

PATENT SPECIFICATION

(11) 1 391 808

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- (21) Application No. 47991/72 (22) Filed 18 Oct. 1972
 (31) Convention Application Nos. 83336/71, 83337/71 and 83338/71
 (32) Filed 22 Oct. 1971
 (31) Convention Application No. 95850/71 (32) Filed 30 Nov. 1971
 (31) Convention Application No. 46487/72 (32) Filed 12 May 1972
 (31) Convention Application No. 52528/72 (32) Filed 29 May 1972
 (31) Convention Application No. 66624/72 (32) Filed 5 July 1972 in
 (33) Japan (JA)
 (44) Complete Specification published 23 April 1975
 (51) INT CL^a C25D 11/14, 11/08, 11/10, // 11/12, 11/16
 (52) Index at acceptance C7B 13 15X 17 2F
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(54) ANODIZING METHODS FOR FORMING A COLORED OXIDE COATING ON SURFACES OF ALUMINUM OR ALUMINUM ALLOY MATERIALS

(71) We, RIKEN KEIKINZOKU KOGYO KABUSHIKI KAISHA, a company organised according to the laws of Japan, of No. 100, 2-Chome, Margarikane, Shizuoka City, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method for forming a colored oxide coating on surfaces of aluminum or aluminum alloy materials and particularly a method for forming colored oxide coatings having a broad color tone of bronze series colors by subjecting aluminum or aluminum alloy materials to an anodic oxidation in an aqueous solution containing oxalic acid and sulfuric acid by means of direct current.

In the specification, aluminum or aluminum alloys are referred to as merely "aluminous materials" and the direct current includes ripple obtained by rectifying alternating current as well as current from an accumulator.

Recently, aluminous building materials have been utilized broadly and various coloring processes for these materials have been studied. However, the range of coloration of the aluminous materials is not said to be broader than that of the other building materials and for obtaining a certain color, for example, bronze, strict treating conditions are required and further the color tone range is narrow and the chemicals for such a treatment are usually expensive. Conventional processes for coloring aluminous materials to bronze are as follows:—

(1) Anodic oxidation is effected in an aqueous solution of oxalic acid used as the electrolytic bath.

(2) Anodic oxidation is effected in an electrolytic bath containing an aromatic sul-

fonic acid and either sulfuric acid or a metal sulfate.

In the above described first process, oxalic acid to be used in the electrolytic bath is inexpensive and in this respect this process is most valuable commercially. However, the color tone range of the obtained oxide coatings is very narrow and even if the color tone is bronze, it belongs to the yellow series. Even if the quality of the aluminous material itself or the thickness of oxide coating is varied, the color tone range is limited and consequently this process has not been used practically so much.

The above described second process can provide a clear bronze color tone and a broad range and therefore this process has been used most widely. However, the aromatic sulfonic acid which is the main component of the electrolytic bath is expensive and this point is a great drawback in this process.

Recently, such colored aluminous materials have been in great demanded and in order to increase the yield amount, it is required to reduce the treating time but the above described processes do not fully satisfy this requirement.

We have made efforts to solve the above described drawbacks and accomplished the present invention.

It has been found possible to obtain colored oxide coatings having a broad range of bronze series color by a simple electrolytic bath, that is an aqueous solution of oxalic acid and sulfuric acid.

According to the present invention there is provided a method of producing colored oxide coatings on aluminum or aluminum alloy material, which comprises electrolytically anodizing the aluminum or aluminum alloy material in an aqueous solution of 0.5—5 grams per 100 ml of oxalic acid and 0.05—0.5

[Price 33p]

grams per 100 ml of sulfuric acid at a temperature of 0—12° C for 3—15 minutes.

By using this method it has been found that the desired color tone can be obtained independently of the thickness of the formed oxide coating layer. Thus colored oxide coatings from amber to bronze having excellent various properties can be obtained.

The preferred conditions of the anodic oxidation are as follows:—

- (1) current: direct current.
- (2) current density: 0.5 to 5 A/dm².
- (3) voltage: 5 to 150 V.

In the above described treatment, the desired color tone can be obtained by keeping the bath temperature low. In general, the color tone of the oxide coating is influenced by the thickness of said coating layer but as described above it has been found that the above described color tone can be attained at the low bath temperature in the above described short time. The upper limit of the bath temperature is important and if the bath temperature is higher than 12° C, it is necessary to increase the electric power per unit area, that is, to increase the thickness of the oxide coating in order to obtain a given coloration. For this purpose, the treating time has to be prolonged and the object of the present invention for shortening the treating time can not be attained and therefore the desired economic effect can not be attained. While, in this treatment, the desired color tone can be attained without increasing the thickness of the oxide coating and particularly since the bath temperature is low as described above, the amount of anode aluminum dissolved off is small and therefore it is possible to prevent the aging of the electrolytic bath and such a treatment is very advantageous also in this point.

When the amount of oxalic acid is less than 0.5 grams per 100 ml, the colored oxide coating is not fully formed and the mechanical strength is not sufficient and the color is not fully developed. Accordingly, the above limitation of amount of oxalic acid is defined based on the above described reason.

When the amount of sulfuric acid is less than 0.05 grams per 100 ml, the coloration of bronze is not sufficient.

It appears that oxalic acid and sulfuric acid contribute to the hue of the oxide coating and sulfuric acid mainly contributes to the value (luminosity).

It has been previously proposed to effect the anodic oxidation in the presence of aluminum ions which may have been obtained from an aluminum article during anodizing. The purpose of the presence of the aluminum ions in this previous proposal is to prevent local corrosion caused by excess current which flows on the aluminous materials upon the anodic oxidation treatment. The amount of aluminum in this case is, for example about 0.1—0.4

g/l in an aqueous solution of oxalic acid. The upper limit is defined by the reason that the electric corrosion on the whole surface can be prevented by such an amount and the lower limit is defined by the reason that the effect for preventing the excess current can be attained from such an amount.

We have found that the presence of aluminum ions in an aqueous solution containing oxalic acid and sulfuric acid can reduce the treating time and give uniform color tone in addition to the prevention of the above described excess current.

Furthermore, there is another prior art process in which the anodic oxidation for forming the colored oxide coatings is carried out in the presence of aluminum ions or the salts thereof. However, the functions of the aluminum ions in these prior art processes are as follows:—

- (1) Aluminum ions themselves give the inherent function for generating color in the oxide coating.
- (2) Aluminum ions coprecipitate with colored oxide or hydroxide in the oxide coating to develop color.

Accordingly, in the above described prior art processes, it is very difficult to obtain the colored oxide coating on the aluminous materials in a short time.

Preferably the aluminous material to be treated is degreased with an aqueous solution of sodium hydroxide and then washed with water and successively neutralized with an aqueous solution of nitric acid and then washed with water.

Aluminum ions promote the formation of a colored oxide coating, shortens the treating time and stabilizes the color tone of the oxide coatings. As mentioned above, aluminum ions generally have the effect of preventing excess current but this is a negative effect. On the contrary, the preferable addition of a relatively large amount of aluminum ions does not directly aim to prevent the excess current but to accomplish the anodic oxidation even at a lower current density, whether or not the excess current is formed. Aluminum ions themselves promote the coloration reaction and from this point the treating time also may be reduced and such a function may be attained by the addition of 0.05—6.0 g/l of aluminum ion in the electrolytic bath containing sulfuric acid in addition to oxalic acid.

The preferable conditions for the anodic oxidation are as follows:—

- (a) Bath temperature: 0—12° C.
- (b) Current density: 0.5—5 A/dm².
- (c) Voltage: 30—80 V.
- (d) Treating time: about 10 minutes.

The above described aluminum ions may be obtained by the following means.

- (1) Dissolving off the anode aluminum during the anodic oxidation step.

(2) Addition of aluminum oxalate or aluminum sulfate.

(3) Immersing a fresh anode aluminum in a pre-used electrolytic bath containing oxalic acid and sulfuric acid, the temperature of which has been raised by continuing the anodic oxidation.

For obtaining aluminum ion, the combination of the above described means (1) and (3) is commercially advantageous, because the means (2) needs the addition of the above described chemicals to the electrolytic bath.

The above described explanation is made with respect to the case where the aluminous materials after being degreased and washed with water, are directly subjected to the anodic oxidation, but if a porous oxide coating has been previously formed on the aluminous material by a usual anodic oxidation, the treating time can be reduced and further the color tone of the oxide coating can be stabilized.

We have further found that when nitric acid is added to an electrolytic bath containing oxalic and sulfuric acids, the resulting bath can provide colored oxide coatings having stable bronze series colors. In addition these colors can be obtained in a shorter time than is possible with a bath containing only sulfuric and oxalic acids.

Further according to the present invention there is provided a method of producing colored oxide coatings on aluminum or aluminum alloy material, which comprises electrolytically anodizing the aluminum or aluminum alloy material in an aqueous solution of 0.5—5 grams per 100 ml of oxalic acid and 0.05—0.5 grams per 100 ml of sulfuric acid and 0.05—0.5 grams per 100 ml of nitric acid at a temperature of 10—30° C.

The addition of nitric acid lowers the electric conductivity of the electrolyte bath containing sulfuric acid and oxalic acid. Accordingly, when a given current density is applied to the electrolytic bath containing nitric acid in addition to oxalic acid and sulfuric acid, the increase rate of voltage in said bath is earlier than that of the electrolytic bath containing oxalic and sulfuric acid and consequently the colored oxide coating having a desired color tone can be obtained in a shorter time.

However, nitric acid is apt to cause electric corrosion of the aluminous material during the anodic oxidation and therefore nitric acid should preferably not be added until the electric corrosion occurs. The upper limit of nitric acid is defined by considering the advantages gained by lowering the electric conductivity and the disadvantage in incurring electric corrosion.

The lower limit of nitric acid is defined based on the reason that the effect for adding nitric acid does not clearly appear in the amount less than 0.05%.

The preferable conditions of the anodic

oxidation in this case are as follows:—

(a) A bath temperature of 10—30° C and preferably

(b) A current density of 0.5—5 A/dm² and preferably

(c) A voltage of 15—80 V.

Still further we have found that when the electrolytic bath contains oxalic, sulfuric, nitric and boric acids oxide coatings having stable greyish green to brown series colors are obtained.

Therefore still further according to the present invention there is provided a method of producing colored oxide coatings on aluminum or aluminum alloy material, which comprises electrolytically anodizing the aluminum or aluminum alloy material in an aqueous solution of 0.5—5 grams per 100 ml of oxalic acid and 0.05—0.5 grams per 100 ml of sulfuric acid and a mixture of 0.05—0.5 grams per 100 ml of nitric acid and 0.1—10.0 grams per 100 ml of boric acid at a temperature of 10—40° C for 3—120 minutes.

Boric acid also has a function for decreasing the electric conductivity of the electrolytic bath as in nitric acid but has no danger of the electric corrosion. Accordingly, it has been found that when boric acid is added to further decrease the electric conductivity, the time for the anodic oxidation can be further reduced as compared with the case when only nitric acid is added.

Furthermore, it has been found that the addition of boric acid can impart a bluish bronze color to the oxide coating.

In this case the preferred conditions for the anodic oxidation are as follows:—

(a) Bath temperature: 10—40° C.

(b) Current density: 0.5—5 A/dm².

(c) Voltage: 15—120 V.

(d) Treating time: 3—120 minutes.

The treating time is sufficient in about 3 minutes.

The following Examples are given for the purpose of illustration of this invention and are not intended as limitations thereof.

The term aluminum 1100 used in the Examples means an aluminum alloy containing by weight 0.05 to 0.20% of copper, 1.0% of a mixture of silicon and iron, 0.05% of manganese and 0.10% of zinc.

Example 1.

Aluminum 1100 was immersed in 8.0% by weight of an aqueous solution of sodium hydroxide at 60° C for 1 minute and washed with water and then the thus degreased aluminous material was immersed in 16% by weight of nitric acid at room temperature for 20 seconds to effect neutralization and washed with water. Then, the thus pretreated aluminous material was anodized as an anode in an electrolytic bath of an aqueous solution containing oxalic acid and sulfuric acid as shown in the following Table 1 at a tempera-

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ture of $11 \pm 1^\circ \text{C}$, with a direct current of a current density of 1 A/dm^2 and a highest voltage of 70 V for 3 minutes or 15 minutes

to obtain colored oxide coatings showing from bronze to amber on the aluminous material as shown in Table 1.

Table 1

Composition of electrolytic bath (% by weight)		Thickness of coating (μ)		Color	
Oxalic acid	Sulfuric acid	3 min.	15 min.	3 min.	15 min.
0.5	0.05	3	8	bluish light amber	bluish bronze
3.0	0.05	3	8	light amber	bronze
	0.3	3	8	light amber	bronze
5.0	0.05	3.5	8	light amber	bronze
	0.3	3	8	light amber	bronze
	0.5	3	8	light amber	bronze

10 The sample obtained in this Example and a comparative sample obtained by a conventional sulfuric acid electrolytic bath were determined with respect to the following properties to obtain results as shown in the following Table 2.

- (1) Abrasion resistance: Test of falling sand according to JIS H-8601.
 (2) Corrosion resistance: Alkaline dropping test according to JIS H-8601.
 (3) Corrosion resistance: CASS test according to JIS H-8601.

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Table 2

Test	Comparative sample obtained by conventional sulfuric acid bath	Sample plate of Example 1
	6 μ	3.5 μ
1	350 sec.	310 sec.
2	60 sec.	70 sec.
3	more than RN9	more than RN10

From the results of Table 2, it was confirmed that the properties of the oxide coatings according to the present invention are superior to those of the comparative sample even when the thickness of the coating is thinner.

As mentioned above, the present invention is a method of obtaining a color of from bronze to amber in a very short time by using inexpensive oxalic acid and sulfuric acid and in this point, has a very industrial and economical merit.

Moreover, the obtained oxide coatings have a broad range of color tone and are the same as those obtained with the expensive aromatic sulfonic acid bath in weather resistance, abrasion resistance and the like.

Example 2.

Aluminum 1100 was immersed in 8% by weight of an aqueous solution of sodium hydroxide at 70° C for 30 seconds and washed with water and then the thus degreased aluminous material was immersed in 16% by weight of an aqueous solution of nitric acid at room temperature for 10 seconds to effect neutralization and washed with water. Then, the thus pretreated aluminous material was anodized as an anode in an electrolytic bath of an aqueous solution containing oxalic acid, sulfuric acid and nitric acid as shown in the following Table 2 at a temperature of $20 \pm 2^\circ$ C, with a direct current of a current density of 2 A/dm² and a voltage of 50—60 V for 30 minutes to obtain colored oxide coatings showing bronze as shown in Table 3.

Table 3

Oxalic acid (% by weight)	Sulfuric acid Nitric acid (% by weight)	Voltage (V)	Thickness of coating (μ)	Color tone	
				Color	Munsell notation
2	— 0.05	~ 60	14	light greyish brown	7.3 GY 5.4/1.0
	— 0.05	"	16	greyish brown	8.1 GY 5.5/1.2
	— 0.10	"	16	brown	3.3 G 4.3/1.2
	— 0.10	"	15	dark greyish brown	9.7 GY 3.3/1.4
	— 0.15	"	17	dark brown	9.5 GY 4.0/1.3
	— 0.05	~ 50	15	greyish yellow	6.2 GY 5.6/1.2
3	— 0.10	"	16	light brown	6.3 GY 5.3/1.0
	— 0.10	"	15	greyish brown	6.5 GY 5.1/1.2
	— 0.15	"	14	greyish brown	3.8 GY 4.3/0.9
	— 0.15	"	15	greyish brown	8.2 GY 4.6/1.2
	— 0.15	"	15	light brown	8.7 GY 4.9/1.4
	— 0.20	"	17	light brown	9.1 GY 3.2/1.0

Table 3 (continued)

Oxalic acid (% by weight)	Sulfuric acid Nitric acid (% by weight)	Voltage (V)	Thickness of coating (μ)	Color tone	
				Color	Munsell notation
3	0.20 0.10	~ 50	16	greyish brown	9.2 GY 3.4/0.9
	0.25 0.05	"	16	light brown	6.4 GY 3.9/1.3
	0.05 0.20	"	17	light yellow	2.9 GY 5.7/1.4
5	0.10 0.20	"	16	greyish yellow	2.7 GY 5.6/1.4
	0.15 0.15	"	16	greyish yellow	3.1 GY 4.9/1.5
	0.15 0.20	"	15	greyish yellow	3.1 GY 5.2/1.4
	0.20 0.15	"	17	greyish yellow	3.0 GY 5.3/1.3
	0.20 0.20	"	15	greyish yellow	2.7 GY 5.5/1.7
	0.25 0.10	"	15	greyish yellow	3.5 GY 5.2/1.2
	0.25 0.15	"	15	light brown	4.3 GY 5.1/0.9
	0.25 0.20	"	14	light brown	4.0 GY 5.0/0.9
	0.30 0.05	"	14	light greyish yellow	4.2 GY 5.2/1.1

Table 3 (continued)

Oxalic acid (% by weight)	Sulfuric acid Nitric acid (% by weight)	Voltage (V)	Thickness of coating (μ)	Color tone	
				Color	Munsell notation
5	— 0.30 — — 0.10 —	~ 50	16	greyish yellow	3.7 GY 5.4/1.3
	— 0.30 — — 0.15 —	"	14	greyish yellow	3.6 GY 5.6/1.4
	— 0.30 — — 0.20 —	"	17	greyish yellow	2.9 GY 5.5/1.7
	— 0.35 — — 0.05 —	"	16	light greyish yellow	3.3 GY 4.9/1.3
	— 0.35 — — 0.10 —	"	16	greyish yellow	3.8 GY 4.8/1.2
	— 0.35 — — 0.15 —	"	16	greyish yellow	4.1 GY 5.0/0.9
	— 0.40 — — 0.05 —	"	17	greyish yellow	4.2 GY 5.1/1.1
	— 0.40 — — 0.10 —	"	15	light yellow	3.7 GY 5.8/1.5
	— 0.45 — — 0.05 —	"	15	light greyish yellow	3.8 GY 4.9/1.4

Example 3.

Aluminum 1100 was immersed in 8% by weight of an aqueous solution of sodium hydroxide at 70° C for 30 seconds and washed with water and then the thus degreased aluminous material was immersed in 16% by weight of an aqueous solution of nitric acid at room temperature for 10 seconds to effect neutralization and washed with water.

The thus pretreated aluminous material was anodized as an anode in an electrolytic bath of an aqueous solution containing oxalic acid, sulfuric acid, nitric acid and boric acid as shown in the following Table 4 at a temperature of $20 \pm 2^\circ \text{C}$, with a direct current under the same electrolytic conditions as shown in Table 4 to obtain colored oxide coatings showing greyish green to greyish brown on the aluminous material as shown in Table 4.

Table 4

Composition of electrolytic bath (% by weight)				Electrolytic condition		Thickness of coating (μ)	Color tone	
Oxalic acid	Sulfuric acid	Nitric acid	Boric acid	Time (min.)	Voltage (V)	Current density (A/dm^2)	Color	Munsell notation
2.0	0.1	0.05	0.5	30	47 - 70	2.0	bluish brown	5.7 G 4.4/1.4
	"	"	1.0	"	47 - 72	"	bluish brown	7.1 G 4.2/1.4
	"	"	3.0	"	45 - 72	"	deep bluish brown	7.1 G 4.2/1.4
3.0	0.15	0.1	0.5	"	42 - 53	"	slightly light bronze	1.1 G 4.8/1.2
	"	"	1.0	"	42 - 47	"	bronze	1.1 G 4.5/1.2
	"	"	3.0	"	40 - 60	"	bluish brown	2.2 G 4.2/1.2
	0.20	"	0.5	"	40 - 52	"	bronze	1.8 G 4.4/1.1
	"	"	1.0	"	40 - 54	"	bronze	0.7 G 4.2/1.4
	"	"	3.0	"	38 - 55	"	bluish brown	0.5 G 4.0/1.2

As mentioned above, the present invention uses an electrolytic bath containing oxalic acid and sulfuric acid as base solution, so that it provides an extremely economical colored surface treatment showing bronze.

WHAT WE CLAIM IS:—

1. A method of producing colored oxide coatings on aluminum or aluminum alloy material, which comprises electrolytically anodizing the aluminum or aluminum alloy material in an aqueous solution of 0.5—5 grams per 100 ml of oxalic acid and 0.05—0.5 grams per 100 ml of sulfuric acid at a temperature of 0—12° C for 3—15 minutes.

2. A method as claimed in claim 1, wherein said aqueous solution contains 0.05—6.0 g/l of aluminum or aluminum ion.

3. A method of producing colored oxide coatings on aluminum or aluminum alloy material, which comprises electrolytically anodizing the aluminum or aluminum alloy material in an aqueous solution of 0.5—5 grams per 100 ml of oxalic acid and 0.05—0.5 grams per 100 ml of sulfuric acid and 0.05—0.5 grams per 100 ml of nitric acid at a temperature of 10—30° C.

4. A method of producing colored oxide coatings on aluminum or aluminum alloy material, which comprises electrolytically anodizing the aluminum or aluminum alloy material in an aqueous solution of 0.5—5

grams per 100 ml of oxalic acid and 0.05—0.5 grams per 100 ml of sulfuric acid and a mixture of 0.05—0.5 grams per 100 ml of nitric acid and 0.1—10.0 grams per 100 ml of boric acid at a temperature of 10—40° C for 3—120 minutes.

5. A method of producing colored oxide coatings on aluminum or aluminum alloy material according to claim 1, substantially as hereinbefore described and with reference to Example 1.

6. A method of producing colored oxide coatings on aluminum or aluminum alloy material according to claim 3, substantially as hereinbefore described and with reference to Example 2.

7. A method of producing colored oxide coatings on aluminum or aluminum alloy material according to claim 4, substantially as hereinbefore described and with reference to Example 3.

8. A colored oxide coating whenever produced by the method claimed in any one of the preceding claims.

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2. A method as claimed in claim 1, wherein said aqueous solution contains 0.05—6.0 g/l of aluminum or aluminum ion.

3. A method of producing colored oxide coatings on aluminum or aluminum alloy material, which comprises electrolytically anodizing the aluminum or aluminum alloy material in an aqueous solution of 0.5—5 grams per 100 ml of oxalic acid and 0.05—0.5 grams per 100 ml of sulfuric acid and 0.05—0.5 grams per 100 ml of nitric acid at a temperature of 10—30° C.

4. A method of producing colored oxide coatings on aluminum or aluminum alloy material, which comprises electrolytically anodizing the aluminum or aluminum alloy material in an aqueous solution of 0.5—5

grams per 100 ml of oxalic acid and 0.05—0.5 grams per 100 ml of sulfuric acid and a mixture of 0.05—0.5 grams per 100 ml of nitric acid and 0.1—10.0 grams per 100 ml of boric acid at a temperature of 10—40° C for 3—120 minutes.

5. A method of producing colored oxide coatings on aluminum or aluminum alloy material according to claim 1, substantially as hereinbefore described and with reference to Example 1.

6. A method of producing colored oxide coatings on aluminum or aluminum alloy material according to claim 3, substantially as hereinbefore described and with reference to Example 2.

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