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[54] PROCESS FOR COLORING ALUMINUM OR ALUMINUM ALLOYS BY ANODIZING WITH IMPERFECTLY RECTIFIED CURRENT

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[58] **Field of Search** .... 204/58, 35 N, 38 A

[56] **References Cited**

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[57] **ABSTRACT**

Aluminum or aluminum alloys are colored by anodizing the aluminum or aluminum alloys in a sulfuric acid electrolytic solution containing oxyacid anion and/or metal salt by imperfectly rectified current.

6 Claims, No Drawings

PROCESS FOR COLORING ALUMINUM OR ALUMINUM ALLOYS BY ANODIZING WITH IMPERFECTLY RECTIFIED CURRENT

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for coloring aluminum or aluminum alloys by anodizing by imperfectly rectified current to form a colored film.

2. Description of the Prior Art

Heretofore, there have been used various methods for coloring aluminum or aluminum alloys by anodizing with imperfectly rectified current to form a colored film.

(1) According to Japanese Patent Publication No. 9805/1969, aluminum or aluminum alloys are anodized to form a film and the resulting film is colored with an organic dye or inorganic coloring materials. (2) Japanese Patent Publication Nos. 14053/1967, 12566/1969 and 19842/1971 and "Studies on coloring of aluminum for architectural purposes using inorganic matierials," published by Aluminum Kenchiku Yohin Hyomen Shori Gijutsu Kenkyu Kumiai, Mar. 1, 1972 disclose a coloring process comprising adding various materials to an electrolytic solution and anodizing by AC, DC or a superimposed AC on DC, a so called "one step electrolytic process." (3) Japanese Patent Publication No. 1715/1963, "electrolytic coloring of an aluminum anodized film" in "Denki Kagaku," Vol. 3, p. 20, 1935, and "Study on Electrolytic coloring method" read before the 44th Meeting of Kinzoku Hyomen Gijutsu Kyokai, 1971 discloses a so called "two step electrolytic method" comprising producing an anodized oxide film on aluminum or aluminum alloy according to conventional procedure in the first step and subjecting the anodized article to AC or DC electrolysis by dipping the aluminum or aluminum alloy thus anodized in a solution of a metal salt where the aluminum of aluminum alloy is used as one electrode.

Among the above mentioned known methods, the method in item (1) above necessitates two vessels, i.e. an electrolytic vessel and a coloring vessel for soaking in a separate coloring bath. The two step electrolytic method in item (3) above necessitates two electrolytic vessels so that the operation is complicated. The method in item (2) above gives a monotonous color tone, and can not give varied color. Furthermore, the process of superimposed alternating current on direct current necessitates AC source, DC source and a rectifier-transformer.

SUMMARY OF THE INVENTION

According to the present invention, there is provided a process for coloring aluminum or aluminum alloys which comprises anodizing the article of aluminum or alloy of aluminum in a sulfuric acid electrolytic solution containing at least one ingridient selected from the group consisting of oxyacid anion and metal salt by imperfectly rectified current.

An object of this invention is to provide a novel coloring process capable of producing commercially excellent colored anodized film easily.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A method of imperfectly rectifying current employed in this invention is that the rectifying is effected imperfectly by by-passing a part of the current by using a resistance upon rectifying single phase or three phase alternating current. This method is much more simple than the conventional process of superimposed alternating current on direct current the apparatus point of view. Further, current obtained by the method of imperfectly rectifying current has a negative component and a positive component which have the same cycle and thereby there can be produced uniform colored anodized film.

According to the present invention, coloring is conducted in such a manner as shown below. While the oxyacid anion and/or metal salt added to the sulfuric acid electrolytic solution produced an anodized film on the aluminum or aluminum alloy article by imperfectly rectified current, S^{2-} ion or negative ion components formed by decomposition of sulfuric acid in the electrolytic solution combines with the positive ion components formed by decomposition of oxyacid anion and/or metal salt to produce a sulfur compound, a coloring component, in the oxide film layer. Since such coloring component is formed in the anodized film, a highly weatherproof colored film of excellent color can be easily obtained.

Examples of the oxyacid ions which may be added to the sulfuric acid electrolytic solution are SeO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, TeO_4^{2-}, CrO_7^{2-}, AsO_3^{3-}, AsO_4^{3-}, and VO_4^{3-}.

Representative metal salts include sulfates, nitrates, phosphates, sulfamates, borates, chromates, dichromates, chlorides, silicates and organic acid salts such as oxalates, malonates, tartarates, succinates and the like of nickel cobalt, tin, copper, lead, titanium, cadmium, iron, molybdenum, zirconium and manganese. Preferable metal salts are sulfates of nickel, cobalt, tin, copper, lead, titanium and cadmium.

The amount of the oxyacid anion and/or metal salt to be added depends upon the type of oxyacid and metal salt. In general, the amount is determined by taking into consideration solubility in the sulfuric acid electrolytic solution, coloring property and economy, and usually ranges from about 0.1 to 200 g./l., preferred with from about 1 to 100 g./l. However, when the solubility in the electrolytic solution is too low, the coloring disadvantageously lowered.

The ratio of positive component to negative component in the imperfectly rectified current is at least 2:1. Preferably such ratio is 2-20:1. For the purpose of adjusting the ratio to this range, the current density of the positive component is 0.5 – 6.0 A/dm^2, with 1.0 – 3.0 A/dm^2 preferred and that of the negative component is 0.05 – 6.0 A/dm^2, with 0.1 – 3.0 A/dm^2 preferred.

When the current density of the positive component is lower than the above mentioned range, the anodized film is formed with difficulty and decomposition of the oxyacid and decomposition of sulfuric acid to S^{2-} are very poor, and thereby coloring, weatherproof property and fastness are deteriorated. On the contrary, when the current density of positive component is higher than the above mentioned range, formation of film is very good, but there are disadvantages such as powdery oxide film, burning, and interference fringe.

When the current density of negative component is lower than the above mentioned range, decomposition and deposition of the metal is poor. When that is higher than the above mentioned range, there can not be obtained uniform coloring.

The following Examples are given for illustrating the present invention, but should not be construed as restricting the present invention.

EXAMPLE 1

An aluminum plate, A 1050 P-H 24, 60 × 40 × 1 mm. was soaked in a 5 percent caustic soda bath at 70°C for 10 seconds to degrease it. It was washed with water, and then soaked in a 30 percent nitric acid bath to neutralize the caustic and washed again with water sufficiently.

The aluminum plate thus treated was subjected to electrolysis in an electrolytic bath having the following composition (aqueous solution) at a bath temperature of 20°C.

Sulfuric acid	100 g./l.
Stannous sulfate	10 g./l.

The electrolysis was effected by using a carbon plate as one electrode with imperfectly rectified current, i.e. wherein the positive component has a current density of 2.0 A/dm² and the negative component has a current density of 0.2 A/dm², for 30 minutes to produce a film of bronze color.

The colored film was treated with boiling water to seal.

EXAMPLE 2

An aluminum plate treated in a way similar to Example 1 above was subjected to electrolysis in an electrolytic bath having the following composition at a bath temperature of 20°C.

Sulfuric acid	100 g./l.
Copper sulfate	10 g./l.

The electrolysis was conducted by using a carbon plate as one electrode with imperfectly rectified current, i.e. wherein the of positive component has the current density of 2.0 A/dm² and the negative component has a current density of 0.1 A/dm², for 30 minutes to produce a brown film. The resulting colored film was treated with boiling water to seal.

EXAMPLE 3

An aluminum plate treated in a way similar to Example 1 above was subjected to electrolysis in an electrolytic bath having the following composition at a bath temperature of 20°C.

Sulfuric acid	200 g./l.
Selenic acid	5 g./l.

The electrolysis was effected by using a carbon plate as one electrode with imperfectly rectified current, i.e. wherein the positive component has a current density of 3.0 A/dm² and the negative component has a current density of 0.2 A/dm², for 40 minutes to produce a deep orange film. The resulting colored film was treated with boiling water to seal.

EXAMPLE 4

An aluminum plate treated in a way similar to Example 1 above was subjected to electrolysis in an electrolytic bath having the following composition at a bath temperature of 25°C.

Sulfuric acid	200 g./l.
Sodium stannate	100 g./l.

The electrolysis was conducted by using a carbon plate as one electrode with imperfectly rectified current, i.e. wherein the positive component has a current density of 3.0 A/dm² and the negative component has a current density of 1.2 A/dm², for 30 minutes to produce a grayish film. The resulting colored film was treated with boiling water to seal.

EXAMPLE 5

An aluminum plate treated in a way similar to Example 1 was subjected to electrolysis in an electrolytic bath having the following composition at a bath temperature of 25°C.

Sulfuric acid	220 g./l.
Sodium tungstate	1 g./l.

The electrolysis was conducted by using a carbon plate as one electrode with imperfectly rectified current, i.e. wherein the positive component has a current density of 3.0 A/dm² and the negative component has a current density of 1.4 A/dm², for 20 minutes to form a grayish film.

The resulting film was treated with boiling water to seal.

EXAMPLE 6

An aluminum plate treated in a way similar to Example 1 was subjected to electrolysis in an electrolytic bath having the following composition at a bath temperature of 20°C.

Sulfuric acid	100 g./l.
Stannous sulfate	10 g./l.
Selenic acid	5 g./l.

The electrolysis was conducted by using a carbon plate as one electrode with imperfectly rectified current, i.e., wherein the positive component has a current density of 2.5 A/dm² and the negative component has a current density of 0.2 A/dm², for 30 minutes to produce a film of bronz color. The resulting colored film was treated with boiling water to seal.

EXAMPLE 7

An aluminum plate treated in a way similar to Example 1 was subjected to electrolysis in an electrolytic bath having the following composition at a bath temperature of 20°C.

Sulfuric acid	100 g./l.
Sodium tungstate	10 g./l.
Selenic acid	5 g./l.

The electrolysis was effected by using a carbon plate as one electrode with imperfectly rectified current, i.e. wherein positive component has a current density of 3.0 A/dm^2 and the negative component has a current density of 0.3 A/dm^2, for 30 minutes to produce a grayish orange film. The resulting colored film was treated with boiling water to seal.

It is believed that the advantages and improved results furnished by the invention will be apparent from the foregoing description. Various modifications and changes may be made without departing from the spirit and scope of the invention as sought to be defined in the following claims.

I claim:

1. A process for coloring an article of aluminum or alloys of aluminum comprising anodizing the article in a sulfuric acid electrolytic solution containing at least one ingredient selected from the group consisting of SeO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, TeO_4^{2-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, AsO_3^{3-}, AsO_4^{3-}, VO_4^{3-}, sulfates, nitrates, phosphates, sulfamates, borates, chromates, dichromates, chlorides, silicates, oxalates, malonates, tartarates, and succinates of nickel, cobalt, tin, copper, lead, titanium, cadmium, iron, molybdenum, zirconium and manganese by subjecting the article to imperfectly rectified current having a ratio of positive component to negative component of at least 2:1, the current density of the positive component being approximately 0.5 to 6.0 A/dm^2 and that of the negative component being approximately 0.05 to 6.0 A/dm^2, the amount of the ingredient in the sulfuric acid electrolytic solution being approximately 0.1 to 200 g./l.

2. A process according to claim **1** wherein the ingredient contained in the sulfuric acid electrolytic solution is selected from the group consisting of a sulfate of nickel, cobalt, tin, copper, lead, titanium and cadmium.

3. A process according to claim **1** wherein the amount of the ingredient in the sulfuric acid electrolytic solution is approximately 1 to 100 g./l.

4. A process according to claim **1** wherein the current density of the positive component is approximately 1.0 to 3.0 A/dm^2 and that of the negative component is approximately 0.1 to 3.0 A/dm^2.

5. A process according to claim **1** wherein the ratio of positive component to negative component is approximately 2–20:1.

6. A process according to claim **5** wherein the ingredient contained in the sulfuric acid electrolytic solution is selected from the group consisting of a sulfate of nickel, cobalt, tin, copper, lead, titanium and cadmium; wherein the amount of the ingredient in the sulfuric acid electrolytic solution is approximately 1 to 100 g./l.; and wherein the current density of the positive component is approximately 1.0 to 3.0 A/dm^2 and that of the negative component is approximately 0.1 to 3.0 A/dm^2.

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