	20	5	D	53.0	-1.7	-3.1	1.66
10	0.63	25	5	B	64.5	-1.6	-2.5	1.89
11	1.25	15	5	D	60.3	-1.9	-3.2	0.94
12	1.25	20	5	A	63.7	-1.2	-2.9	1.88
13	1.25	25	5	C	53.9	-1.5	-3.2	2.34
14	Control sample*				53.9	-4.8	1.2	—

* Control sample (Double layered film)

A : White with perfect homogeneity

B : White with partial inhomogeneity

C : White with inhomogeneity

D : Not colored

1.25 V/sec, the L value is highest at 15 V and 20 V, while it is lowest at 25 V, with the rate at 0.63 V/sec, the highest value of L is registered at 25 V.

Preparation of white film on aluminum with titanium oxide as the coloring component was made by an electrolytic coloring method with a hydrosol of hydrated titanium oxide as the electrolytic solution. This film, however, is not sufficiently white, although it gives the highest whiteness compared to other method. This white film has outstanding dye absorbcency, so that it is feasible to produce films with beautiful pastel shades by way of dyeing this coating.

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Fig. 9. V - L value relation (A.C. Electrolytic coloring)

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水和酸化チタンゾル中でのアルミニウム 陽極酸化皮膜の白色電解着色

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要 旨

白色のアルミニウム陽極酸化皮膜を得ることを目的として、陽極酸化皮膜を形成させたアルミニウム板を水和酸化チタンのヒドロゾル中で二次電解し、電気泳動によって皮膜の細孔中に水和酸化チタンのコロイド粒子を析出させて着色する方法について検討した。

その結果、硫酸浴を用いて陽極酸化して得た皮膜でも、このものを水和酸化チタンのヒドロゾル中で二次電解すると白色に着色するが、白さが十分ではなく、より白色度の強い、均一に着色した皮膜を得るには、硫酸浴を用いて皮膜を形成させたのち、さらに、これをリン酸浴中で陽極酸化して得た二重皮膜に対して電気泳動させる必要があった。これは、二重皮膜の方が硫酸浴だけで陽極酸化して得た皮膜よりも皮膜の細孔径が大きく、より多くの酸化チタン（水和酸化チタン）が析出するためである。

酸化チタン粒子の皮膜中への泳動、析出は直流電位走査法によって得た分極曲線から、 -3 V ～ -3.5 V 位で起こっていることがわかった。また、この白色皮膜は交流で電解した方がより均一な白色となるが、この場合は交流電圧走査法から、 16 V 近傍がもっとも析出しやすいことがわかった。