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I-20133 Milano (MI)(IT)(54) **Process for electrolytic colouring, by optical interference, the anodic oxide on aluminum and aluminum alloys.**

(57) Process for electrolytic colouring ("electrocolouring") aluminum and its alloys by optical interference, which process comprises the steps of pickling and neutralization of material surface,

anodic oxidizing, modification of oxide layer by anodizing in phosphoric acid, acidic conditioning of said modified oxide layer, electrolytic colouring and fixation.

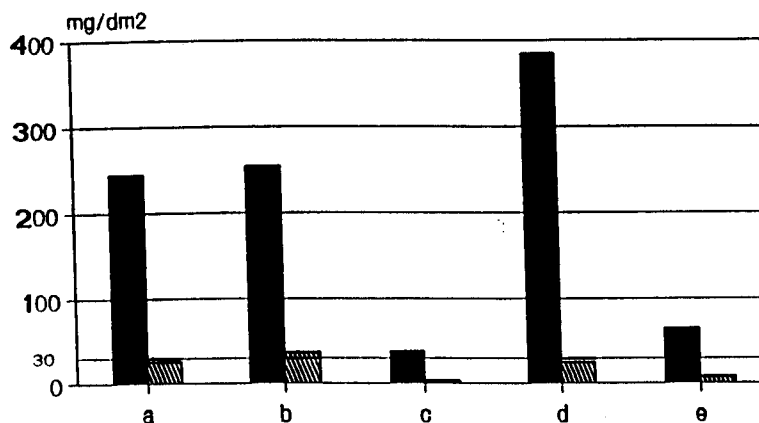


FIG.1

■ na ▨ na2

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The subject-matter of the present invention is a process for electrolytic colouring layers of anodic oxide on aluminum and its alloys by optical interference.

It is well known that for electrolytic colouring ("electrocolouring") aluminum and its alloys, aluminum is first submitted to anodic oxidizing, in such a way that an oxide layer is formed on its surface, and then is submitted to an electrolysis, in either DC or AC current operating mode, in an electrolytic solution containing a metal salt, e.g., a nickel salt. In that way, a deposit of this metal or an oxide thereof inside still open pores of the anodically oxidized layer, and a consequent colouring of aluminum surface are obtained. Eventually pores are closed, i.e. the coloured oxide layer is fixed by following the well known fixation processes, so that also colour results to be fixed. The most commonly used metals for electrolytic aluminum colouring are nickel, cobalt, tin and copper.

Unfortunately, as well known, one of the limits and drawbacks shown by the traditional electrocolouring technique is constituted by the matter of fact that the range of colours which can be obtained is very limited, and ranges from golden bronze colour to dark bronze colour, and to black colour, as a function of operating conditions, in particular of treatment time and voltage, with only slight differences as regards the type of metal ion used.

Already many years ago, a methodology was disclosed which makes it possible a very wide range of colours to be obtained, still by electrolytic way, which comprises violet, blue, grey and also red, by taking advantage of the optical interference effects which occur when the electromagnetic waves falling in the visible region interact between the thin layer of metal particles deposited inside the pores of the oxide layer, and aluminum-oxide interface. In order to obtain such an effect, the distance between the surface of the metal deposit and the underlying aluminum support should be of the same order of magnitude as of the wave lengths corresponding to colours which one wishes to reproduce, i.e. 400-700 nanometres. In order to be able to obtain such limited thicknesses, the bottom of the pores should be expanded in such a way that the metal salt subsequently deposited by electrolytic way is distributed to a larger extent in horizontal direction, instead of tending to "fill" the pore, as it normally occurs.

It is well known that such a process of modification of the porous oxide structure can be accomplished by carrying out a short electrolytic treatment in a solution of phosphoric acid, such as disclosed, e.g. in GB 1,532,235 (P.G. Sheasby et al.), soon after the treatment of anodic oxidation carried out, e.g., as in most cases, in sulfuric acid.

The studies carried in the past, aiming at transferring the methodology of electrocolouring by interference to the large industrial level, have anyway evidenced the matter of fact that such a modification in phosphoric acid renders ineffective the fixation, i.e. the end step of oxide colouring process, during which the closure of pores takes place. As known, the fixation is essential if one wishes to secure the stability of colour over time, and in order to supply the protecting oxide film with the necessary corrosion resistance. Such a serious drawback seems to be due to the presence of phosphate ions in the layer, which are thought to inhibit the fixation (Interference colouring of anodized aluminum, by P.G. Sheasby et al. "Ossidare e verniciare oggi" II - 1985).

Still according to said Authors, by carefully controlling the rinsing and fixation operations, a satisfactory fixation would be obtained. In reality, it does not seem that the process has ever found an industrial success on a large industrial scale: this witnesses the serious application difficulties of the process above all, as said, as regards the fastness and resistance of obtained colour.

A purpose of the present invention is of providing a process for electrocolouring aluminum and its alloys by optical interference, with a wide range of colours being obtained which comprise, for example, violet, blue, grey and red, which makes it possible an effective fixation to be obtained and which therefore secures the stability of colour over time and a very good corrosion resistance of the protective film of coloured oxide.

Still another purpose of the present invention is a process of electrocolouring by optical interference which makes it possible an evenness of colour and a very good quality of fixation to be accomplished.

Still a further purpose of the finding is a process for electrocolouring aluminum by optical interference, which is highly reproducible and easily realizable on the large industrial scale, and which is furthermore easy to be carried out, by means of simple adaptations, and without having to resort to substantial modifications, also on already existing electrocolouring facilities.

These and still other purposes, and relevant advantages which will be evidenced more clearly by the following disclosure, are achieved by a process for electrolytic colouring the anodic oxide on aluminum and on aluminum alloys by optical interference, which process, according to the present invention, comprises the following steps:

- treatment of pickling and neutralization of aluminum or aluminum alloy surface;
- anodic oxidation with a layer of oxide being formed with a thickness of from 10 to 25 microns;

- modification of said oxide layer by anodizing in either alternating current or direct current operating mode, or in pulsated current operating mode, inside a solution of phosphoric acid;
- conditioning of said so-modified oxide layer by means of a treatment with a diluted aqueous solution of an acid;
- electrocolouring said modified, so-conditioned oxide layer;
- fixation of said modified, conditioned and coloured oxide layer.

More particularly, said pickling and neutralization steps are carried out according to traditional processes known in the art, such as, for example pickling with sodium hydroxide in solution at 60-80° C, and neutralization with 1:1 nitric acid.

The anodic oxidation is preferably carried out in sulfuric acid solution, also according to techniques known from the prior art, which makes it possible an oxide layer with regular porosity to be obtained, which is later on submitted to a modification by anodizing in a suitably concentrated phosphoric acid solution, in order to modify the shape and the size of open pores and render said pores suitable for receiving the metal deposit, in such a way as to accomplish the phenomenon of optical interference.

The modified layer of anodic oxide is then submitted to an acidic conditioning treatment, which consists in treating said layer with an aqueous solution of an inorganic acid, or also an organic acid, by keeping the article of aluminum or aluminum alloy immersed inside a bath of said acid for a time period of from 1 to 15 min at room temperature, while keeping said bath simultaneously stirred. In fact, the present Applicant could surprisingly observe that thus conditioned oxide layer, after being coloured, can be fixed without any drawbacks, by using the traditional fixation processes, with a colour being thusly obtained which is very stable and uniform, and very corrosion resistant.

Said inorganic or organic acid used for said conditioning, is advantageously selected from the group comprising sulfuric acid, perchloric acid, hydrochloric acid and hydrobromic acid, oxalic acid, sulfamic acid, trifluoroacetic acid, and is used, in aqueous solution, at a concentration, which preferably is comprised within the range of from 1 to 15% by weight, based on total solution weight, according to the acid nature, and its characteristics and solubility.

The process according to the present invention can be advantageously applied by using, for the electrocolouring, any types of known and commonly used salts. However, it has been seen, as is better illustrated in the following, that particularly

advantageous results are obtained when nickel electrocolouring is carried out.

The following examples, supplied for merely illustrative, non-limitative purposes, will be used in order to better illustrate the invention according to the present finding.

The fixation was carried out by using the main, most common fixation solutions available from the market, both on samples coloured by interference according to the process of the present invention and, for comparison purposes, on samples coloured by interference according to the processes known from the prior art. The fixation quality check was carried out according to the destructive test of weight loss in phosphochromic mixture according to ISO Standard 3210, after 24 h of same fixation.

The material used in the tests was constituted by samples of extruded flats made from AA6060 alloy, of 100 mm x 50 mm x 2 mm of size.

Example 1

The aluminum supports which constituted the test samples were submitted to the following pickling and neutralization treatment:

- pickling with 10% NaOH at 70°C for 3 min
- neutralization with 1:1 HNO₃ at room temperature, for 30 sec.

The samples were then submitted to anodic oxidation in sulfuric acid at 18%, with an electric current density of 1.5 A/dm² at 20° for 35 min, with a class 15-thickness of oxide layer being obtained.

Later on, some samples were submitted to modification by anodizing in a 100 g/l H₃PO₄ solution, at the temperature of 20°C, in direct current mode (ΔV = 20 v for 10 min), whilst the residual samples were submitted to modification with a same solution, but by operating in alternating current mode (Δv = 10V for 4 min).

Some of the modified samples were then submitted to acidic conditioning in H₂SO₄ at the concentration of 10 g/l, at room temperature for 5 min and were then electrocoloured, whilst the residual portion of said modified samples were directly electrocoloured, for comparison purposes, without acidic conditioning.

Electrocolouring was carried out by using a nickel electrocolour of "CARMIOLE" type (registered trade mark of Company ALUMINIA of Portovesme (CA), Italy), using baths having the following composition:

NiSO₄ 47.5 g/l, (NH₄)₂SO₄ 22.5 g/l, H₃BO₃ 30 g/l.

All samples were then submitted to fixation by means of deionized water at 100°C, for a time of 2,5 min/micron ("a" fixation).

The following samples were obtained:
na: modification in alternating-current operating mode, without conditioning (comparison);

nc: modification in direct-current operating mode, without conditioning (comparison);

naz: modification in alternating-current operating mode, with conditioning (according to the present invention);

ncz: modification in direct-current operating mode, with conditioning (according to the present invention).

The samples, evaluated according to ISO Standard 3210 gave the following results, expressed as weight loss values:

na	= 244 mg/dm ²
nc	= 241 mg/dm ²
naz	= 26 mg/dm ²
ncz	= 79 mg/dm ²

Example 2

The operating steps were kept equal to those of Example 1, with only the fixation step being changed, which was carried out by means of a solution of NiSO₄ at the concentration of 10 g/l, at the temperature of 100°C, over a time of 2,5 min/micron ("b" fixation).

The measurements carried out on treated samples yielded the following results:

na	= 254 mg/dm ²
nc	= 299 mg/dm ²
naz	= 37 mg/dm ²
ncz	= 45 mg/dm ²

Example 3

All the operating steps were kept equal to those of Example 1, with only the fixation step being changed, which was carried out by means of a solution of Sandoz AS salt at the concentration of 7 g/l, at the temperature of 100°C, over a time of 2,5 min/micron ("c" fixation), with the following results being obtained:

na	= 38 mg/dm ²
nc	= 89 mg/dm ²
naz	= 4 mg/dm ²
ncz	= 20 mg/dm ²

Example 4

All operating steps are equal to those of Example 1, but the fixation step, which was carried out by means of a solution containing 1.6 g/l of Ni and 800 ppm of F, at 28°C, for a time of 1 min/micron ("d" fixation), with the following results being obtained:

na	= 385 mg/dm ²
nc	= 320 mg/dm ²
naz	= 25 mg/dm ²
ncz	= 267 mg/dm ²

Example 5

The operating steps are equal to those of Example 1, but the fixation step, which was carried out by means of a solution containing 1.6 g/l of Ni and 800 ppm of F, for 1 min/micron at 28°C, (same as "d" fixation), with a second step in NiSO₄ solution at 10 g/l at 60°C for 20 min, ("e" fixation), with the following results being obtained:

na	= 66 mg/dm ²
nc	= 190 mg/dm ²
naz	= 8 mg/dm ²
ncz	= 27 mg/dm ²

The test results reported in above examples clearly evidence that the treatment of conditioning in acid according to the present invention makes it possible the fixation of interference-electrocoloured articles to be carried out with extremely good results, with the known drawbacks being thus eliminated which occur with the interference electrocolouring processes according to the prior art.

The results of the above 5 examples are reported in the histograms of the accompanying drawing table, in which

Figure 1 shows, for the five "a", "b", "c", "d" and "e" fixation types, of the above Examples 1-5, the values of weight losses shown by the samples modified in alternating current operating mode obtained without the acidic conditioning treatment ("na"), as compared to analogous samples obtained according to the process of the present invention ("naz"), and

Figure 2 shows, still for the same five fixation types as of above Examples from 1 to 5, the weight loss values shown by the samples modified by operating in direct current mode, obtained without the acidic conditioning treatment ("nc"), as compared to analogous samples obtained with the process according to the present invention ("ncz").

The process for electrocolouring by interference according to the present invention can be advantageously accomplished also on already existing electrocolouring facilities, by simply adding, besides the tank for the modification by anodizing in phosphoric acid, an additional tank for the step of acidic conditioning, i.e. without having to resort to substantial and consequently burdensome modifications of the same facility.

To the invention, as disclosed and exemplified hereinabove, technically equivalent modifications can obviously be supplied, all falling within the scope of protection of the same invention.

Claims

1. Process for electrolytic colouring ("electrocolouring") the anodic oxide on alu-

minum and on aluminum alloys by optical interference, which process, according to the present invention, comprises the following steps:

- treatment of pickling and neutralization of aluminum or aluminum alloy surface; 5
 - anodic oxidation with a layer of oxide being formed with a thickness of from 10 to 25 microns;
 - modification of said oxide layer by anodizing in alternating current operating mode or in direct current operating mode, or in pulsated current operating mode, inside a solution of phosphoric acid; 10 15
 - conditioning of said so-modified oxide layer by means of a treatment with a diluted aqueous solution of an acid;
 - electrocolouring said modified, so-conditioned oxide layer; 20
 - fixing said modified, conditioned and coloured oxide layer.
2. Process according to claim 1, characterized in that said acid solution for said conditioning step is constituted by an acid selected from the group comprising sulfuric acid, perchloric acid, hydrochloric acid, hydrobromic acid, oxalic acid, sulfamic acid, trifluoroacetic acid, in aqueous solution, and the concentration of said acid in said solution is comprised within the range of from 1 to 15% by weight, based on total solution weight. 25 30
3. Process according to claim 1, characterized in that the duration of said treatment with said diluted acid aqueous solution is comprised within the range of from 1 to 15 min. 35
4. Process according to claim 1, characterized in that said electrolytic colouring of said modified and conditioned oxide layer is a nickel colouring, obtained by using baths based on nickel sulfate. 40

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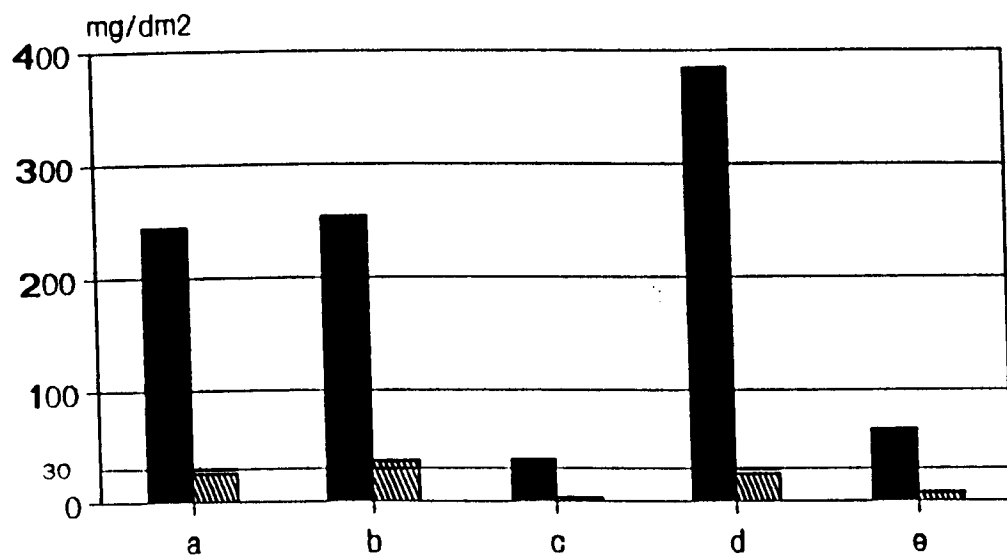


FIG.1

na naz

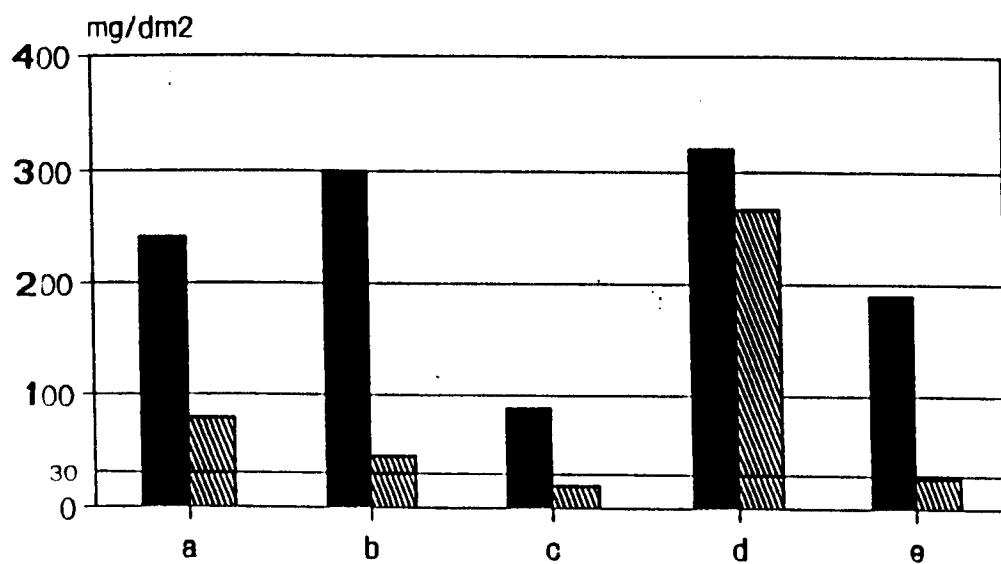


FIG.2

nc ncz



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EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 92110964.1
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	<u>US - A - 4 737 245</u> (BEFELD) * Column 3, lines 20-22 *	1, 3	C 25 D 11/22
D, A	<u>GB - A - 1 532 235</u> (ALCAN RESEARCH) * Claims 5-13 *	1	
A	<u>US - A - 3 989 605</u> (YANAGIDA et al.) * Column 5, line 65 - column 6, line 1 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 25 D
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
VIENNA	19-10-1992	LUX	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	