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[54] **METHOD FOR FORMING A COLORED COATING ON ALUMINOUS MATERIALS**

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[58] **Field of Search** 204/58

[56] **References Cited**

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[57] **ABSTRACT**

Colored oxide coatings from yellow to brown on aluminum or aluminum alloy are formed by an anodic oxidation with an aqueous solution of 0.5 – 10.0 percent by weight of oxalic acid and 0.05 – 4.0 percent by weight of an ammonium salt, a metal acetate or a metal nitrate.

7 Claims, No Drawings

METHOD FOR FORMING A COLORED COATING ON ALUMINOUS MATERIALS

The present invention relates to a method for forming a colored oxide coating on the surfaces of aluminum or aluminum alloy materials and particularly a method for forming a colored oxide coating having a broad yellowish color tone on aluminum or aluminum alloy materials by an anodic oxidation.

In the specification, aluminum or aluminum alloys are referred to as merely "aluminous material(s)."

Recently, aluminous building materials have been utilized broadly, because aluminous materials have excellent abrasion resistance and weather resistance and fulfill the requirements desired of building materials and have a beautiful appearance and a broader coloration range than the other metal materials.

However, it can be said that, while the coloration range of aluminous materials is broader than that of the other metal materials it is not always possible to color such aluminous materials in various color tones to the maximum desired extent. Thus, various investigations have been made to widen the color tone but a satisfactory method which can color the aluminous materials to the color tones desired by the user and particularly to a broad range of yellowish color, has never heretofore been developed. Among the processes known for coloring aluminous materials yellow are the following features:

1. Oxalic acid is used as an electrolytic bath.

2. Anodic oxidation is effected in an electrolytic bath containing an aromatic sulfonic acid and sulfuric acid or a metal sulfate.

3. An aluminous material is previously subjected to an anodic oxidation and then applied with an alternate current in an electrolytic bath containing a metal salt.

In any of the above known processes, the obtained range of the color tones is narrow and for example, in the above described first process which is the most practical process among these known processes, the color tone of the obtained oxide coating is of a very narrow range and even if the thickness of oxide coating or the quality of aluminous materials is varied, the remarkable variation in color cannot be obtained. Accordingly, colored oxide coatings having the broad yellowish color tone required by the user, have not heretofore been obtained.

The above described second and third processes can provide oxide coatings having a relatively broad color tone but the second process uses an electrolytic bath consisting mainly of an aromatic sulfonic acid which is a specific chemical and therefore the electrolytic bath is expensive. In the third process, after the usual anodic oxidation, an alternating current must be applied and consequently there are problems in view of productivity and cost.

The present invention aims to solve the above described deficiencies and provides a method for producing colored oxide coatings of aluminous materials wherein colored oxide coatings of aluminous materials having a broad yellowish color tone are formed by an anodic oxidation using an electrolytic bath having a simple composition.

For the practice of the method of the present invention, firstly, an aluminous material to be treated is degreased with an aqueous solution of sodium hydroxide and then washed with water and successively neutralized in an aqueous solution of nitric acid and then washed with water. Then, the thus treated aluminous material is subjected to an anodic oxidation with direct current by using an aqueous solution containing 0.5 – 10.0 percent by weight of oxalic acid and 0.05 – 4.0 percent by weight of ammonium salt, 0.05 – 1.5 percent by weight of acetate or 0.05 – 0.7 percent by weight of nitrate as an electrolytic bath.

In this case, the above limitation of the composition of the electrolytic bath is based on the following reason.

The addition of oxalic acid serves to improve the electric conductivity of the bath and facilitate the electrolysis, whereby the yellow oxide coating is formed on aluminous materials. This has been previously known as shown in the above described first process. Accordingly, for the same reasons as in the above first process, oxalic acid is added as an essential component of the bath, i.e., in order to obtain the yellow color tone and at least 0.5 percent of oxalic acid is necessary to generate the yellow color; when the amount of oxalic acid is larger than 10.0 percent, the dissolution of such an amount of oxalic acid is difficult at room temperature.

The addition of ammonium salts, acetates or nitrates serves to widen the color range of the oxide coating on aluminous materials and to obtain an yellowish color tone and these salts improve the luminosity. An amount less than the lower limit cannot develop the effect of addition, while even if amounts more than the upper limits are added, the effect of coloration does not vary. It has been found that these ranges can provide colored oxide coatings of a broad color tone from yellow to greyish yellow.

As an ammonium salts, use can be made of ammonium phosphate and ammonium dichromate.

As acetates, use can be made of manganese acetate and chromium acetate.

As nitrates, use can be made of ferric nitrate and chromium nitrate.

The optimum conditions when aluminous materials are treated by defining the bath composition to the above range are as follows:

Base solution	Metal salt	Current type	Current density (A/dm^2)	Voltage (V)	Bath temperature (°C)	Time (min.)
Oxalic acid	Ammonium salt	Direct	0.05–3	5–160	10–40	10–120
	Acetate	do.	0.5–3	5–130	10–40	10–120
	Nitrate	do.	0.5–5	5–150	0–50	10–120

It is assumed that in the above described bath composition, oxalic acid contributes to the hue of the oxide coatings and that the metal salts provide an auxiliary

contribution. Furthermore, it is assumed that the metal salts mainly contribute to the luminosity range of the colored oxide coating.

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

Example 1

An aluminous material 1,100 was immersed in 7.5 percent by weight of an aqueous solution of sodium hydroxide at 80°C for 30 seconds and washed with water and then the thus treated aluminous material was immersed in 10 percent by weight of an aqueous solution of nitric acid 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 and stannous sulfate as shown in the following Table 1 at a temperature of 20±1°C, with a direct current of a current density of 2 A/dm² and a voltage of 30 – 105 V for 60 minutes to obtain colored oxide coatings showing greyish yellow as shown in Table 1.

Table 1

Composition of electrolytic bath (% by weight)		Voltage (V)	Thickness of coating (μ)	Color tone*
Oxalic acid	Stannous sulfate			
1	0.05	65–105	30	7.5 GY 4.8/1.6
	0.1	60–85	29	2.6 G 4.6/1.9
	0.1	55–75	31	4.2 GY 5.4/1.7
3	0.3	45–65	29	7.5 GY 4.7/1.6
	0.5	40–55	28	6.1 GY 4.2/1.6
5	0.75	35–45	30	4.6 GY 5.5/1.5
	1.0	35–40	30	5.0 GY 4.9/1.6
10	1.5	30–35	31	7.0 GY 6.2/1.4
	2.0	30–33	30	6.9 GY 6.2/1.4

*Munsell notation

When ferrous sulfate was used instead of stannous sulfate, the similar results were obtained.

Example 2

The same aluminous material as used in Example 1 was pretreated in the same manner as described in Example 1. The pretreated material was anodized as an anode in an electrolytic bath of an aqueous solution containing oxalic acid and titanium sulfate as shown in the following Table 2 at a temperature of 20±1°C with a direct current of a current density of 2 A/dm² and a voltage of 30 – 95 V for 60 minutes to obtain colored oxide coatings showing greyish yellow as shown in Table 2.

Table 2

Composition of electrolytic bath (% by weight)		Voltage (V)	Thickness of coating (μ)	Color tone*
Oxalic acid	Titanium sulfate			
1	0.05	60–95	28	4.8 GY 4.7/1.7
	0.1	55–75	29	4.9 G 4.5/1.8
3	0.05	55–70	30	5.5 GY 5.6/2.0
	0.5	40–45	28	7.3 GY 4.1/1.8
5	0.75	35–45	30	7.8 GY 5.0/1.7

Table 2-Continued

Composition of electrolytic bath (% by weight)		Voltage (V)	Thickness of coating (μ)	Color tone*
Oxalic acid	Titanium sulfate			
7.5	0.75	35–40	27	0.2 G 5.8/1.4
	1.0	35–37	31	0.2 G 5.6/1.4
10.0	1.0	30–35	30	1.3 G 6.0/1.4
	1.5	30–33	31	1.5 G 6.0/1.2

*Munsell notation

Example 3

The same aluminous material as used in Example 1 was pretreated in the same manner as described in Example 1. The pretreated material was anodized as an anode in an electrolytic bath of an aqueous solution containing oxalic acid and manganese sulfate as shown in the following Table 3 at a temperature of 20±2°C with a direct current of a current density of 2 A/dm² and a voltage of 30 – 85 V for 60 minutes to obtain colored oxide coatings having a color tone ranging from amber to brown as shown in Table 3.

Table 3

Composition of electrolytic bath (% by weight)		Voltage (V)	Thickness of coating (μ)	Color tone*
Oxalic acid	Manganese sulfate			
1	0.10	60–85	30	2.5 G 4.4/1.6
1	0.20	55–75	31	4 G 4.0/2.0
2	0.20	55–74	30	9.3 GY 4.2/1.7
2	0.25	45–67	30	9.0 GY 4.0/1.9
3	0.25	40–58	30	8.0 GY 4.5/1.7
3	0.50	40–48	32	7.5 GY 4.1/1.9
3.5	0.25	40–60	31	5.0 GY 4.2/1.7
3.5	0.50	40–54	32	6.8 GY 4.0/1.8
3.5	0.75	40–48	32	7.2 GY 4.1/1.8
4.0	0.25	40–63	29	2.9 GY 6.8/1.3
4.0	0.50	40–55	32	5.2 GY 5.2/1.4
4.0	0.75	40–46	32	6.8 GY 4.8/1.5
5.0	0.10	40–69	31	2.0 GY 7.2/1.2
5.0	0.25	40–65	31	3.8 GY 6.0/1.5
5.0	0.50	35–53	32	4.2 GY 5.4/1.6
5.0	0.75	35–48	32	4.5 GY 5.4/1.4
10.0	0.50	30–46	32	3.0 GY 7.4/1.2
10.0	0.75	30–43	32	4.2 GY 7.0/1.2
10.0	1.00	30–45	30	6.6 GY 6.2/1.4

*Munsell notation

Example 4

In this example, the influence of the quality of aluminous material upon the color tone and thickness of the resulting coating was examined. Various aluminous materials as shown in the following Table 4 were anodized as an anode in an electolytic bath of an aqueous solution containing 3 percent by weight of oxalic acid and 0.5 percent by weight of manganese sulfate at a temperature of 20±1°C with a direct current of a current density of 2 A/dm² for 60 minutes to obtain a result as shown in Table 4.

Table 4

Aluminum alloy (AA)	Highest voltage at the electrolysis (V)	Thickness of coating (μ)	Color tone*	
1100	48	32	7.4 GY	4.2/1.8
3003	52	30	3 G	4.2/1.9
5052	49	30	7.1 GY	4.6/1.6
6063	49	32	4.8 GY	5.8/1.4

*Munsell notation

Example 5

The same aluminous material as used in Example 1 was pretreated in the same manner as described in Example 1. The pretreated material was anodized as an anode in an electrolytic bath of an aqueous solution containing oxalic acid and ammonium phosphate as shown in the following Table 5 at a temperature of 20±1°C with a direct current of a current density of 2 A/dm² and a voltage of 60 – 150 V for 60 minutes to obtain colored oxide coatings showing yellowish green as shown in Table 5.

Table 5

Composition of electrolytic bath (% by weight) Oxalic acid	Ammonium phosphate	Voltage (V)	Thickness of coating (μ)	Color tone*
1	0.05	80–150	28	5.9 GY 5.2/1.5
	0.1	85–140	30	7.7 GY 4.7/1.6
	0.1	60–85	30	2.7 GY 5.4/3.0
	0.3	70–85	31	1.3 GY 5.2/2.2
3	0.5	75–90	31	0.3 GY 5.3/2.3
	0.75	85–95	32	2.5 GY 5.5/1.9
	1.0	95–110	31	7.4 GY 4.7/1.8
5	1.5	80–90	29	2.8 GY 5.0/1.8
10	1.5	60–70	29	7.4 Y 5.7/2.9

*Munsell notation

Example 6

The same aluminous material as used in Example 1 was pretreated in the same manner as described in Example 1. The pretreated material was anodized as an anode in an electrolytic bath of an aqueous solution containing oxalic acid and ammonium dichromate as shown in the following Table 6 at a temperature of 20±1°C with a direct current of a current density of 2 A/dm² and a voltage of 50 – 150 V for 60 minutes to obtain colored oxide coatings having a color tone ranging from yellowish green to greyish yellow as shown in Table 6.

Table 6

Composition of electrolytic bath (% by weight) Oxalic acid	Ammonium dichromate	Voltage (V)	Thickness of coating (μ)	Color tone*
1	0.05	80–130	30	3.5 GY 5.7/1.6
	0.1	125–135	30	8.2 GY 5.6/1.1
	0.3	70–80	28	6.9 BG 5.6/1.6
	0.5	60–75	27	0.2 B 5.2/1.8
	0.05	50–80	29	8.6 Y 5.6/2.7
3	0.3	50–80	29	0.1 GY 5.4/2.4
	0.7	50–135	30	2.9 GY 5.8/1.7
	1.5	100–150	31	1.0 GY 6.1/10.9
	0.05	45–60	28	7.0 Y 5.9/3.2
	0.3	45–60	28	7.4 Y 5.9/2.5
10	0.7	50–60	28	7.1 Y 5.8/3.1
	1.5	50–85	29	9.1 Y 5.4/2.5
	3.0	80–135	31	4.6 GY 5.7/1.9

* Munsell notation

Example 7

The same aluminous material as used in Example 1 was pretreated in the same manner as described in Example 1. The pretreated material was anodized as an anode in an electrolytic bath of an aqueous solution containing oxalic acid and manganese acetate as shown in the following Table 7 at a temperature of 20±1°C with a direct current of a current density of 2 A/dm² and a voltage of 45 – 130 V for 60 minutes to obtain colored oxide coatings having a color tone ranging from yellow to dark yellowish green as shown in Table 7.

Table 7

Composition of electrolytic bath (% by weight) Oxalic acid	Manganese acetate	Voltage (V)	Thickness of coating (μ)	Color tone*
1	0.05	80–120	29	5.7 Y 5.5/1.7
	0.1	80–115	30	2.4 GY 5.7/1.8
	0.3	85–130	30	4.4 GY 5.5/1.9
3	0.05	60–75	29	7.3 Y 5.8/2.7
	0.1	60–80	29	7.7 Y 5.7/2.7
	0.3	100–130	31	8.8 Y 5.7/2.7
	0.5	110–130	31	5.1 GY 5.5/1.6
	0.7	130 (constant)	32	5.4 GY 5.4/1.2
	1.0	do.	32	5.2 GY 5.6/0.6
5	0.05	50–60	28	7.2 Y 5.7/3.1
	0.7	50–65	28	8.2 Y 5.6/2.9
10	0.05	45–55	27	7.1 Y 5.9/3.1
	0.7	50–60	28	3.6 Y 5.6/3.2

*Munsell notation

Example 8

The same aluminous material as used in Example 1 was pretreated in the same manner as described in Example 1. The pretreated material was anodized as an anode in an electrolytic bath of an aqueous solution containing oxalic acid and chromium acetate as shown in the following Table 8 under the same condition and procedure as described in Example 1 to obtain colored oxide coatings having a color tone ranging from yellow to dark yellowish green as shown in Table 8.

Table 8

Composition of electrolytic bath (% by weight)		Voltage (V)	Thickness of coating (μ)	Color tone*
Oxalic acid	Chromium acetate			
1	0.05	75–130	31	4.3 GY 5.6/1.8
	0.05	60–80	30	8.8 Y 5.6/2.6
	0.1	60–80	30	9.0 Y 5.6/2.6
3	0.3	60–80	30	8.5 Y 5.6/2.7
	0.5	65–110	31	1.0 GY 5.2/2.4
	1.0	65–105	31	10 Y 5.4/2.5
5	0.05	55–70	28	5.1 GY 5.6/2.7
7.5	0.05	50–60	28	5.6 Y 5.9/3.1
10.0	0.05	45–55	27	7.2 Y 5.8/3.1

* Munsell notation

Example 9

The same aluminous material as used in Example 1 was pretreated in the same manner as described in Example 1. The pretreated material was anodized as an anode in an electrolytic bath of an aqueous solution containing oxalic acid and ferric nitrate as shown in the following Table 9 at a temperature of 20±1°C with a direct current of a current density of 2 A/dm² and a voltage of 45 – 110 V for 60 minutes to obtain colored oxide coatings showing greyish yellow as shown in Table 9.

Table 9

Composition of electrolytic bath (% by weight)		Voltage (V)	Thickness of coating (μ)	Color tone*
Oxalic acid	Ferric nitrate			
1	0.05	70–110	28	6.4 GY 5.7/1.7
3	0.05	55–75	30	1.0 GY 5.7/2.4
	0.1	60–80	29	2.6 GY 5.5/2.1
5	0.3	55–65	30	3.4 GY 5.6/1.8
	0.5	65–65	30	3.4 GY 5.6/1.8
	0.5	65–75	31	0.2 G 4.9/1.5
7.5	0.5	45–55	31	2.5 GY 5.9/1.9
10.0	0.75	45–50	29	2.5 GY 5.8/1.9

* Munsell notation

Example 10

The same aluminous material as used in Example 1 was pretreated in the same manner as described in Example 1. The pretreated material was anodized as an anode in an electrolytic bath of an aqueous solution containing oxalic acid and chromium nitrate as shown in the following Table 10 at a temperature of 22±1°C with a direct current of a current density of 2 A/dm² and a voltage of 45 – 110 V for 60 minutes to obtain colored oxide coatings showing greyish and yellowish green as shown in Table 10.

Table 10

Composition of electrolytic bath (% by weight)		Voltage (V)	Thickness of coating (μ)	Color tone*
Oxalic acid	Chromium nitrate			
1	0.05	70–110	29	6.7 GY 5.7/1.8
3	0.05	60–75	29	1.9 GY 5.6/2.1
	0.10	60–80	30	5.0 GY 5.6/2.6
5	0.30	50–60	28	2.0 GY 5.9/2.3
10	0.50	45–50	28	1.2 GY 6.2/2.1
	0.75	45–50	29	1.0 GY 6.2/2.1

* Munsell notation

As described above, in the method of the present invention, an aluminous material which has been previously degreased and washed with water is anodized in an electrolytic aqueous bath containing oxalic acid and a metal salt to obtain a colored oxide coating. Therefore, the method of the present invention has the following merits.

1. Electrolyte is inexpensive.
2. High technique is not required.
3. Efficiency is high.
4. Oxide coatings having a broad range of color tone from yellow to brown can be obtained.

That is, the above merit (1) is that the electrolytic bath is composed of usual chemicals and therefore the cost is inexpensive, and the above merit (2) is that satisfactorily colored oxide coatings can be easily obtained by using an electrolytic bath maintained at room temperature, and therefore the bath can be easily controlled. Accordingly, in the method of the present invention, aluminous materials can be treated in the same manner as in the case of conventional anodic oxidation process. Moreover, the oxidized coating obtained by the method of the present invention is excellent in the corrosion resistance, abrasion resistance and weather resistance.

What is claimed is:

1. A method of producing colored oxide coatings ranging from yellow to brown on aluminum or aluminum alloy, which consists essentially of electrolytically anodizing with direct current, an aluminum material selected from the group consisting of aluminum and an alloy thereof in an aqueous solution of 0.5 – 10.0 percent by weight of oxalic acid and 0.05 – 4.0 percent by weight of a salt selected from the group consisting of ammonium phosphate, ammonium dichromate, a metal acetate and a metal nitrate at a temperature of between 0° and 50°C; a voltage of between 5–160 volts, a current density of between 0.05 – 5 A/dm², and for a time of between 10–120 minutes.

2. A method as claimed in claim **1**, wherein said acetate is selected from the group consisting of manganese acetate and chromium acetate.

3. A method as claimed in claim **1**, wherein said metal nitrate is selected from the group consisting of ferric nitrate and chromium nitrate.

4. A method of producing colored oxide coatings ranging from yellow to brown on aluminum or aluminum alloy, which consists essentially of electrolytically anodizing with direct current, an aluminum material selected from the group consisting of aluminum and an alloy thereof in an aqueous solution of 0.5 – 10.0 percent by weight of oxalic acid and 0.05 – 4.0 percent by

weight of a salt selected from the group consisting of ammonium phosphate, ammonium dichromate, manganese acetate, chromium acetate, ferric nitrate and chromium nitrate at a temperature of between 0° and 50°C; a voltage of between 5–160 volts, a current density of between 0.05 – 5 A/dm², and for a time of between 10–120 minutes.

5. A method as claimed in claim **4,** wherein the amount of said ammonium salt is 0.05 – 4.0 percent by weight.

6. A method as claimed in claim **1,** wherein the amount of said acetate is 0.05 – 1.5 percent by weight.

7. A method as claimed in claim **4,** wherein the amount of said metal nitrate is 0.05 – 0.7 percent by weight.

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