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COLORING AN OXIDIZED COATING ON ALUMINUM AND ITS ALLOYS

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ABSTRACT OF THE DISCLOSURE

Coloring of anodic oxide film on aluminum and aluminum alloys is accomplished by direct current electrolysis in an electrolyte containing an acid or metal salt, using the aluminum article as cathode.

The present invention relates to a novel method for coloring anodic oxide film on aluminum and aluminum alloy articles, and more particularly to a method for obtaining colored film by direct current electrolysis on aluminum or aluminum alloy (hereinafter referred to simply as aluminum) articles disposed and arranged as the cathode, which has been subjected to anodizing by the ordinary method.

As the methods of coloring anodic oxide film on aluminum articles, there are the dyeing method in which the oxide film is dyed with dye or pigment, and the integral color anodizing. The dyeing with dye provides clear colored film with a variety of shades, but the film has a great disadvantage of poor resistance to weathering. Also, the film colored with pigment has disadvantages of being limited in colors, and, in addition requiring a particular skill in its preparation. The colored film on the aluminum articles produced by the integral color anodizing is tough and highly resistant to weathering, because of which it is accepted as one of the most suitable materials for use in the exterior of buildings. This method, however, requires much electric power and consequently is of high cost.

This invention is characterized in that an aluminum article having been subjected to anodizing in an electrolyte containing an organic or inorganic acid is colored by direct current electrolysis in an aqueous solution containing acids or metal salts with the aluminum article being disposed and arranged as the cathode.

In this invention, anodizing is intended to form anodic film on the surface of aluminum articles, and the acid used in this method is not specifically limited, but usually sulfuric acid is used. The film thus formed is preferably colorless or pale-colored, although appreciably deep-colored ones can be changed in color according to the method of this invention.

The treatment for coloring an aluminum article having been provided with anodic oxide film thereon is performed by direct current electrolysis while the aluminum article is disposed and arranged as the cathode in an aqueous solution containing one or more acids or metal salts as the electrolyte.

The acids or water-soluble metal salts used in the method of this invention can include, for example, acids or water-soluble salts of Ag, As, Ca, Cd, Cu, Co, Fe, Se, Sn, Zn, Mn, Mo, Mg, Ni, Pb, V, Ti, etc.

The duration of time required for electrolysis varies depending on the composition of the aluminum articles and of the electrolyte, but usually a period of several tens of seconds to several minutes is sufficient for coloration. A longer duration of electrolysis gives deeper colors.

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The voltage used for electrolysis varies depending on the composition of the electrolyte and the thickness of the film. The temperature of the electrolyte exerts no substantial effect on the coloring, and thus room temperature is available.

The advantages according to the method of this invention can be enumerated as follows:

(1) Coloration can be achieved in a much shorter time in comparison with the conventional integral color anodizing.

(2) The method of this invention not only permits change in colors depending on the composition of the electrolyte, but also it permits change in colors depending on the composition of the aluminum material to be treated, thus enabling aluminum articles to obtain a very wide range of colors. Table 1 gives some examples of the color changes of aluminum alloys when treated in an electrolyte containing nickel sulfate as the metal salt.

TABLE 1

Shape	Nominal composition of the material	Color
Extrusions.....	Al-4Cu-0.5Mn-0.5Mg.....	Pure black.
Do.....	Al-1.2Mn.....	Brown.
Do.....	Al-2.5Mg-0.25Cr.....	Yellowish brown.
Do.....	Al-0.4Si-0.7Mg.....	Brown.
Do.....	Al-1.6Cu-2.5Mg-0.3Cr-5.6Zn.....	Pure black.
Castings.....	Al-4.5Mg.....	Deep brown.
Do.....	Al-9Si-0.5Mg-0.5Mn.....	Grayish green.

(3) Because of lower electrolytic voltage, no special additional equipment is required for the power source, cooling apparatus for the electrolyte, etc., and thus an ordinary apparatus used for sulfuric acid anodizing is available.

(4) Not only sheets, plates and extrusions but also various castings can be colored.

(5) The method of coloring aluminum according to this invention has no effect on the thickness of the film formed by anodizing, while it is frequently effective in elevating the hardness of the film, thus improving the toughness, particularly the abrasion resistance thereof.

(6) The coloring operation is easy to perform and the reproducibility of color is excellent.

In the following the method of the invention is illustrated more in detail by examples, but the invention is not limited thereto.

EXAMPLE 1

An aluminum plate (purity: 99.2%) was immersed in a 10% (by weight) sodium hydroxide solution at 70° C. for two minutes, and was then neutralized and rinsed in water according to the usual method. The plate was then subjected to direct current anodizing at a current density of 1.5 a./dm.² in a 15% (by weight) aqueous sulfuric acid solution at 20±0° C. for 40 minutes. The resulting anodized plate was set up as the cathode in a solution comprising 50 g./l. of nickel sulfate, 25 g./l. of ammonium chloride and 25 g./l. of boric acid, with a carbon plate as the anode, and was subjected to direct current electrolysis at a current density of 2.0 a./dm.² for 30 seconds at an electrolyte temperature of 20±1° C. The voltage during the electrolysis varied from 10 to 12 v. After being subjected to the ordinary sealing treatment, the resulting plate had a film of brown color whose thickness and Vickers hardness number (Hv) was found to be 18μ and Hv: 480 respectively. The film before coloration was colorless and transparent, and had a thickness and hardness of 18μ and Hv: 310 respectively.

EXAMPLE 2

An aluminum extrusion (Al-0.7Mg-0.4Si) was subjected to preparation similar to that of Example 1 and then to direct current electrolysis at a current density of 1.5 a./dm.² in a 15% aqueous sulfuric acid solution at 20±1° C. for 20 minutes.

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The resulting anodized extrusion was set up as the cathode in a solution comprising 50 g./l. of nickel sulfate, 2 g./l. of ammonium chloride and 30 g./l. of boric acid, with a carbon plate as the anode, and was subjected to direct current electrolysis at a current density of 0.7 a./dm.² for one minute at a temperature of 20°±1° C.

The color of the film was yellowish brown. The cell voltage during this treatment varied from 41 to 48 v.

EXAMPLE 3

An aluminum plate (purity: 99.2%) was subjected to preparations under the same conditions as in Example 1 and was then anodized in a 15% aqueous sulfuric acid solution under the same conditions as in Example 2.

The anodized plate was set up as cathode in an aqueous solution containing 50 g./l. of nickel sulfate and 30 g./l. of boric acid, with a carbon plate as the anode and was subjected to direct current electrolysis at a current density of 0.2 a./dm.² for 3 minutes at 20°±1° C. The variation of the cell voltage during this treatment was within the range of 11 to 14 v. The color of the film was deep brown.

EXAMPLE 4

An aluminum plate (purity: 99.2%) was subjected to pretreatments similar to that of Example 1 and then to direct current electrolysis at a current density of 2.0 a./dm.² in an aqueous electrolyte containing 10% naphthalenedisulfonic acid and 1% sulfuric acid at 20°±1° C. for 40 minutes. The plate was then set up as the cathode, and treatment was performed under the same electrolytic conditions and using the same composition of the electrolyte as in Example 1. The surface film of the sample became brown. The variation of the voltage during the treatment was within the range of 11 to 13 v.

EXAMPLE 5

An aluminum plate (purity: 99.2%) was prepared under the same conditions as in Example 1. The plate was then subjected to direct current electrolysis in a 15% aqueous sulfuric acid solution at 20°±1° C. at a current density of 5.0 a./dm.² for 15 minutes. The anodized sample was disposed and arranged as the cathode in an aqueous solution comprising 50 g./l. of nickel chloride, 25 g./l. of ammonium chloride and 15 g./l. of boric acid to undergo direct current electrolysis at 15 v. for 30 seconds. The surface film of the sample was colored deep brown.

EXAMPLE 6

An aluminum plate (purity: 99.2%) which had undergone sulfuric acid anodizing as in Example 1 was set up as the cathode in an aqueous solution containing 60 g./l. of cobalt acetate, 10 g./l. of boric acid and 10 g./l. of ammonium acetate. The plate then underwent direct current electrolysis under the same conditions as in Example 1. The surface film of the plate was colored pale brown. The variation in the voltage during the coloration treatment was 9 to 10 v.

EXAMPLE 7

An aluminum alloy plate (Al-4.0Cu-0.5Mn-0.5Mg) which had undergone sulfuric acid anodizing as in Example 1 was set up as the cathode, with a carbon plate as the anode, in an aqueous solution containing 2.5% selenic acid to undergo direct current electrolysis at a current density of 2.5 a./dm.² at a temperature of 20°±1° C. for two minutes. The surface film of the sample plate was colored clear reddish orange. The voltage during the treatment was kept at a constant value of 4 v.

EXAMPLE 8

An aluminum plate (purity: 99.2%) which had undergone sulfuric acid anodizing as in Example 1 was set up as the cathode, with a carbon plate as the anode, in a solution comprising 100 g./l. of chromic acid and 10 g./l. of sulfuric acid, and was subjected to direct current elec-

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trolysis at a current density of 2.0 a./dm.² at 20°±1° C. for two minutes. The surface film of the sample was colored yellowish brown. The voltage during the coloration treatment was maintained constant at 7 v.

EXAMPLE 9

An aluminum alloy extrusion (Al-0.7Mg-0.4Si) which had undergone sulfuric acid anodizing as in Example 1 was set up as the cathode, with a carbon plate as the anode, in an aqueous solution comprising 25 g./l. of cobalt sulfate and 25 g./l. of boric acid, and was subjected to direct current electrolysis at a current density of 0.5 a./dm.² at 20°±1° C. for one minute. The surface film of the sample was found to be golden. The variation of voltage during the treatment was from 12 to 6 v.

EXAMPLE 10

An aluminum alloy extrusion (Al-0.7Mg-0.4Si) which had undergone sulfuric acid anodizing as in Example 1 was set up as the cathode, with a carbon plate as the anode, in an aqueous solution comprising 35 g./l. of cobalt sulfate, 15 g./l. of nickel sulfate and 25 g./l. of boric acid, and was subjected to direct current electrolysis at a current density of 0.5 a./dm.² at 20°±1° C. for two minutes. The surface film of the sample was found to be blackish brown. The variation of voltage during the treatment was from 11 to 7 v.

In the following Table 2, there are listed some of the resulting colors obtained by certain combinations of metal salts used in the treatment with compositions of the materials treated.

TABLE 2

Metal salt added in the electrolyte	Composition of the material treated	Color of the film
Cupric sulfate.....	99.0% Al.....	Reddish brown.
Cobalt sulfate.....	99.0% Al.....	Brown.
Manganese sulfate.....	99.0% Al.....	Grayish white.
Ferrous sulfate.....	99.0% Al.....	Yellow.
Chromic sulfate.....	Al-4.0Cu-0.5Mn-0.5Mg.	Pale green.
Silver nitrate.....	99.0% Al.....	Yellowish brown.
Chromic nitrate.....	99.0% Al.....	Pale green.
Lead acetate.....	99.0% Al.....	Grayish brown.
Nickel acetate.....	Al-4.0Cu-0.5Mn-0.5Mg.	Black.
Zinc acetate.....	99.0% Al.....	Pale yellowish brown.
Magnesium sulfate.....	99.0% Al.....	Yellowish brown.
Cadmium acetate.....	99.0% Al.....	Do.
Stannous chloride.....	99.0% Al.....	Blackish brown.

The colors of the films obtained in the above examples are not those of the nature derived from electrodeposition of metals produced by plating. Also, no change was observed in these colors even after atmospheric exposure for one year. According to the method of this invention, deep colored film with a variety of shades can be obtained at a lower voltage in the coloring process, because of which the electrolysis operation can be simplified. Furthermore, the method can provide excellent reproducibility of colors, i.e. by proper selection of the conditions of electrolysis and the composition of the electrolyte, products having no difference in color can be easily obtained.

The colored material obtained according to the method of this invention is of lower cost and more excellent in resistance to weathering. For this reason, a wide range of uses of this product is contemplated in exterior building materials as well as other structural materials.

What we claim is:

1. A method for forming and coloring an anodic oxide film on an aluminum or aluminum alloy article which comprises anodizing the article with direct current in an aqueous solution consisting essentially of water and sulfuric acid to produce an anodic oxide film thereon, coloring the anodized film by means of subjecting the anodized article, used as a cathode, to direct current electrolysis in an aqueous solution containing at least one water-soluble salt selected from the group consisting of nickel sulfate, nickel chloride, nickel acetate, cobalt acetate, cobalt sulfate, cupric sulfate, manganese sulfate, ferrous sulfate,

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chromic sulfate, chromic nitrate, silver nitrate, lead acetate, zinc acetate, magnesium sulfate, cadmium acetate and stannous chloride, or in an aqueous solution containing an acid selected from the group consisting of chromic acid and selenic acid, for a period of from 30 seconds to 3 minutes, and subjecting the resultant article to a sealing treatment.

2. The method according to claim 1, wherein the direct current electrolysis is carried out at room temperature.

3. The method according to claim 1, wherein anodizing is carried out in an aqueous solution containing 15% by weight of sulfuric acid for 40 minutes and the resultant anodized article is subjected to direct current electrolysis in an aqueous solution containing 50 g./l. of nickel sulfate, 25 g./l. of ammonium chloride and 25 g./l. of boric acid with a current density of 2.0 a./dm.² at a temperature of 20°±1° C.

4. The method according to claim 1, wherein the direct current electrolysis is carried out in an aqueous solution containing 50 g./l. of nickel sulfate, 2 g./l. of ammonium chloride and 30 g./l. of boric acid.

5. The method according to claim 1, wherein the direct current electrolysis is carried out in an aqueous solution containing 50 g./l. of nickel sulfate and 30 g./l. of boric acid.

6. The method according to claim 1, wherein the direct current electrolysis is carried out in an aqueous solution containing 50 g./l. of nickel chloride, 25 g./l. of ammonium chloride and 15 g./l. of boric acid.

7. The method according to claim 1, wherein the direct

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current electrolysis is carried out in an aqueous solution containing 60 g./l. of cobalt acetate, 10 g./l. of boric acid and 10 g./l. of ammonium acetate.

8. The method according to claim 1, wherein the direct current electrolysis is carried out in an aqueous solution containing 25 g./l. of cobalt sulfate and 25 g./l. of boric acid.

9. The method according to claim 1, wherein the direct current electrolysis is carried out in an aqueous solution containing 35 g./l. of cobalt sulfate, 15 g./l. of nickel sulfate and 25 g./l. of boric acid.

10. The method according to claim 1, wherein anodizing is carried out in an aqueous solution containing 15% by weight of sulfuric acid for 15 to 40 minutes.

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