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PATENT OFFICE

COMPLETE SPECIFICATION

Improvements in and relating to Coloring Aluminium Articles by Electrolytic Depositions of Colored Compounds

I TAHEI ASADA, Nishi Hirano, Mikagecho, Higashi Nada-ku, Kobe City, Japan, a Japanese National, do hereby declare the invention, for which I pray that a patent may be granted to me, 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 process for producing anticorrosive coloring coatings on aluminium and its alloys by an alternating current electrolytic method.

Various studies on inorganic coloring of aluminium by using metallic salts, such as nickel, cobalt, chromium, copper, cadmium, titanium, manganese, silver, gold and lead, have been continued for many years.

The coloring method are in general classified into two different processes, chemical and electrochemical.

However, it is well known that both these two methods are based on an electrical irreversible absorption between aluminium and the above-described metallic salt selected.

By employing the chemical method, defects occur such as that the coloring is very light and not homogeneous, because only one or more molecular layers of a metallic oxide or hydroxide are precipitated on the surface of aluminium, or that a specified coloring is not obtainable because of the accompanied interference of light.

By using electrochemical method, on the other hand, it is possible to obtain a layer of metallic salt with an increased thickness by introducing a metallic salt into the film of aluminium oxide, during the oxide treatment.

Thus electrical methods of Max Schenk D.R.P. 672,268 1939) and Alexander Jenny (D.P 562,615 1930, U.S.P. 1,923,539 1933) are put to practical use. The former is a process of producing a milky white coating on aluminium by passing direct current at a potential of 120 volts in a bath of borax solution which contains Ti, Zr or Th salts, and the latter a dark grey coating on aluminium by passing alternating current between two articles of aluminium.

It is well known that the resistance to corrosion of aluminium is greatly improved when coated with a colored coating. In such an instance the above-mentioned inorganic salts precipitate and plug the crevices of oxidised film on the aluminium surface.

According to the present invention there is provided a process for the production of colored protective coatings on articles of aluminium or an aluminium alloy, which comprises passing an alternating current through an aqueous bath containing a salt which yields a colored metal oxide or hydroxide between such an article having been previously oxidized in a prior operation and a carbon, carborundum or aluminium electrode.

The strong irreversible absorption of the added metallic cation on the aluminium surface is attributable to the fact that the aluminium oxide functions as a semiconductor and a condenser. Therefore, the present invention effects electrolytic oxidation of an aluminium surface (or an aluminium alloy surface) by using an acid liquor, such as, for example, sulphuric acid, oxalic acid, or chromic acid, as an electrolyte for 20 to 45 minutes to completely form a film of oxide. In other respects conventional electrolytic processes are employed.

Then, an alternating current (5—75V, 10—25 Amp/m^2) is supplied to the electrolyte comprising a solution of mineral acid or organic carboxylic acid (or salt thereof, pH 1—6.5) to which is added a small amount of the metals nickel, cobalt, chromium, copper, cadmium, vanadium, gold, silver iron or lead as the cation of a salt such as, a nitrate, sulphate, oxalate, acetate, citrate, or phosphate

[*Price 4s. 6d.*]

or as the anion of metallic oxyacids, such as, manganate, selenite, tellurite, permanganate using the aluminium which bears the oxide film as one electrode and carbon, carborundum or aluminium as the other electrode.

The inventor considers, in this case, the aluminium oxide layer to be an electrical condenser and so the surface of the aluminium, coated with its oxide layer, consists of two parts, i.e., a greater part electrically negative and a smaller part electrically positive.

In other words, the inventor considers the aluminium oxide layer to be an electrical condenser. When the particles in solution are attracted to the oxide layer, and are thereby deposited in the crevices of the oxidised film on the surface of the aluminium during the several minutes while generating hydrogen gas. This deposition of the metallic hydroxide or oxide on the aluminium causes various colors, the colors depending on the different metallic salts employed. In this process, when carborundum or aluminium is employed as an anode instead of the conventional carbon, brighter colorings of deposits are obtained on the surface of aluminium.

The above effects differ somewhat according to the electrodes selected, the degree of the coloring effect being expressed by the following

C>SiC>Al

When a carbon electrode is used as the other one, the deepest color is obtained. The inventor considers that the aluminium behaves as a semiconductor and a condenser in this coloring process.

The following examples are provided in order to illustrate the characteristic aspects of the present invention.

EXAMPLES:

(1) A sheet of aluminium (99.7—99.8%) is oxidised with direct current in a bath of aqueous, 10% ~~sulphuric~~ Sulphric acid at ordinary temperature. After 30—45 minutes' treatment, the sheet of uniformly oxide coated aluminium and a carbon electrode are connected to a source of alternating current in a bath of 1.5% ~~sulphuric~~ Sulphric acid which contains 0.15% silver nitrate (pH 1.0) at room temperature for 5 minutes at a potential of about 20 volts. After sealing in boiling water for about 30 minutes, a brown color (Ag_2O) is created.

(2) A sheet of aluminium (99.7—99.8%) is oxidised with direct current in a bath heated to 45—50° C of aqueous, 8% chromic acid. After 30—45 minutes' treatment the sheet of uniformly oxide coated aluminium and a carbon electrode are connected to a source of alternating current in a bath of 1.5% boric acid which contains 1.5% nickel sulphate (pH 5.8) at room temperature for 10 minutes at a potential of about 25 volts.

After sealing in boiling water for about 30 minutes, a black color (Ni_3O_4) is created.

(3) A sheet of aluminium (99.7—99.8%) is oxidised with direct current in a bath heated to 45—50° C of aqueous, 8% chromic acid. After 30—45 minutes' treatment, the sheet of uniformly oxide coated aluminium and a carbon electrode are connected to a source of alternating current in a bath of 1.5% boric acid which contains 1.5% cobalt sulphate (pH 5.8) at room temperature for 10 minutes at a potential of about 30 volts.

After sealing in boiling water for about 30 minutes, a blue-black color is created.

(4) A sheet of aluminium (99.7—99.8%) is oxidised with direct current in a bath containing 8% chromic acid at 45—50° C. After 30—45 minutes, treatment, the sheet of uniformly oxide coated aluminium and a carbon electrode are connected to a source of alternating current in a bath of 1.5% phosphoric acid which contains 1.3% cupric sulphate (pH 1.5) at room temperature for 8 minutes at a potential of about 30 volts.

After sealing in boiling water for about 30 minutes, a red-brown color (Cu_2O) is created.

(5) A sheet of aluminium (99.7—99.8%) is oxidised with direct current in a bath heated to 45—50° C of aqueous, 8% chromic acid. After 30—45 minutes' treatment, the sheet of uniformly oxide coated aluminium and a carborundum electrode are connected to a source of alternating current in a bath of 1.5% phosphoric acid which contains 1.3% cupric sulphate (pH 1.5) at room temperature for 2 minutes at a potential of about 50 volts.

After sealing in boiling water for about 30 minutes, a blue-green color ($Cu(OH)_2$) is created.

(6) Two sheets of uniformly oxide coated aluminium and a carbon electrode are connected to a source of alternating current in a bath of 1.5% phosphoric acid which contains 1.3% cupric sulphate (pH 1.5) at room temperature for 1.5 minutes at a potential of about 50 volts.

After sealing in boiling water for about 30 minutes, a blue color ($Cu(OH)_2$) is created.

(7) A sheet of aluminium (99.7—99.8%) is oxidised with direct current in a bath heated to 45—50° C of aqueous, 8% chromic acid. After 30—45 minutes' treatment, the sheet of uniformly oxide coated aluminium and a carbon electrode are connected to a source of alternating current in a bath of 1.5% ~~sulphuric~~ Sulphric acid which contains 0.15% sodium selenite (pH 1.1) at room temperature for 8 minutes at a potential of about 20 volts.

After sealing in boiling water for about 30 minutes, an orange color is created.

(8) A sheet of aluminium (99.7—99.8%) is oxidised with direct current in a bath heated to 45—50° C of aqueous, 8% chromic acid. After 30—45 minutes' treatment, the sheet of uniformly oxide coated aluminium and a

carbon electrode are connected to a source of alternating current in a bath 1.5% boric acid solution which contains 1.0% cadmium sulphate (pH 5.8) at room temperature for 10 minutes at a potential of about 30 volts.

After sealing in boiling water for about 30 minutes, a brown-black color (CdO) is created.

(9) A sheet of aluminium alloy (1—2% Mg.) is oxidised with direct current in a bath heated to 45—50° C of aqueous, 8% chromic acid.

After 30—45 minutes' treatment, the sheet of uniformly oxide coated aluminium and a carbon electrode are connected to a source of alternating current in a bath of 2% sulfamic acid solution which contains 1.5% lead acetate (pH 1.5) at room temperature for 10 minutes at a potential of 30 volts.

After sealing in boiling water for about 30 minutes, a grey-black (PbO) color is created.

(10) A sheet of aluminium is oxidised with direct current in a bath of aqueous, 10% sulphric acid at ordinary temperature.

After 40 minutes' treatment, the sheet of uniformly oxide coated aluminium and a carbon electrode are connected to a source of alternating current in a bath of 1.5% ~~sulphuric~~ sulphric acid which contains 0.15% potassium permanganate (pH 1.6) at room temperature for 8 minutes at a potential of about 20 volts.

After sealing in boiling water for about 30 minutes, a yellow-brown color is created.

(11) A sheet of aluminium is oxidised with direct current in a bath of aqueous, 10% ~~sulphuric~~ sulphric acid at ordinary temperature.

After 45 minutes' treatment, the sheet of uniformly oxide coated aluminium and a carbon electrode are connected to a source of alternating current in a bath of 2% ammonium-sulphate which contains 0.2% chrome alum (pH 5.7) at room temperature for 10 minutes at a potential of about 50 volts.

After sealing in boiling water for about 30 minutes, a green color is created.

(12) A sheet of aluminium is oxidised with direct current in a bath heated to 45—50° C of aqueous, 8% chromic acid.

After 30—45 minutes' treatment, the sheet of uniformly oxide coated aluminium and a carbon electrode are connected to a source of alternating current in a bath of 1.5% boric acid solution which contains 0.5% ferric sulphate (pH 5.8) at room temperature for 10 minutes at a potential of about 50 volts.

After sealing in boiling water for about 30 minutes, a grey-brown color is created.

(13) A sheet of aluminium (99.0 to 99.5%) is oxidised with a direct current in a bath of aqueous 15% sulphuric acid at room temperature. After 40 minutes' treatment, the sheet of uniformly oxide coated aluminium and a carbon electrode are connected to a source of alternating current in a bath of 1.5% sulphuric acid which contains 0.15% sodium selenite (pH 1.1) at room temperature for 10 minutes at a potential of about 20 volts.

After sealing in boiling water for about 30 minutes, a gold color is created.

(14) A sheet of aluminium (99.0 to 99.5%) is oxidised with a direct current in a bath of aqueous, 15% sulphuric acid at room temperature. After 40 minutes' treatment, the sheet of uniformly oxide coated aluminium and a carbon electrode are connected to a source of alternating current in a bath of 1.5% sulphuric acid which contains 0.15% sodium ~~telluride~~ tellurite (pH 1.1) at room temperature for 10 minutes at a potential of about 20 volts.

After sealing in boiling water for about 30 minutes, a dark gold color is created.

WHAT I CLAIM IS:—

1. A process for the production of colored protective coatings on articles of aluminium or an aluminium alloy, which comprises passing an alternating current through an aqueous bath containing a salt which yields a coloured metal oxide or hydroxide between such an article having been previously oxidised in a prior operation and a carbon, carborundum or an aluminium electrode.

2. A process as claimed in claim 1 in which the article of aluminium is one which has been previously oxidised with direct current in chromic, sulphric or sulfamic acid solution.

3. A process as claimed in claim 1 or 2 in which the aqueous bath contains an acid solution of a salt of nickel, cobalt, chromium, copper, silver, iron, lead, cadmium or a manganate, selenite or tellurite.

4. A process as claimed in any of the preceding claims in which the aqueous bath is maintained at room temperature.

5. A process as claimed in any of the preceding claims in which the alternating current is passed at a potential of 20 to 50 volts through the electrolytic bath.

6. A process as claimed in claim 5 in which the potential is 50 volts.

7. A process for the production of colored protective coatings substantially as hereinbefore described with reference to and as illustrated in any of the Examples.

8. An aluminium article when coated by the process as claimed in any of the preceding claims.

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