

Aug. 7, 1973

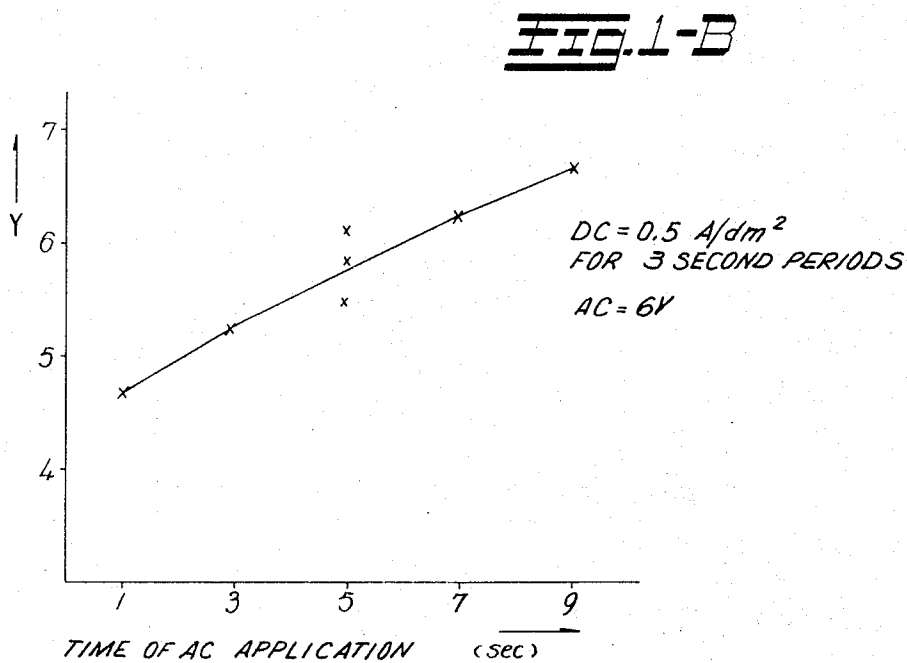
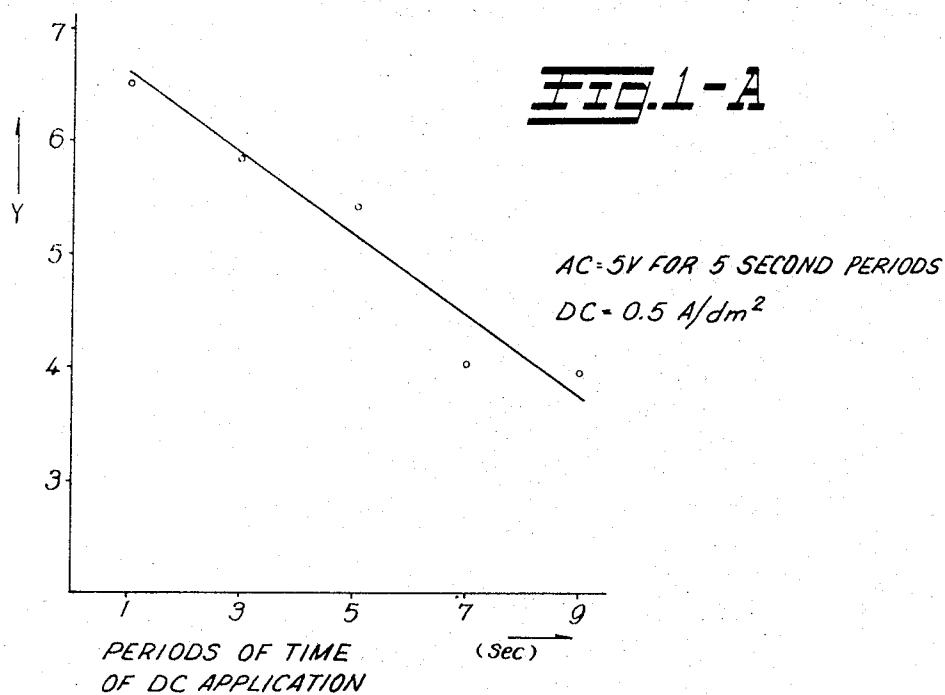
SHIGERU UEKI

3,751,350

PROCESS FOR COLORING AN ALUMINUM ANODIC OXIDE FILM

Filed March 3, 1972

3 Sheets-Sheet 1



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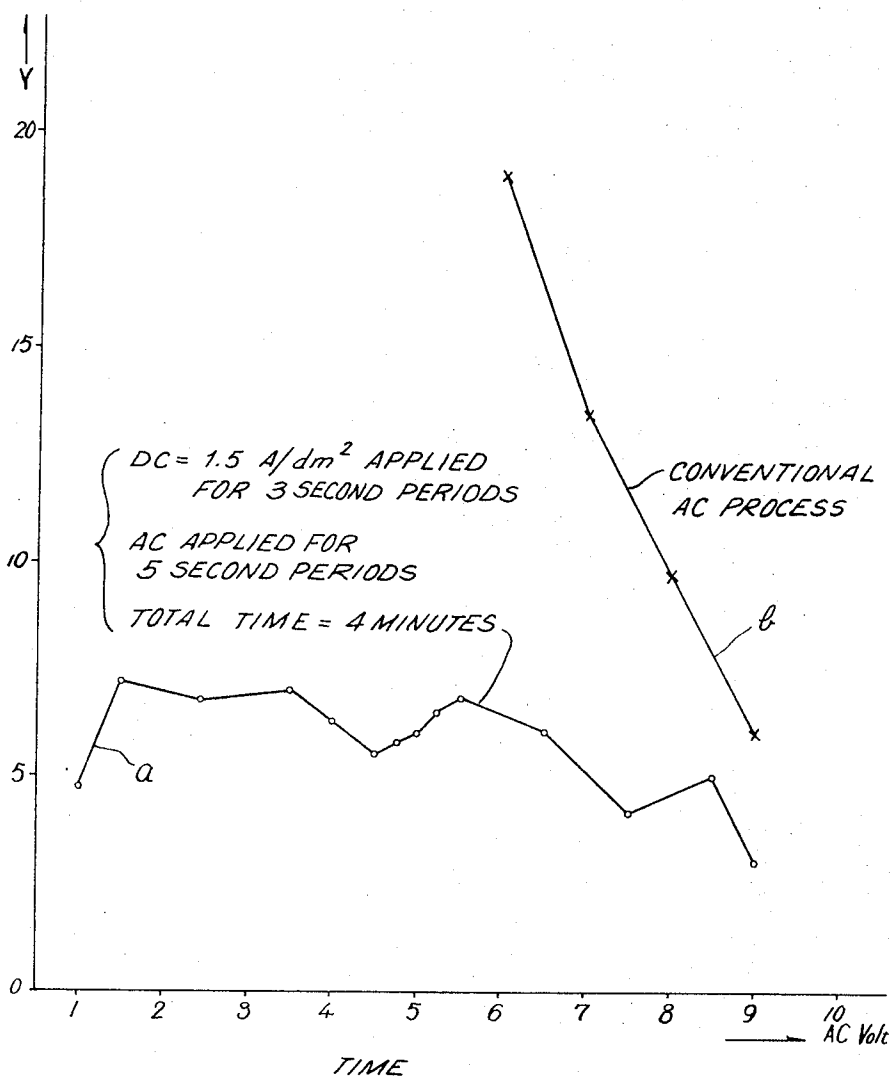
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PROCESS FOR COLORING AN ALUMINUM ANODIC OXIDE FILM

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3 Sheets-Sheet 2

FIG. 2



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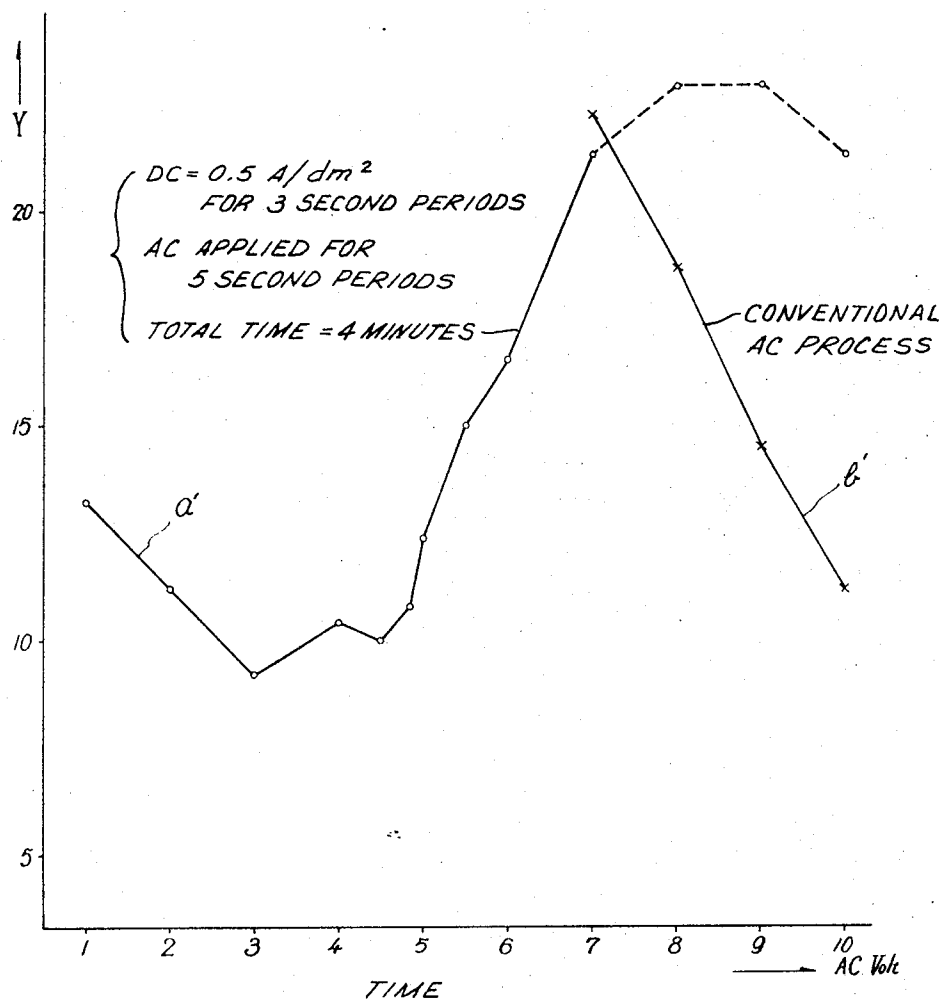
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Filed March 3, 1972

3 Sheets-Sheet 3

FIG. 3



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PROCESS FOR COLORING AN ALUMINUM ANODIC OXIDE FILM

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5 Claims

ABSTRACT OF THE DISCLOSURE

A process for coloring aluminum anodic oxide films in which aluminum or an aluminum alloy with an anodic oxide film is used as a cathode and is alternately subjected, in an acidic electrolyte containing metallic salts, to a direct current electrolysis from 0.2 a./dm.² to 2 a./dm.² and an alternating current electrolysis from about 1 v. to about 5 v.

BACKGROUND

(a) Field of the invention

This invention relates to a process for coloring aluminum anodic oxide films.

(b) Prior art

There is known an alternating current coloring process in which aluminum or an aluminum alloy having an anodic oxide film formed thereon is subjected to an alternating voltage of from 5 to 75 v. in an electrolyte containing metallic salts in order to color the anodic oxide film.

In this known process, the metallic salts become deposited in the corner regions of the film and a uniform coloring is not obtained.

In a known direct current coloring process, hydrogen is accumulated between a barrier layer located between the anodic oxide film and the aluminum metal base and this causes cracks in the film.

SUMMARY OF THE INVENTION

An object of this invention is to provide a process in which the above deficiencies in the known alternating and direct current coloring processes are avoided while at the same time providing any desired color density.

According to the invention, an aluminum or aluminum alloy having an anodic oxide film is used as a cathode and is placed in an acidic electrolyte in which a metallic salt is dissolved, and the alloy is subjected alternately to a direct current electrolysis at a current density of from 0.2 a./dm.² to 2 a./dm.² and an alternating current electrolysis of from about 1 v. to about 5 v.

The acidic electrolyte comprises an acidic aqueous solution having a pH below 6 which is prepared by dissolving a proper amount of metallic colorant salt in any inorganic or organic acid.

The frequency of the A.C. voltage given hereinabove is 50 cycles and this frequency will be employed throughout this case. The A.C. frequency can, however, be varied within wide limits without substantial departure from the results obtained.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1-A is a graphical representation showing the variation of luminous reflectance Y for a constant A.C. voltage in constant periods and varying periods of application of D.C. voltage;

FIG. 1-B is similar to FIG. 1-A but in which the D.C. current is constant and applied in constant periods and the A.C. voltage is applied for varying time periods; and

FIGS. 2 and 3 are graphical illustrations respectively

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showing luminous reflectance Y for different alternating current voltages.

DETAILED DESCRIPTION

The relation between the time ratio of the AC flow and the DC flow and the color density is shown in FIG. 1-A and FIG. 1-B. In FIG. 1-A, the color density, obtained in the case when the alternating current is 5 v. and 5 seconds while the passing time of the direct current with a density of 0.5 a./dm.² is varied, is indicated by Y (luminous reflectance value) of the tristimulus values of the CIE standard colorimetric system (XYZ color system).

Here, it will be clear that the decrease in the luminous reflectance Y, that is, the increase in the color density is the result of increase of the length of time of direct current flow.

In FIG. 1-B, the color density obtained in the case when the flow time of the direct current of current density 0.5 a./dm.² is fixed at 3 seconds while the time of flow of alternating current of 6.0 v. is varied is indicated by Y (luminous reflectance) of the tristimulus values. Here, it will be clear that an increase in the luminous reflectance Y, that is, the decrease in the color density is the result of increase of the length of time of alternating current flow.

Thus, any desired color density can be obtained by carrying the time ratio of application of alternating current flow and direct current flow.

FIGS. 2 and 3 shows the change of Y of the color density with respect to the change of the voltage of the alternating current under the following conditions.

Coloring condition in FIG. 2

Coloring time	-----min--	4
D.C. current density	-----a./dm. ² --	1.5
Coloring time periods for the D.C. and A.C. current flows:		
D.C.	-----sec--	3
A.C.	-----sec--	5

Coloring electrolyte:

Nickel sulfate	-----g./l--	30
Stannous sulfate	-----g./l--	15
Ammonium chloride	-----g./l--	10
Sulfuric acid	-----g./l--	7
Cresolsulfonic acid	-----g./l--	8

Coloring condition in FIG. 3

Coloring time	-----min--	4
D.C. current density	-----a./dm. ² --	0.5
Coloring time periods for the D.C. and A.C. current flows:		
D.C.	-----sec--	3
A.C.	-----sec--	5

Coloring electrolyte:

Nickel sulfate	-----g./l--	100
Ammonium chloride	-----g./l--	10
Boric acid	-----g./l--	30

Each of the lines, a, a' in FIG. 2 and FIG. 3 shows the change of Y with respect to the change of the voltage of the alternating current under the respective conditions as given above, and each of curved lines b, b' shows the change of Y obtained by the conventional alternating current coloring process using the same coloring time (4 minutes) and the same electrolyte as above.

The curve a in FIG. 2 indicates that an almost constant thick-coloring condition can be kept even by increase in the alternating current voltage, whereas the curve b of the conventional process shows that the color density is too low below about 7 v. to be practical. The curve a' in FIG. 3 shows that the color density is too low above about 5 v. to be practical, and the curve b' of the conventional process is similar to the line b in FIG. 2 and has the same deficiency as noted with respect thereto.

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Thus, as shown in FIGS. 2 and 3, good coloring can be obtained according to the invention in a range of about 1 to 5 v. A.C., and by properly setting the ratio of the time of direct current application and the time of application of alternating current as shown in FIGS. 1-A and 1-B, any desirable color density can be preferably obtained within the range of predetermined time.

The difference between the curves a , a' in FIG. 2 and FIG. 3 is based on the difference between the coloring electrolyte containing sulfuric acid and that containing boric acid. The first electrolyte with sulfuric acid makes the barrier thin and thereby good coloring can be effected even in the high voltage range such as 9 v. as shown in FIG. 2. The electrolyte with boric acid does not make the barrier thin and impairs the coloring at voltages above about 5 v.

As for the direct current density in the direct current electrolysis coloring, a range of 0.2 a./dm.²–2 a./dm.² is suitable. When the density is below 0.2 a./dm.², an extension of the coloring time is necessitated, and when it is above 2 a./dm.², peeling of the coating film occurs.

The invention will next be described with reference to the following examples.

EXAMPLE 1

A sheet of 99% pure aluminum was put in a bath (20° C.) containing sulfuric acid of 15%, by weight, and the sheet is anodized for 30 minutes with a direct current density of 1.5 a./dm.² (the opposite electrode is lead). The anodized plate, after being washed in water, is immersed in an electrolyte constituted by an aqueous solution (20° C.) containing 150 g./l. of boric acid. Electrical current is passed to the plate and to a nickel plate used as an opposite electrode to subject the anodized plate to a coloring treatment for 6 minutes under the voltage conditions and periods as indicated in the following table. As a result, bronze-colored beautiful coating films of different thicknesses are obtained.

The colors, when indicated by the tristimulus values in the CIE, are as follows (A color difference meter of CH-G type manufactured by Rika Kogyo is used):

	Sample 1			Sample 2			Sample 3		
D.C., 0.5 a./dm. ² —	3 sec.			3 sec.			3 sec.		
A.C., 4.5 v.-----	5 sec.			7 sec.			9 sec.		
	Y	X	Z	Y	X	Z	Y	X	Z
	5.10	5.00	4.42	8.30	7.95	7.55	9.84	9.52	8.63

EXAMPLE 2

Three 99.0% pure aluminum sheets (each 50 mm. x 120 mm. x 0.6 mm.) are subjected to alternating current of 1.0 a./dm.² (the opposite electrode is lead) for 45 minutes in a solution (20° C.) containing 10%, by volume, of sulfuric acid so as to form an anodic oxide film thereon. Each of the resultant sheets, after being washed in water, is used as a cathode, with the opposite electrode being carbon, and is subjected to direct current of 0.4 a./dm.² and alternating current of 4.0 v., alternately, under the time conditions as indicated in the following table, in an electrolyte (30° C.) consisting of 15 g./l. of stannous sulfate, 30 g./l. of nickel sulfate, 1.5 g./l. of ammonium chloride, 12 g./l. of cresolsulfonic acid and 20 g./l. of sulfuric acid. The total of treatment was 5 minutes.

The following bronze-colored sheets were obtained.

	Sample 4			Sample 5			Sample 6		
D.C., 0.4 a./dm. ² —	4 sec.			4 sec.			4 sec.		
A.C., 4 v.-----	3 sec.			5 sec.			7 sec.		
	Y	X	Z	Y	X	Z	Y	X	Z
	4.22	4.05	3.65	7.17	6.78	6.74	10.23	9.60	9.96

EXAMPLE 3

An L-shaped elongated extruded aluminum member (280 mm. x 70 mm. x 25 mm., 2 mm. thick) was sub-

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jected for 30 minutes to direct current of a density of 1.5 a./dm.² (the opposite electrode was lead) in a solution of 11%, by volume, of sulfuric acid to form an anodic oxide film thereon. The member then is washed in water and subjected to alternating current and direct current, alternately, under the conditions as shown in the table, while a nickel bar is used as the opposite electrode, in an aqueous solution (20° C.) containing 100 g./l. of nickel sulfate, 10 g./l. of ammonium chloride and 30 g./l. of boric acid. The resulting products obtained under the respective conditions are shown below. The visual results of the state of the film and color thereof are indicated in the following table.

The state of the film is indicated by R.E. meaning remarkably existent, S.E. meaning slightly existent and N.E. meaning non-existent. The color is indicated by ⊙ meaning somewhat thick bronze, ○ meaning ordinary bronze and Δ meaning thin bronze.

	D.C. a./dm. ²	A.C. volt	Coloring time (min.)	Color	Film crack
D.C., 3 sec.-----	0.4	0	4	Δ	R.E.
		2	4	○	N.E.
		4.5	6	○	S.E.
		4.5	4	○	N.E.
		0	6	○	N.E.
	0.6	2	4	○	N.E.
		4.5	4	○	S.E.
		2	6	○	R.E.
A.C., 5 sec.-----		4.5	4	○	N.E.
		0	4	Δ	R.E.
	0.8	2	4	○	S.E.
		4.5	6	⊙	N.E.
		4	4	⊙	N.E.
D.C., 8 sec.-----	0.4	4	4	○	S.E.
		5	4	○	N.E.
A.C., 8 sec.-----	0.6	4	4	○	N.E.
		5	4	○	N.E.

In the case when the alternating current voltage is 0 v., the process is the direct current intermittent process and is indicated merely for purposes of comparison.

As indicated in Examples 1, 2 and 3 the process of the invention avoids the deficiencies of the conventional processes that is, film cracks, non-uniform coloring and difficulty in the production of the desired color. The colored samples obtained by the method in Examples 1, 2 and 3 were subjected to fading tests and no fading was detected.

What is claimed is:

1. A process of coloring an anodic oxide film on an aluminum or aluminum alloy member, said process comprising immersing the alloy member in an acidic electrolyte containing metallic salts as colorants, connecting the alloy member as a cathode in a circuit and subjecting the alloy member to A.C. and D.C. electrolysis intermittently and in alternation, the D.C. current density being between 0.2 a./dm.² and 2 a./dm.² and A.C. voltage between 1 and 5 volts.

2. A process as claimed in claim 1 wherein the D.C. is applied for 3–4 seconds and the A.C. for 3–9 seconds.

3. A process as claimed in claim 2 wherein the electrolyte contains an acid having a pH below 6.

4. A process as claimed in claim 3 wherein the acid is organic or inorganic.

5. A process as claimed in claim 2 wherein the total time of current application is 4 to 6 minutes.

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