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IMPROVEMENTS IN OR RELATING TO ELECTROLYTIC BATH COMPOSITION FOR COLOUR ANODISING OF ALUMINIUM AND ITS ALLOYS.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rabindra Bhavan, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies (Act XXI of 1860).

This is an invention by BAIKUNJEE ANANTHA SHENOI, Scientist, KANDADAI RAJAGOPALACHARI NARASIMHAM, Scientist, VENKATESHVARASWAMI LAKSHMIMANARASIMHAM, Senior Scientific Assistant and THIRUMANAMCHERI SESHADRI KRISHNAN, Senior Laboratory Assistant, all are employed in Central Electrochemical Research Institute, Karaikudi-3, India, all Indian citizens.

PROVISIONAL

The following Specification describes the nature of this invention:

This invention relates to improvements in or relating to integral colour anodising of aluminium and its alloys.

Historically, it has been proposed to adopt the following electrolyte processes for producing coloured anodic films on aluminium alloys:

1. Dilute sulphuric acid at very low temperature near 0°C
2. 2-Sulphosalicilic acid-d-sulphuric acid or metallic sulphate
3. 4-Sulphophthalic acid-d-sulphuric acid
4. 5-Sulphosalicilic acid-d-sulphuric acid
5. 5-Sulphosalicylic acid-d-sulphuric acid-d-maleic acid
6. Anodizing process.

This is open to objection that the disadvantages present in the above processes are as follows:

1. The sulphuric acid process, the bath is operated at very low temperature and hence, the refrigerating cost will be high. Higher voltages are required to produce the anodic film and the colour of the film is determined by the thickness of the anodic coating.

2. Special electrolyte mixtures containing aromatic sulphonic acids are employed for producing coloured anodic films. In such processes, the organic electrolytes are costly, extremely sensitive to chloride contamination and build up aluminium much faster than oxalic acid bath. These acids require special plastic-lined vessels with stainless steel fittings. The intensity/depth of particular colour increases with increase in thickness of the anodic film and hence, certain light shades cannot be produced with thick coating. The organic acids are not available in India.

3. In the Anodizing process, the aluminium alloys are pre-anodised with direct current in chromic, sulphuric or sulphamic acid solution to produce the minimum thickness as specified for architectural purposes. Then the anodized samples are immersed in an aqueous bath of an acid solution containing sulphates of the following metals such as iron, nickel, cobalt, cadmium copper and an alternating current is passed through the bath to produce the coloured oxide coatings. While passing alternating current, the sulphur gets precipitated inside the oxide coatings and hence, such films have poor corrosion-resistance. The films do not have high abrasion resistance.

The object of this invention is to obviate these disadvantages by employing oxalic acid as anodizing electrolyte containing soluble salts of any one of metal-ions belonging to group IB, VIIIB or VIII of the periodic system, namely, copper, manganese, iron, cobalt and nickel to produce integrally coloured anodic coatings on various aluminium alloys.

To these ends, the invention broadly consists in anodising aluminium and its alloys in a bath containing oxalic acid and salt of the above said group. Generally, the patented electrolytes for integral colour anodising processes stress the presence of sulphate ion for producing the colour.

In this invention, we find that the presence of any one of the metal ions belong to the above said groups is responsible for producing colour of the oxide film. So, the addition of 0.1 to 2% w/v of salts of any one of the above said metals, as sulphate, carbonate, sulfamate or as complex to 2% to 5% of the oxalic acid bath gives the coloured oxide coating on aluminium and its alloys. Different colours such as straw yellow, light grey, brown, dark brown, dark grey and jet black are obtained when architectural alloys are anodized at the above bath. The colour of the oxide coating depends on the current density, duration of anodising and the composition of the alloy.

The addition of the same metal salts to patented baths such as oxalic-maleic acid mix or aromatic sulphonic acids, gives much deeper black colour than shades produced in the above patented electrolytes.

The aluminium alloys are first anodised in standard sulphuric acid bath for half-an-hour using conditions suitable for producing films of 50μ thickness as specified for architectural purposes. Then the alloys are again anodised in the bath containing oxalic acid and the metal salt mixture. The clear transparent oxide film produced by sulphuric acid anodising process is changed to light grey to dark black colour depending on the current density and the duration of anodising. Hence, different shades can be obtained even after having minimum thickness of 25μ as specified for architectural purposes.

The following typical examples are given to illustrate the invention:

Example 1

The D548M architectural alloy is degreased with trichloroethylene and then anodised in the following electrolyte:

- Oxalic acid diphotrate: 5% w/v
- Manganese sulphate: 0.1% w/v

The anodising is carried out at 20±2°C for one hour.

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using a current density of 12 asf. A light grey coloured smooth anodic film is produced.

Example II
The B15SwP alloy is degreased with trichloroethylene and anodised in the following electrolyte:
- Sulphuric acid: 10% w/v
- Current density: 16 asf
- Temperature: 20±2°C
- Duration of treatment: 40 minutes

The alloy is again anodised in the following electrolyte:
- Oxalic acid dihydrate: 5% w/v
- Manganese sulphate: 0.5% w/v
- Temperature: 20±2°C
- Current density: 24 asf
- Duration of treatment: 15 minutes

The clear transparent film produced in sulphuric acid anodising is changed to dark grey brown colour.

Example III
The 50 SW architectural alloys is degreased with trichloroethylene and then anodised in the following bath:
- Oxalic acid dihydrate: 5% w/v
- Manganese carbonate: 0.5% w/v

The alloy is anodised for one hour at 20±2°C using a current density of 24 asf.
A brown anodic film is produced.

Example IV
The B15SwP alloy is degreased with trichloroethylene and anodised in the following electrolyte:
- Oxalic acid dihydrate: 5% w/v
- Nickel sulphate: 0.5% w/v
- Temperature: 20±2°C
- Duration of treatment: 1 hour
- Current density: 24 asf

A brownish grey colour film is obtained.

Example V
The 50SW alloy is degreased with trichloroethylene and anodised in the following electrolyte:
- Oxalic acid dihydrate: 5% w/v
- Nickel carbonate: 0.5% w/v
- Temperature: 20±2°C
- Current density: 24 asf
- Duration of treatment: 1 hour

A cement grey colour film is produced.

Example VI
A 50SW alloy is degreased in trichloroethylene and anodised in the following electrolyte:
- Oxalic acid dihydrate: 5% w/v
- Copper carbonate: 0.5% w/v
- Temperature: 20±2°C
- Duration of treatment: 1 hour
- Current density: 24 asf

A dark brown coloured oxide film is produced.

The following are among the main advantages of the invention:
- The electrolyte employed in the present work namely the oxalic acid is very cheap in comparison with aromatic sulphonic acids. Aluminium build-up in the bath is slow. Hence, the ion exchange equipment is not required. This organic acid is readily available in India. For a given thickness of the coating, the abrasion resistance of the integrally coloured film produced in the bath is much greater than the film produced in sulphuric acid at 20 to 25°C.

Since we employ a single organic acid for anodising, control, maintenance and analysis of the bath are easy. The acid may be kept in lead lined tanks and hence, no special plant or fittings are necessary.

The process of first anodising in sulphuric acid manganese salt mix carries two advantages:

1. It is possible to get light shades with thicker film because the required film thickness is built in sulphuric acid anodising.
2. Since major portion of the anodising is carried out in sulphuric acid, the anodising cost is minimised.

Dated this 23rd day of June 1970

COMPLETE

The following specification particularly describes and accentuates the nature of this invention and the manner in which it is to be performed:

This invention relates to improvements in, or relating to, electrolytic bath composition for colour anodising of aluminium and its alloys. Henceforth it has been proposed to adopt the following electrolyte/procemdes for producing coloured anodic film on aluminium alloys:
- (1) Dilute sulphuric acid at very low temperature near 0°C
- (2) 5-Sulphoacrylic acid + Sulphuric acid or metallic sulphate
- (3) 4-Sulphoplastic acid + Sulphuric acid
- (4) 5-Sulphoacrylic acid + Sulphuric acid
- (5) 4-Sulphoacrylic acid + Sulphuric acid + Molybdenum acid

Anodol Process:
This is open to objection that the disadvantages present in the above processes are as follows:

1. In the sulphuric acid process, the bath is operated at very low temperature and hence, the refrigeration cost will be higher. Higher voltages are required to produce the anodic film and the colour of the film is determined by the thickness of the anodic coating.
2. Special electrolyte mixtures containing aromatic sulphonic acids are employed for producing coloured anodic films. In such processes, the organic electrolytes are costly, extremely sensitive to chloride contamination and build-up aluminium much faster than oxalic acid bath. These acids require special plastic-lined vessels with stainless steel fittings. The intensity/depth of particular colour increases with increase in thickness of the anodic film and hence, certain light shades cannot be produced with thick coating. The organic acids are not available in India.

(6)—In the Anodol Process, the aluminium alloys are pre-anodised with direct current in chromic, sulphuric or sulphamic acid solution to produce the minimum thickness as specified for architectural purposes. Then the anodised samples are immersed in an aqueous bath of an acid solution containing sulphates of the following metals such as iron, nickel, cobalt, cadmium, copper and an alternating current is passed through the bath to produce the coloured oxide coatings. Such films have poor corrosion-resistance and they do not have high abrasion resistance.

The object of this invention is to obviate these disadvantages by employing oxalic acid as anodising electrolyte containing soluble salts of any one of metals ions belonging...
to group IB, VIIIB or VII of the periodic system, namely, copper, manganese, iron, cobalt and nickel to produce integrally coloured anodic coatings on various aluminium alloys.

To these ends, the invention broadly consists in anodising aluminium and its alloys in a bath containing oxalic acid and salt of the above said group. Generally, the patented electrolytes for integral colour anodising processes stress the presence of sulphate ion for producing the colour. But, in this invention, we find that the presence of any one of the metal ions belong to the above said groups is responsible for producing colour of the oxide film. So, the addition of 0.1 to 2% w/v of salts of any one of the above said metals, as sulphate, carbonate, sulfamate or as complex to 2% to 9% of the oxalic acid bath gives the coloured oxide coating on aluminium and its alloys. Different colours such as straw yellow, light grey, brown, dark brown, grey and jet black are obtained when architectural alloys are anodised in the above bath. The colour of the oxide coating depends on the current density, duration of anodising and the composition of the alloy.

The addition of the same metal salts to patented baths such as oxalic-malic acid mix or aromatic sulphonic acids, gives much deeper black colour than shades produced in the above patented electrolytes.

In the integral colour anodising of architectural alloys, the depth of the shades depends upon the thickness of the oxide film and the end anodising voltage. In any single stage patented process light shades cannot be produced with 25 microm thick Oxide film as specified for architectural anodising process. To obviate the above disadvantage, we are recommending the following two-stage anodising process for producing light shades with desired film thickness.

The aluminium alloys are first anodised in standard sulphuric acid bath for half-an-hour using conditions suitable for producing films of 25a thickness as specified for architectural purposes. Then the alloys are again anodised in the bath containing oxalic acid and the metal salt mixture. The clear transparent oxide film produced by sulphuric acid anodising process is changed to light grey to dark black colour depending on the current density and the duration of anodising. Hence, different shades can be obtained even after having having thickness of 25a as specified for architectural purposes.

The following typical examples are given to illustrate the invention:

**Example 1**
The BS4SM architectural alloy is degreased with trichloroethylene and then anodised in the following electrolyte:

- Oxalic acid diborate: 5% w/v
- Manganese sulphate: 0.5% w/v

The anodising is carried out at 20±2°C for one hour using a current density of 12 a/sf. A light grey coloured smooth anodic film is produced.

**Example 2**
The BS155WP alloy is degreased with trichloroethylene and anodised in the following electrolytes:

- Sulfuric acid: 10% w/v
- Current density: 16 a/sf
- Temperature: 20±2°C
- Duration of treatment: 40 minutes

The alloy is again anodised in the following electrolyte:
- Oxalic acid diborate: 5% w/v
- Manganese sulphate: 0% w/v
- Temperature: 20±2°C
- Current density: 24 a/sf
- Duration of treatment: 15 minutes

The clear transparent film produced in sulphuric acid anodising is changed to dark grey brown colour.

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**Example 3**
The 50 SW architectural alloy is degreased with trichloroethylene and then anodised in the following bath:

- Oxalic acid diborate: 5% w/v
- Manganese carbonate: 0.5% w/v

The alloy is anodised for one hour at 20±2°C using a current density of 24 a/sf. A brown anodic film is produced.

**Example 4**
The BS155WP alloy is degreased with trichloroethylene and anodised in the following electrolyte:

- Oxalic acid diborate: 5% w/v
- Nickel sulphate: 0.5% w/v
- Temperature: 20±2°C
- Duration of treatment: 1 hour
- Current density: 24 a/sf

A brownish grey colour film is obtained.

**Example 5**
The 505 SW alloy is degreased with trichloroethylene and anodised in the following electrolyte:

- Oxalic acid diborate: 5% w/v
- Nickel carbonate: 0.5% w/v
- Temperature: 20±2°C
- Current density: 36 a/sf
- Duration of treatment: 1 hour

A cement grey colour film is produced.

**Example 6**
A 505 SW alloy is degreased in trichloroethylene and anodised in the following electrolyte:

- Oxalic acid diborate: 5% w/v
- Copper carbonate: 0.5% w/v
- Temperature: 20±2°C
- Duration of treatment: 1 hour
- Current density: 36 a/sf

A dark brown coloured oxide film is produced.

**Example 7**
The super purity aluminium sheet degreased with trichloroethylene and then anodised in the following electrolyte:

- Oxalic acid diborate: 5% w/v
- Manganese sulphate: 0.5% w/v
- Temperature: 20±2°C
- Current density: 24 a/sf
- Duration of treatment: 45 minutes

A light yellow colour film is produced.

The following are among the main advantages of the invention:

The electrolyte employed in the present work, namely the oxalic acid is cheap in comparison with aromatic sulphonic acids. Aluminium build-up in the bath is slow. Hence, equipments using ion exchange resins for the purification of solution are not required. This organic acid is readily available in India. Further, the oxide film produced in oxalic acid electrolyte is known to possess higher abrasion resistance compared to the film produced in sulphuric acid at 20°C.

Since we employ a single organic acid for anodising, control, maintenance and analysis of the bath are easy. The
acid may be kept in leadlined tanks and hence, no special plant or fittings are necessary. The bath is also less sensitive to chloride ion contamination.

The process of anodising first in sulphuric acid followed by anodising in oxalic acid manganese salt mixture carries two advantages:

(1) It is possible to get light shades with thicker film because the required film thickness is built in sulphuric acid anodising.

(2) Since major portion of the anodising is carried out in sulphuric acid, the anodising cost is minimised.

Sd.

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