

1.121.228



PATENT SPECIFICATION

NO DRAWINGS

1.121.228

Date of Application and filing Complete Specification: 7 Dec., 1966.

No. 54871/66.

(Patent of Addition to No. 1,022,927 dated 26 Feb., 1963)

Complete Specification Published: 24 July, 1968.

© Crown Copyright 1968.

Index at acceptance:—C7 B(2F, 2H, 13, 16X)

Int. Cl.:—C 23 b 9/02

COMPLETE SPECIFICATION

Process for Colouring Anodised Aluminium by Electrolytic Deposition

I, TAHEI ASADA, a Japanese National, of 14—5, Okamoto Aza Shoya, Motoyama-cho, Higashinada-ku, Kobe, Japan, 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 coloured coatings on aluminium, and more particularly relates to the production of inorganic-coloured coatings on aluminium articles. References to "aluminium" herein will be understood to include aluminium of ordinary commercial purity and aluminium-base alloys that are suitable for conventional anodising treatments. The term "aluminium article" as used herein is intended to include semi-fabricated products, such as rolled aluminium sheet and aluminium extruded sections.

The present invention relates to improvements in the two-stage process already described in Patent No. 1,022,927 for producing a coloured coating which comprises anodically oxidising an aluminium article and thereafter treating the anodised article by passing an alternating current between such aluminium article and a counter-electrode, while such aluminium article and electrode are immersed in an electrolyte that contains a dissolved compound of a selected metal in an aqueous acidic medium. Under these circumstances the anodic oxide coating on the aluminium article becomes coloured and such colouring is substantially permanent.

It has however now been discovered in accordance with the present invention that exceptionally satisfactory colours can be produced in anodic oxide films on aluminium by subjecting them to a process in which alternating current is passed between the anodised aluminium and a nickel counter-electrode whilst both are immersed in an acidic electrolyte, which is maintained at pH 3.5—5.5, and contains a dissolved nickel compound.

Although in Patent No. 1,022,927 the use of a nickel-containing electrolyte with a carbon counter-electrode had already been described, it was in no way apparent that when a nickel-containing electrolyte was used improved results could be obtained by the use of nickel counter-electrodes. It has however been found that it is possible to deposit desirable dark colours in anodic oxide films from nickel-containing electrolytes more readily when nickel counter-electrodes are employed than with carbon electrodes.

In general it is found that the colour developed in a given length of time is dependent on the applied voltage. It is found possible to apply higher voltages with nickel counter-electrodes than with carbon electrodes without leading to spalling (local detachment) of the anodic oxide film. The cause of spalling is not fully known, but is believed to be due to evolution of hydrogen at the surface of the metal beneath the anodic oxide film.

The use of a nickel counter-electrode in conjunction with a nickel-containing electrolyte for the described alternating current electrolytic colouring treatment of anodised aluminium articles appears to present particular advantages. It appears that a somewhat higher voltage may be employed than when a carbon electrode is employed, resulting in darker or more intense shades of colour, without the anodic coating becoming blotchy, as may sometimes occur because of over-treatment with alternating current.

A further important advantage resulting from the use of a nickel counter-electrode in a nickel-containing electrolyte resides in the decrease in the rate of variation of pH value, as compared with carbon electrodes. Since it is desirable, for uniform results, to maintain suitable uniformity of the physical and chemical nature of the bath, the use of a nickel counter-electrode has special value in that the pH of the solution then remains sub-

stantially unchanged during a considerable time interval, in contrast to operations with a carbon counter-electrode where it was found that preferred results would necessitate several conventional adjustments of pH, by suitable chemical additions, to maintain constancy during such interval. This is an advantage of great significance in the commercial operation of the colouring process.

- 10 In carrying out the complete process, the aluminium article, after cleaning, is first treated to apply an anodic coating. For example, the article can be anodised by the use of direct current with the article as anode in an appropriate acid bath for a suitable time, such as 30 to 60 minutes, at a conventionally appropriate voltage and current density. The bath may comprise an aqueous solution of a suitable acid, such as sulphuric acid, aryl sulphonic acids or chromic acid, and mixtures of such acids; that is to say, the treatment is one which is appropriate, in nature and concentration of the electrolyte, for producing a good, permanent anodic coating. The anodic coating is preferably formed under conditions requiring the application of voltages below about 40 volts; anodic oxide films formed at higher voltages can exhibit poor colour-accepting properties. It is, in fact, usually preferred that the anodic coating should be produced by direct-current anodising at an applied voltage of not more than about 40 volts. The article, which has thus been anodised to give it an adherent anodic oxide coating, is then subjected to a second stage treatment in which the original anodic oxide coating is transformed to a coloured coating, of essentially the same adherent, protective nature, but characterised by one of a variety of shades depending on the conditions of the second stage treatment.

- 45 In the following specific example of treating aluminium articles, the article, being sheet aluminium of commercial purity, was first anodised in a conventional acidic bath. While other anodic treatments can be employed, as already explained, a convenient treatment that was utilised for the example involved anodisation in 15% (by weight) sulphuric acid solution, with direct current using the aluminium article as anode, employing a

current density of 15 amperes per square foot and voltage of about 17 volts for 30 minutes at 21°C. By this operation, an anodic film having a thickness of 15 microns was obtained. Prior to the anodising step, the surfaces of the sheet aluminium were cleaned by conventional decreasing, etched for 5 minutes in 5% sodium hydroxide solution, and treated to remove or obviate so-called "smut", as is conventional in anodising operations for aluminium.

During the colouring treatment the spacing of the aluminium article and counter-electrode was about 6—18 inches, to reduce difficulties of uneven colouring of areas more remote from the counter-electrode, as for example recesses in extruded aluminium sections. The final, coloured article, was subjected to a conventional treatment for sealing the coating, i.e. a sealing treatment in boiling or near-boiling water.

EXAMPLE

A nickel counter-electrode was used with a bath containing a nickel salt. The anodised aluminium article and the nickel electrode were immersed in an aqueous electrolyte having the following concentration of ingredients: $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 30 grams per litre; H_2BO_3 , 30 grams per litre; $(\text{NH}_4)_2\text{SO}_4$, 15 grams per litre. The pH was adjusted by the addition of ammonium hydroxide or sulphuric acid as necessary, to have a value between 3.5 to 5.5. Outside this pH range it is found to be difficult to obtain the production of smooth, uniform coloured coatings when nickel salts are used in the electrolyte. Alternating current at 15 volts was passed between the anodised article and the counter-electrode for 5 minutes. The anodic coating acquired a dark bronze colour, of unusually satisfactory permanence and uniformity.

In general, the use of nickel salts in the bath with a nickel electrode provides bronze colours of various shades, approaching black.

The following table summarises briefly the results of a series of tests carried out to compare the coatings obtained with carbon counter-electrodes and nickel counter-electrodes, using the same electrolyte. In each case the electrolyte used corresponds to the electrolyte used in the Example.

	Metal in Electrolyte	Counter Electrode	Deposition Conditions	Colour	Comments
1.	Ni	Ni	10V—5 min.	lt. bronze	
2.	Ni	C	10V—5 min.	lt. bronze	
3.	Ni	Ni	15V—10 min.	dk. bronze	no spalling
4.	Ni	C	15V—10 min.	dk. bronze	some spalling
5.	Ni	Fe*	15V—10 min.	dk. bronze	no spalling but AC corrosion of steel
6.	Ni	Ni	13V—3 min. + 17V—10 min.	dk. bronze	slight spalling
7.	Ni	C	13V—3 min. + 17V—10 min.	lt. bronze	severe spalling

* Type 304 stainless steel

The above results exhibit the fact that significant improvements are obtained with a nickel counter-electrode in a nickel-containing electrolyte as compared with those obtainable with carbon electrodes.

It will be understood that different desirable shades may be obtained by variation of the treatment times and voltages. For example, it is possible to produce colouring on an aluminium article with treatment times varying from 3 to 30 minutes and an applied A.C. voltage of 5 to 25 volts.

WHAT WE CLAIM IS:—

1. A process for colouring an anodic oxide film on aluminium in which alternating current is passed between the anodised aluminium and a nickel counter-electrode whilst both are immersed in an acidic electrolyte containing a dissolved nickel compound, the electrolyte being held at a pH value of 3.5 to 5.5.
2. A process according to Claim 1 in which the electrolyte also contains an ammonium salt.

3. A process according to Claim 2 in which the electrolyte contains nickel sulphate and ammonium sulphate.

4. A process according to Claim 1, 2 or 3 in which the electrolyte also contains boric acid.

5. A process according to any preceding claim in which the treatment time is 3—30 minutes with an applied voltage of 5—25 volts.

6. An aluminium article bearing a coloured anodic oxide film produced by the process claimed in any of Claims 1 to 5.

7. A process for producing coloured protective coatings on aluminium articles substantially as herein described.

STEVENS, LANGNER, PARRY &
ROLLINSON,
Chartered Patent Agents,
Agents for the Applicants.

	Metal in Electrolyte	Counter Electrode	Deposition Conditions	Colour	Comments
1.	Ni	Ni	10V—5 min.	lt. bronze	
2.	Ni	C	10V—5 min.	lt. bronze	
3.	Ni	Ni	15V—10 min.	dk. bronze	no spalling
4.	Ni	C	15V—10 min.	dk. bronze	some spalling
5.	Ni	Fe*	15V—10 min.	dk. bronze	no spalling but AC corrosion of steel
6.	Ni	Ni	13V—3 min. + 17V—10 min.	dk. bronze	slight spalling
7.	Ni	C	13V—3 min. + 17V—10 min.	lt. bronze	severe spalling

* Type 304 stainless steel

5 The above results exhibit the fact that significant improvements are obtained with a nickel counter-electrode in a nickel-containing electrolyte as compared with those obtainable with carbon electrodes.

10 It will be understood that different desirable shades may be obtained by variation of the treatment times and voltages. For example, it is possible to produce colouring on an aluminium article with treatment times varying from 3 to 30 minutes and an applied A.C. voltage of 5 to 25 volts.

WHAT WE CLAIM IS:—

15 1. A process for colouring an anodic oxide film on aluminium in which alternating current is passed between the anodised aluminium and a nickel counter-electrode whilst both are immersed in an acidic electrolyte containing a dissolved nickel compound, the electrolyte being held at a pH value of 3.5 to 5.5.

20 2. A process according to Claim 1 in which the electrolyte also contains an ammonium salt.

3. A process according to Claim 2 in which the electrolyte contains nickel sulphate and ammonium sulphate. 25

4. A process according to Claim 1, 2 or 3 in which the electrolyte also contains boric acid. 30

5. A process according to any preceding claim in which the treatment time is 3—30 minutes with an applied voltage of 5—25 volts.

6. An aluminium article bearing a coloured anodic oxide film produced by the process claimed in any of Claims 1 to 5. 35

7. A process for producing coloured protective coatings on aluminium articles substantially as herein described. 40

STEVENS, LANGNER, PARRY &
ROLLINSON,
Chartered Patent Agents,
Agents for the Applicants.

