

Complete Specification No. 140537 dated 6th December 1974. Application and Provisional Specification No. 2050/Cal/1973 dated 6th September 1973. Acceptance of the complete specification advertised on 27th November 1976.

Index at acceptance—70C5 [LVIII(5)] 129G [XXXV]

International classification—B44c 1/00

### PROVISIONAL SPECIFICATION

“IMPROVEMENTS IN OR RELATING TO ELECTROLYTIC COLOURING OF ALUMINIUM AND ITS ALLOYS FOR DECORATIVE AND ARCHITECTURAL USES”

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJ MARG, NEW DELHI-11 INDIA.  
AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following specification describes the nature of this invention:—

This is an invention by BALKUNJE ANANTHA SHENOI, Scientist, KANDADAI RAJAGOPALACHARI NARASIMHAN, Scientist and VENKATARAMAN BALASUBRAMANIAN, Junior Scientific Assistant, all of them employed in Central Electrochemical Research Institute, Karaikudi-3 and all are Indian Nationals.

This invention relates to improvements in or relating to electrolytic colouring of aluminium and its alloys for decorative and architectural uses.

Hitherto it has been proposed to colour aluminium and its alloys electrolytically by treating anodised aluminium or its alloys with alternating current employing a voltage of the order of 9-15 volts in metallic salt solutions containing organic or mineral acid or their salts using counter electrodes such as nickel, tin, graphite, lead or copper. Colours such as bronze, light brown maroon and similar light shades are obtained depending upon the metal salt solution, voltage and period of treatment.

The above mentioned process has the following shortcomings in that, when anodised aluminium or its alloy is subjected to electrolytic colouring using alternating current in nickel salt solution, the anodised aluminium is not uniformly coloured and spalling (local detachment) of the anodic oxide film above 14 volts are observed. Moreover, alternating current below 14 yields only light colours.

The object of the present invention is to obviate these disadvantages by anodising aluminium and its alloys first in sulphuric acid and then follow it up by anodising the same in chromic acid or oxalic acid or in borax solution with pH 10 (adjusted with NaOH) for a period of three to ten minutes. These duplex film on aluminium when used for A.C. colouring in metallic salt solution containing nickel or copper or silver or in combination of any two of the metal salt solutions in succession using counter-electrodes such as nickel, lead, stainless steel or tin uniform colouring without spalling is obtained. Moreover, deeper shades are obtained at A.C. voltages above 9.

To these ends, the invention broadly consists in anodically oxidising degreased and cleaned aluminium or its alloys with direct current under 15A/sq. ft current density for 30-45 minutes in 15% sulphuric acid solution at  $21 \pm 1^\circ\text{C}$ . Subsequently, the anodised aluminium alloy is further anodised (second stage anodising) in 10% chromic acid solution at  $40^\circ\text{C}$  for 1-5 minutes at 30-50 volts or in 5% oxalic acid at 15-20 volts for 5-10 minutes or in 5% borax solution with pH 10 (pH adjusted with NaOH) at 20-50 volts for 5-10 minutes.

After double anodising, the aluminium or its alloys, they were subjected to electrolytic colouring using A.C. at 5-40 volts for 30 seconds to 10 minutes in nickel salt solution, with a pH of 3.0-5.5. When nickel or stainless steel is used as counter-electrode uniform light bronze or dark bronze or jet black colour is obtained without spalling of the oxide film depending upon the A.C. voltage.

A.C. colouring can also be carried out over double anodised aluminium and its alloys in other metal salt solutions like copper sulphate (15-30 g/l), silver nitrate or silver sulphate (0.15 to 5 g/l) containing sulphuric acid (5-20 g/l) and the pH maintained at 1-5. A.C. colouring can be carried out in a single metallic salt solution or in two metallic salt solutions in sequence or in a mixture of metallic salt solutions under suitable current density, pH and metal salt concentrations using counter electrodes such as nickel, copper, lead, stainless steel or tin or graphite.

The following are the typical examples given to illustrate the invention and not to limit the scope of the invention:

#### Example 1

2S aluminium alloy specimen of 7.5 cm x 5 cm was mechanically polished and degreased with trichlorethylene. Later, this was cleaned in 5% NaOH solution for 5 minutes and washed. Further this was cleaned in 10% nitric acid solution for three minutes for desmutting and later thoroughly washed with tap water and further rinsed with distilled water. The specimens thus cleaned were anodised in 15% sulphuric acid solution at  $21 \pm 1^\circ\text{C}$  under 15-A/sq. ft. current density for 30 minutes. The anodised aluminium plates were further anodised in 10% chromic acid solution at 40 volts and at  $40^\circ\text{C}$  for three minutes. The double anodised aluminium plates thus obtained was subjected to a.c. electrolytic colouring in the undermentioned bath at 40 volts.

Nickel sulphate	100 g/l
Boric acid	50 g/l
Ammonium sulphate	50 g/l
pH	4
Counter electrode	Nickel
Time	10 minutes

A jet black colour was obtained without any spalling of the oxide film. The coloured plate was hot water sealed. The colour obtained was fast to ultraviolet rays.

**Example 2**

65S aluminium alloy of size 5 cm x 7.5 cm was mechanically polished, degreased and pre-cleaned as described in Example 1. It was first anodised in 15% sulphuric acid under a current density of 15 A/sq. ft. at  $21^{\circ} \pm 1^{\circ} \text{C}$  for 30 minutes. This plate was further anodised in 5% borax solution (pH adjusted to 10 with sodium hydroxide) at  $70^{\circ} \text{C}$  and 50 volts for five minutes. After double anodising, the specimen was subjected to A.C. colouring in the nickel salt solution as given in Example 1 at 25V for three minutes using stainless steel as counter-electrode. A light bronze colour was obtained without any spalling of the oxide film. This was hot water sealed. The coloured plate was fast to ultra-violet rays.

**Example 3**

26S aluminium alloy of size 5 cm x 7.5 cm was mechanically polished and degreased and pre-cleaned as in Example 1. This specimen was anodised in 15% sulphuric acid under 15A/sq. ft. current density at  $21^{\circ} \pm 1^{\circ} \text{C}$  for 30 minutes. This anodised specimen was subjected to second stage anodising in 5% oxalic acid solution at 30 volts for five minutes at  $21^{\circ} \pm 1^{\circ} \text{C}$ .

After double anodising, the plate was subjected to A.C. colouring in silver sulphate solution (0.15 g/l) and 5 g/l sulphuric acid at 9 volts for 30 seconds using graphite as counter electrode. Further A.C. colouring was continued, in nickel sulphate 30 g/l, boric acid 15 g/l and magnesium sulphate 15 g/l at 20 volts for two minutes, a uniform chocolate brown colour was obtained and there was no spalling of the oxide film. The specimen was hot water sealed. The plate was colour fast to ultraviolet rays.

**Example 4**

3S aluminium alloy of size 7.5 cm x 5 cm was chemically polished and degreased. The pre-treated plate was anodised in 15% sulphuric acid at 15 A/sq. ft. current density at  $21^{\circ} \pm 1^{\circ} \text{C}$  for 30 minutes. After anodising in sulphuric acid, the plates were further anodised in 10% chromic acid at 50 volts at  $40^{\circ} \pm 1^{\circ} \text{C}$  for five minutes.

After double anodising, the aluminium plate was subjected to a.c. colouring in copper sulphate solution (20 g/l) and sulphuric acid (5 g/l) using copper counter electrode at 9 volts for 30 seconds.

Further, the second stage a.c. colouring was carried out in nickel sulphate (30 g/l), boric acid (25 g/l) and ammonium sulphate (15 g/l) at  $35^{\circ} \text{C}$  under a current density of 0.4 A/dm<sup>2</sup> for two minutes.

A uniform chocolate brown colour was obtained without spalling of the oxide film. The plate was hot water sealed. It was colour resistant to ultra-violet source.

**Example 5**

56S alloy aluminium of size 5 cm x 7.5 cm was electropolished, degreased and anodised in 15% sulphuric acid at 15 A/sq. ft. for 30 minutes at  $21^{\circ} \pm 1^{\circ} \text{C}$ . It was further anodised in 10% chromic acid for periods given below and A.C. colouring was carried out in copper sulphate solution using copper counter electrode at 30 volts for one minute.

Period of anodisation in chromic acid bath (in seconds)	Colour obtained
60	light brown
90	light grey
120	blue grey
150	blue colour

The following are among the main advantages of the invention:

1. Electrolytic colouring of anodised aluminium can be carried out without spalling of the oxide film by adopting the present invention of double anodising.
2. Dark shades can be achieved by adopting this process since A.C. colouring can be carried out even at 40 volts without spalling of the oxide film.
3. In addition to black, brown and bronze colours, other shades can be obtained by A.C. colouring double anodised aluminium in nickel salt solution and subsequently colouring the same in different metal salt solution such as copper or silver in sequence by varying the time of second stage anodising as well as A.C. electrolysis.
4. The colours obtained by this process are light fast and hence can be used for decorative as well as for architectural purposes.
5. This double anodisation has one another advantage in that enables us to get a range of colours from the same bath using a single salt solution depending on the period of anodisation in chromic acid bath, as illustrated in Example 5.

Dated this 29th day of August, 1973.

Sd./-

ASST. PATENTS OFFICER

Council of Scientific & Industrial Research.

**COMPLETE SPECIFICATION**

**"IMPROVEMENTS IN OR RELATING TO ELECTROLYTIC COLORING OF ALUMINIUM AND ITS ALLOYS FOR DECORATIVE AND ARCHITECTURAL USES."**

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860),

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

This is an invention by Balkunje Anantha Sheno, Scientist, Kandadai Rajagopalachari Narasimhan, Scientist, and Venkataraman Balasubramanian, Junior Scientific Assistant, all of them employed in

This invention relates to Improvements in or relating to electrolytic colouring of aluminium and its alloys for decorative and architectural uses.

their salts using counter electrode (the other electrode) such as nickel, tin, graphite, lead or copper. Colours such as bronze, light brown, maroon and similar light shades are obtained depending upon the metal salt solution, voltage and period of treatment.

The above mentioned process has the following shortcomings in that, when anodised aluminium or its alloys is subjected to electrolytic colouring using alternating current in nickel salt solution, the anodised aluminium is not uniformly coloured and spalling (local detachment) of the anodic oxide film above 14 volts are observed. Moreover, alternating current below 14 volts yields only light colours.

The object of the present invention is to obviate these disadvantages. This has been achieved by anodising aluminium and its alloys first in sulphuric acid and then following it up by anodising the same in chromic acid or oxalic acid or in Borax solution with pH 10 for a period of 1—10 minutes. These duplex films on aluminium when used for electrolytic colouring with alternating current in metallic salt solution containing nickel or copper or silver or in combination of any two of the metal salt solutions in succession using counter electrodes such as nickel, lead, stainless steel or tin, impart uniform colouring without spalling. Moreover, deeper shades are obtained at AC voltages above 9.

According to the present invention, there is provided a process for the electrolytic colouring of aluminium or its alloys for decorative and architectural uses which consists of anodising aluminium and its alloys in sulphuric acid electrolyte using direct current followed by second stage anodising (double anodising) in chromic acid, oxalic acid or in Borax solution with pH 10 for a period of 1—10 minutes and finally electrolytically coloured in a solution of a metallic salt such as nickel salt, copper salt or silver salt using alternating current.

The electrolytic colouring is done in presence of a 'counter electrode' such as stainless steel, copper, nickel, tin or graphite. By 'counter electrode', we mean the other electrode used in the electrolytic colouring process using alternating current, other than anodised aluminium. Darker shades could be obtained by using higher alternating current voltage (above 20 V) by virtue of double anodising. The electrolytically coloured anodised aluminium thus obtained is uniform and free from spalling (local detachment of the oxide film).

Thus in the process described in this specification, direct current is used for anodising and alternating current for electrolytic colouring.

Degreased and cleaned aluminium or its alloys is anodically oxidised with direct current under 15 A/sq.ft. current density for 30—45 minutes in 15% sulphuric acid solution at  $21^{\circ} \pm 1^{\circ}\text{C}$ . Subsequently, the anodised aluminium alloy is further anodised (second stage anodising) in 10% chromic acid solution at  $40^{\circ}\text{C}$  for 1 to 5 minutes at 30—50 volts or in 5% Borax solution with pH 10 at 2—50 volts for 5—10 minutes.

After double anodising, the aluminium or its alloys, were subjected to electrolytic colouring using A.C. at 5.40 volts for 30 seconds to 10 minutes in nickel salt solution with a pH of 3 to 5.5. When nickel or stainless steel is used as counter electrode, uniform light bronze or dark bronze or jet black colour is obtained without spalling on the oxide film depending upon the alternating current voltage and duration of treatment.

Alternating current colouring can also be carried out over double anodised aluminium and its alloys in other metal salt solutions like copper sulphate (15—30 g/l), silver nitrate or silver sulphate (0.15—5 g/l) containing sulphuric acid (5—20 g/l) and the pH

maintained at 1-5. Alternating current colouring can be carried out in a single metallic salt solution or in two metallic solutions in sequence or in a mixture of metallic salt solutions under suitable current density, pH and metal salt concentrations using counter electrodes such as nickel, copper, lead, stainless steel tin or graphite.

The following are the typical examples given to illustrate the invention and not to limit the scope of the invention. The examples illustrate how different shades of colours can be obtained by using different metal salt solutions such as nickel, copper and silver individually or in sequence.

#### Example 1

2S aluminium alloy specimen of 7.5 cm x 5 cm was mechanically polished and degreased with trichloroethylene. Later, this was cleaned in 5% sodium hydroxide solution for 5 minutes and washed. Further this was cleaned in 10% nitric acid solution for three minutes for desmutting and later thoroughly washed with tap water and further rinsed with distilled water. The specimens thus cleaned were anodised in 15% sulphuric acid solution at  $21^{\circ} \pm 1^{\circ}\text{C}$  under 15 A/sq. ft. current density for 30 minutes. The anodised aluminium plates were further anodised in 10% chromic acid solution at 40 volts and at  $40^{\circ}\text{C}$  for 3 minutes. The double anodised aluminium plates thus obtained were subjected to alternating current electrolytic colouring in the undermentioned bath at 40 volts:

Nickel sulphate	100 g/l
Boric acid	50 g/l
Ammonium sulphate	50 g/l
pH	4
Counter electrode	Nickel
Time	10 minutes

A jet black colour was obtained without any spalling of the oxide film. The coloured plate was hot-water sealed. The colour obtained was fast to ultraviolet rays.

#### Example 2

6S aluminium alloy of 5 cm x 7.5 cm was mechanically polished, degreased and pre-cleaned as described in Example 1. It was first anodised in 15% sulphuric acid under a current density of 15 A/sq. ft. at  $21^{\circ} \pm 1^{\circ}\text{C}$  for 30 minutes. This plate was further anodised in 5% borax solution at  $70^{\circ}\text{C}$  and 50 volts for 5 minutes. After double-anodising, the specimen was subjected to alternating current colouring in the nickel salt solution as given in Example 1 at 25 volts for 3 minutes using stainless steel as counter-electrode. A light bronze colour was obtained without any spalling of the oxide film. This was hot-water sealed. The coloured plate was fast to ultraviolet rays.

#### Example 3

26S aluminium alloy of size 5 cm x 7.5 cm was mechanically polished and degreased and pre-cleaned as in Example 1. This specimen was anodised in 15% sulphuric acid under 15 A/sq. ft. current density at  $21^{\circ} \pm 1^{\circ}\text{C}$  for 30 minutes. This anodised specimen was subjected to second stage anodising in 5% oxalic acid solution at 30 volts for 5 minutes at  $21^{\circ} \pm 1^{\circ}\text{C}$ .

After double anodising, the plate was subjected to alternating current colouring in silver sulphate solution (0.15 g/l) and 5 g/l sulphuric acid at 9 volts for 30 seconds using graphite as counter electrode. Further alternating current colouring was continued in nickel sulphate (30 g/l), boric acid (15 g/l) and magnesium sulphate (15 g/l) at 20 volts for 2 minutes. A uniform chocolate brown colour was

obtained and there was no spalling of the oxide film. The specimen was hot water sealed. The plate was colour fast to ultraviolet rays.

#### Example 4

3S aluminium alloy of size 7.5 cm x 5 cm was chemically polished and degreased. The pre-treated plate was anodised in 15% sulphuric acid at 15 A/sq. ft. current density at  $21^{\circ} \pm 1^{\circ}\text{C}$  for 30 minutes. After anodising in sulphuric acid, the plates were further anodised in 10% chromic acid at 50 volts at  $40^{\circ} \pm 1^{\circ}\text{C}$  for five minutes.

After double-anodising, the aluminium plate was subjected to alternating current colouring in copper sulphate solution (20 g/l) and sulphuric acid (5 g/l) using copper counter electrode at 9 volts for 30 seconds.

Further, the second stage alternating current colouring was carried out in nickel sulphate (30 g/l), boric acid (25 g/l) and ammonium sulphate (15 g/l) at  $35^{\circ}\text{C}$  under a current density of  $0.4 \text{ A/dm}^2$  for two minutes.

A uniform chocolate brown colour was obtained without spalling of the oxide film. The plate was hot-water sealed.

#### Example 5

56S aluminium alloy of size 5 cm x 7.5 cm was electropolished, degreased and anodised in 15% sulphuric acid at 15 A/sq. ft. for 30 minutes at  $21^{\circ} \pm 1^{\circ}\text{C}$ . It was further anodised in 10% chromic acid for periods given below and alternating current colouring was carried out in copper sulphate solution using copper counter electrode at 30 volts for one minute.

Period of anodising in chromic acid bath (in seconds)	Colour obtained
60	Light brown
90	Light grey
120	Blue grey
180	Blue colour

#### Example 6

An aluminium name plate with letters written with bitumen paint or with lacquer was anodised in 15% sulphuric acid at  $20^{\circ} \pm 2^{\circ}\text{C}$  for half an hour at 15 A/sf current density. The anodised plate was washed and rinsed and further anodised in 10% chromic acid for 3 minutes at 30 volts. The double anodised name plate thus obtained is electrolytically coloured in a bath consisting of nickel sulphate (100 g/l), boric acid (50 g/l), ammonium sulphate (30 g/l) and copper sulphate (10 g/l) using nickel as counter electrode. pH of the bath was 4. The electrolytic colouring was carried out for 4 minutes at  $0.4 \text{ A/dm}^2$  current density. Uniform black colour was obtained on the non-lacquered portion of the name-plate. The plate was washed, dried and degreased with trichloroethylene in order to remove the lacquered portion. A bright name-plate with black background was obtained. The name-plate thus obtained was sealed in hot water. This example illustrates the usefulness of this process for preparing name-plates.

The following are among the main advantages of the invention:

1. Electrolytic colouring of anodised aluminium can be carried out without spalling of the oxide film by adopting the present invention of double-anodising.

2. Dark shades can be achieved by adopting this process since alternating current colouring can be carried out even at 40 volts without spalling of the oxide film.

3. In addition to black, brown and bronze colours, other shades can also be obtained by alternating current colouring double anodised aluminium in

nickel salt solution and subsequently colouring the same in different metal salt solution such as copper or silver in sequence by varying the time of second stage anodising as well as alternating current electrolysis.

4. The colours obtained by this process are light fast and hence can be used for decorative as well as for architectural purposes.

5. This double anodisation has another advantage in that it enables us to get a range of colours from the same bath using a single salt solution depending on the period of anodising in chromic acid bath as illustrated in Example 5.

6. This process can be made use of for preparing name-plates as illustrated in Example 6.

#### WE CLAIM:

1. A process for the electrolytic colouring of aluminium or its alloys for decorative and architectural uses which consists of anodising aluminium and its alloys in sulphuric acid electrolyte using direct current followed by electrolytic colouring in a solution of a metallic salt such as nickel salt, copper sulphate, silver nitrate and or silver sulphate using alternating current, characterised in that after the said anodising step and prior to the said electrolytic colouring step, the anodised product is further anodised (double anodised) in chromic acid or oxalic acid or in borax solution with pH 10 for a period of 1 to 10 minutes using direct current.

2. A process as claimed in claim 1 wherein the electrolytic colouring is done using counter-electrode such as stainless steel, copper, nickel, tin or graphite.

3. A process as claimed in claims 1 or 2 wherein darker shades are achieved without spalling of oxide film by using higher alternating current voltage (above 20 V) by virtue of double anodising.

4. A process as claimed in any of the preceding claims wherein direct current is used for anodising and alternating current is used for colouring.

5. A process as claimed in any of the preceding claims wherein degreased and cleaned aluminium or its alloys is anodically oxidised with direct current under 15 A/sq.ft. current density for 30-45 minutes in 15% sulphuric acid solution at  $21^{\circ} \pm 1^{\circ}\text{C}$ , subsequently, the anodised aluminium alloy is further anodised (second stage anodising) in 10% chromic acid solution at  $40^{\circ}\text{C}$  for 1 to 5 minutes at 30-50 volts or in 5% oxalic acid at 15-20 volts for 5-10 minutes or in 5% borax solution with pH 10 at 20-50 volts for 5-10 minutes.

6. A process as claimed in claim 5 wherein, after double-anodising, the aluminium or its alloys, are subjected to electrolytic colouring using AC at 5-40 volts for 30 seconds to 10 minutes in nickel salt solution with a pH of 3 to 5.5.

7. A process as claimed in any of the preceding claims wherein the alternating current colouring is carried out over double-anodised aluminium and its alloys in metal salt solutions like copper sulphate (15-30 g/l), silver nitrate or silver sulphate (0.15-5 g/l) containing sulphuric acid (5-20 g/l) and the pH maintained at 1 to 5.

8. A process for electrolytic colouring of anodised aluminium or its alloys substantially as illustrated in the examples.

9. A process for electrolytic colouring of aluminium or its alloys for decorative and architectural uses substantially as herein before described.

Dated this 3rd day of December, 1974.

Sd/-

R. BHASKARAN PAI  
Patents Officer.

Council of Scientific & Industrial Research