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

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body incorporated under the Registration of Societies (Act XXI of 1860).

This is an invention by BAIKUNJE ANANTHA SHENOI, Scientist, KANDADAI RAJAGOPALACHARI
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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.

Hitherto it has been proposed to adopt the following
electrolyte/processes for producing coloured anodic film on
aluminium alloys :

- (1) Dilute sulphuric acid at very low temperature
nearing 0°C
- (2) 5—Sulphosalicylic acid + sulphuric acid or metallic
sulphate
- (3) 4—Sulphophthalic acid + sulphuric acid
- (4) 5—Sulphoisophthalic acid + sulphuric acid
- (5) 4, 5—Sulphosalicylic acid + sulphuric acid + maleic
acid
- (6) Anolok 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 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.

(2-5)—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 Anolok process, the aluminium alloys are
pre-anodised with direct current in chromic, sulphuric or
sulfamic 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. 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 disad-
vantages by employing oxalic acid as anodising electrolyte
containing soluble salts of any one of metal-ions belonging

to group IB, VIIB 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 anodi-
sing 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 respon-
sible 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, dark 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-maleic acid mix or aromatic sulpho 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 25 μ thickness as specified
for architectural purposes. Then the alloys are again anodi-
sised 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 25 μ as
specified for architectural purposes.

The following typical examples are given to illustrate
the invention :

Example I

The D54SM architectural alloy is degreased with
trichloroethylene and then anodised in the following
electrolyte :

Oxalic acid dihydrate :	5% w/v
Manganese sulphate :	0.5% w/v

The anodising is carried out at 20 \pm 2°C for one hour

Price : Rs. Two Only.

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

Example II

The B51SWP alloy is degreased with trichloroethylene and anodised in the following electrolytes :

Sulphuric acid	:	10% v/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 B51SWP 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 the 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	:	36 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	:	36 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 ascertains the nature of this invention and the manner in which it is to be performed :

This invention relates to improvement in or relating to electrolytic bath composition for colour anodising of aluminium and its alloys.

Hitherto it has been proposed to adopt the following electrolyte/processes for producing coloured anodic film on aluminium alloys :

- (1) Dilute sulphuric acid at very low temperature nearing 0°C
- (2) 5—Sulphosalicylic acid+Sulphuric acid or metallic sulphate
- (3) 4—Sulphophthalic acid+Sulphuric acid
- (4) 5—Sulphoisophthalic acid+Sulphuric acid
- (5) 4, 5—Sulphosalicylic acid+Sulphuric acid+Maleic acid
- (6) Anolok 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 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 to 5)—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 Anolok Process, the aluminium alloys are pre-anodised with direct current in chromic, sulphuric or sulfamic 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 metal-ions belonging

to group IB, VIIB 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. 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, dark 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-maleic acid mix or aromatic sulpho 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 micron 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 required film thickness.

The aluminium alloys are first anodised in standard sulphuric acid bath for half-an-hour using conditions suitable for producing films of 25μ 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 D54SM architectural alloy is degreased with trichloroethylene and then anodised in the following electrolyte :

Oxalic acid dihydrate :	5% w/v
Manganese sulphate :	0.5% w/v

The anodising is carried out at $20\pm 2^\circ\text{C}$ for one hour using a current density of 12 asf. A light grey coloured smooth anodic film is produced.

Example 2

The B51SWP alloy is degreased with trichloroethylene and anodised in the following electrolytes :

Sulphuric acid :	10% v/v
Current density :	16 asf
Temperature :	$20\pm 2^\circ\text{C}$
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 :	$20\pm 2^\circ\text{C}$
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 3

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 $20\pm 2^\circ\text{C}$ using a current density of 24 asf. A brown anodic film is produced.

Example 4

The B51SWP alloy is degreased with trichloroethylene and anodised in the following electrolyte :

Oxalic acid dihydrate :	5% w/v
Nickel sulphate :	0.5% w/v
Temperature :	$20\pm 2^\circ\text{C}$
Duration of the treatment :	1 hour
Current density :	24 asf

A brownish grey colour film is obtained.

Example 5

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 :	$20\pm 2^\circ\text{C}$
Current density :	36 asf
Duration of treatment :	1 hour

A cement grey colour film is produced.

Example 6

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 :	$20\pm 2^\circ\text{C}$
Duration of treatment :	1 hour
Current density :	36 asf

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 dihydrate :	5% w/v
Manganese sulphate :	0.5% w/v
Temperature :	$20\pm 2^\circ\text{C}$
Current density :	24 asf
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 cation 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 lead-lined 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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