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11 Publication number:

0 558 940 A1

12

EUROPEAN PATENT APPLICATION

21 Application number: **93101547.3**

51 Int. Cl.⁵: **C25D 11/22**

22 Date of filing: **02.02.93**

30 Priority: **04.03.92 IT MI920477**

43 Date of publication of application:
08.09.93 Bulletin 93/36

84 Designated Contracting States:
BE CH DE ES FR GB LI

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54 **Process for electrocolouring, by optical interference, aluminium and aluminium alloys, suitable to obtain homogeneous and easily reproducible colourings.**

57 A process for electrocolouring aluminium and its alloys by optical interference, which process comprises the following stages: anodic oxidation; modification in phosphoric acid; possible conditioning by treatment with diluted acids; electrocolouring by means of a solution in which the concentration of colouring metal is comprised between 0.018 and 0.1 moles/l; and final fixing.

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Object of the present invention is an electrocolouring process by optical interference of aluminium and its alloys, which permits to obtain a homogeneous colouring on the whole manufactured article and which is easily reproducible.

It is well known that for the electrolytic colouring or electrocolouring by optical interference of aluminium and its alloys, aluminium is submitted first to anodic oxidation according to traditional techniques, utilizing, for instance, sulphuric acid-based baths, so that an oxide layer forms on its surface, then to an electrolytic treatment of modification in a phosphoric acid solution, such as the one disclosed for instance, in GB 1532235 (P.G.SHEASBY et al.). Such treatment in phosphoric acid has the purpose of modifying the oxide's porous structure, so that the following DC or AC-mode electrolytic treatment in an electrolytic solution containing a coloring metal salt, for instance a nickel salt, permits to obtain colouring by optical interference.

To avoid possible fixing problems, which fixing is indispensable to secure the stability of colour over time, and to give the protective oxide film the necessary corrosion resistance, before carrying out the treatment of electrocolouring by optical interference, a conditioning of the layer of modified oxide is made; such conditioning is made by treatment with a diluted solution of an organic or inorganic acid, for instance sulphuric acid, as disclosed in the patent application no. MI91A 00191932, filed on July 12 1991 on behalf of the same Applicant.

It is well known that the technique of optical interference electrocolouring can produce a very wide range of colours, comprising violet, blue, grey and even red. Such colours are obtained by utilizing conventional electrolytic baths, such as, for instance, a standard "CARMIOLE" bath (Registered Trade Mark of Soc. ALUMINIA of Portovesme (CA) (Italy), having the following composition:

NiSO ₄ 7H ₂ O	47.5 g/l (0.17 moles/l of Ni ²⁺)
(NH ₄) ₂ SO ₄	22.5 g/l (0.17 moles/l)
H ₃ BO ₃	30.0 g/l
pH = 5.7	

As can be seen, in electrolytic baths for electrocolouring of aluminium and its alloys, according to prior art, the concentration of metal useful for colouring, or colouring metal, for instance nickel, has a molar ratio of about 1:1 compared to the concentration of the support electrolyte, which may be a salt, for instance ammonium sulphate or a mixture of analogous salts in suitable quantities.

However, the studies carried out in the past have stressed that several problems are associated to such optical interference electrolytic colouring and in particular the matter of fact that reproducible and easily controllable colourings are difficult to obtain. Another important problem is the poor homogeneity of colourings. The non-homogeneity of colouring as obtained by the techniques of prior art hinders to a large extent the diffusion of the process on an industrial scale.

A purpose of the present invention is to provide an electrocolouring process by optical interference of aluminium and its alloys producing a wide range of colours comprising, for instance, violet, blue, grey and red, with highly reproducible colourings.

Another purpose of the present invention is to realize an optical interference electrocolouring process permitting to obtain an excellent homogeneity and, therefore, an excellent colour quality.

Still another purpose of the present invention is an electrocolouring process by optical interference which is easily realizable by means of simple adjustments without having to resort to basic changes, even in already existing electrocolouring plants.

Another further purpose of the invention is to provide an electrolytic solution permitting to obtain an optical interference electrocolouring process supplying highly reproducible and homogeneous colourings.

These and still other purposes and relevant advantages which will be more clearly stressed in the following disclosure are obtained by a process of optical interference electrocolouring of aluminium and its alloys, comprising the following stages: anodic oxidation; modification by electrolysis in phosphoric acid solution; electrocolouring by utilizing a solution comprising at least a colouring metal salt and a support electrolyte; and a final fixation, the latter electrocolouring stage being carried out, according to the invention, by utilizing an electrolytic solution in which the concentration of the colouring metal is between 0.018 and 0.1 moles/l.

According to the present invention, between said stage of phosphoric acid modification and said stage of electrocolouring, a conditioning stage of the oxide layer by treatment with a diluted aqueous solution of an acid may be advantageously introduced, which acid is chosen among the group comprising sulphuric acid, perchloric acid, hydrochloric acid, hydrobromic acid, oxalic acid, sulphamic acid and trifluoroacetic acid. In particular, said colouring metal in form of salt in said electrolytic solution is chosen among the ones

that are more widely used for aluminium electrolytic colouring, especially nickel and cobalt.

Ammonium salts and/or salts of alkaline metals in general are advantageously used as salts constituting the support electrolyte.

Always according to the present invention, the use of support electrolytes constituted by a mixture of ammonium sulphate and magnesium sulphate in different ratios according to the different operating conditions of the electrocolouring stage has proved advantageous.

Instead of the sulphate anion, other analogous anions may be used that are normally admitted in electrocolouring processes.

According to the present invention, the concentration of the support electrolyte is markedly higher than the one utilized in prior art, in order to increase the conductivity of said electrolytic baths, obtaining in this way an increased penetration of colouring and therefore a greater homogeneity of said colouring.

Quantities and ratios of the various components which constitute the composition of the electrolytic baths according to the invention, change according to the type of colouring wished and to the type and utilization conditions of the electrolytic bath. In general, the electrolytic solution for optical interference electrocolouring of aluminium and its alloys according to the present invention, includes in preference the following quantities of constituents expressed in weight concentrations or in moles with respect to the total volume of the solution:

20	<ul style="list-style-type: none"> - colouring metal (Ni^{2+} or Co^{2+}) - support electrolytes salts - pH regulators, acids and various additives of known type 	<p>0.018 to 0.1 moles/l</p> <p>55 to 75 g/l</p> <p>30 to 100 g/l</p>
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Said pH regulators, acids and various additives are chosen among the most commonly used ones, such as, for instance, boric acid and sodium hydroxide.

The pH value of electrolytic baths according to the process object of the present invention is preferably kept between 4 and 7.

The process of optical interference electrocolouring of aluminium and its alloys according to the invention has surprisingly proved to lead constantly to results that are remarkably better than the ones obtainable through conventional techniques. In particular, it permits to accomplish an electrocolouring which supplies highly reproducible and homogeneous colourings compared to those obtainable according to prior art, with clear advantages from both the aesthetical point of view and the point of view of industrial application in which the poor reproducibility and homogeneity of colourings obtained according to prior art is a severe drawback.

Particularly advantageous results are obtained when electrocolouring is accomplished by utilizing nickel salts, as illustrated in the following examples, supplied to merely illustrative, non-limitative purposes, which will disclose the process object of the present invention.

The material utilized in tests was constituted by samples of extruded flats of 6060 aluminium alloy, of 100 x 100 x 2 mm of size. Samples to be tested had been submitted to the following pickling and neutralization treatment:

pickling with 5% NaOH at 60 °C for 3 min.; additive:

Anodal B2 Sandoz 20 g/l, neutralization with 1:1 HNO_3 at room temperature for 15 sec.

Samples have been then submitted to anodic oxidation in 200 g/l sulphuric acid, 3 g/l Al, with voltage density of 1.5 A/dm² at 20 °C for 35 min., obtaining a class 15 thickness of the oxide layer (about 17 microns). Then, samples have been submitted to modification by treatment in a 100 g/l H_3PO_4 solution at 20 °C in AC mode ($V = 10\text{V}$ for 4 min.), with AC density of 0.7 A/dm².

The so-modified samples have been then submitted to acid conditioning in 10 g/l H_2SO_4 solution at room temperature for 5 min.

50 EXAMPLE 1

Some of the samples treated as described have been electrocoloured by using Hull cell having a capacity of 250 ml of solution at a 10 V voltage, for periods of time of 3 and 10 min and a temperature of 23 °C. As is well known, in Hull cell the sample to be submitted to electrocolouring is placed in oblique position with respect to the electrode.

This permits to reach on said sample different voltage intensities during the electrocolouring stage and, as a consequence, different colouring intensities when the distance of the sample increases with respect to the electrode. By this technique one obtains precise information on the characteristics of the electrolytic

baths used, the electrocolouring velocity and the homogeneity of said colouring. The composition of the electrolytic solution was the following:

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NiSO ₄ 7H ₂ O	7 g/l (0.025 moles/l of Ni ²⁺)
(NH ₄) ₂ SO ₄	40 g/l (0.3 moles/l)
H ₃ BO ₃	30 g/l
MgSO ₄ 7H ₂ O	30 g/l (0.12 moles/l)

10 As can be seen, in this example the molar ratio of the concentration of metal useful for colouring, or colouring metal, is about 1:10 compared to the concentration of the mixture of salts which constitute the support electrolyte.

The pH of the solution has been regulated on value 5.7 by the addition of ammonium hydroxide. Such samples are A-marked.

15 Instead, the remaining samples have been submitted to electrocolouring in Hull cell and in the same operating conditions, but using "Carmiol"-type compositions of electrolytic solutions for electrocolouring. These last samples have been B-marked. Upon completion of colouring, the A and B samples obtained with the two different compositions for electrolytic baths have been examined and compared to one another before the fixing treatment.

20 In particular, A samples showed, compared with B samples, a significant and remarkable colour stabilization for blue shades, as well as a homogeneous distribution of said colouring on the sample surface.

On said A and B samples a qualitative colour measurement has been carried out with Colorflash spectrophotometer (Optronik). Said samples have been subdivided in three measurement zones, with the purpose of comparing the intensity of possible colour variations between zones. Such colour variations are 25 quantified through factors called "a", "b" and "L"; factor L supplies an indication of the brightness degree of the colouring under examination; factor "a" indicates the shade degree comprised between green and red of said colouring, while factor "b" indicates the shade degree comprised between blue and yellow.

Sample A (submitted to optical interference electrocolouring treatment according to the present invention) has been subdivided into three measurement zones, indicated by A1, A2 and A3 respectively, 30 and also sample B (submitted to a treatment of optical interference electrocolouring according to prior art by utilizing a Carmiol-type bath) has been subdivided into the three measurement zones indicated by B1, B2 and B3 respectively.

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SAMPLE A

$$\Delta L_{(A1-A2)} = -2,0 \quad \Delta L_{(A2-A3)} = -3,1$$

$$\Delta a_{(A1-A2)} = -2,1 \quad \Delta a_{(A2-A3)} = -0,1$$

$$\Delta b_{(A1-A2)} = -2,2 \quad \Delta b_{(A2-A3)} = -0,5$$

$$\Delta L_{(A1-A3)} = -5,11$$

$$\Delta a_{(A1-A3)} = -2,19$$

$$\Delta b_{(A1-A3)} = -2,68$$

SAMPLE B

$$\Delta L_{(B1-B2)} = -9,3 \quad \Delta L_{(B2-B3)} = -9,5$$

$$\Delta a_{(B1-B2)} = -2,1 \quad \Delta a_{(B2-B3)} = +8,2$$

$$\Delta b_{(B1-B2)} = -9,3 \quad \Delta b_{(B2-B3)} = +5,8$$

$$\Delta L_{(B1-B3)} = -18,8$$

$$\Delta a_{(B1-B3)} = +6,08$$

$$\Delta b_{(B1-B3)} = -3,47$$

As can be seen from the above values of Δa , Δb and ΔL , in the case of sample A, the colouring variation between the two A1 and A3 extremes of said sample is very low, while in the case of sample B, the colouring variation between the two B1 and B3 extremes is significantly high, involving even a sign inversion for the value of "a" and "b" factors. Said variation, in the case of sample B, corresponds in fact to a colour variation from yellow-green of zone B1 to blue-grey of zone B2 up to bronze of zone B3 of said sample.

Repeating the test, while samples A showed a high reproducibility of colour shades, operating conditions being the same, in samples B the same result could not be observed.

EXAMPLE 2

Part of the samples, treated as described above with respect to pickling, neutralization, modification and conditioning, have been electrocoloured as described in example 1, but utilizing the following composition for the electrocolouring electrolytic bath:

NiSO ₄ 7H ₂ O	20 g/l
(NH ₄) ₂ SO ₄	40 g/l
H ₃ BO ₃	30 g/l
MgSO ₄ 7H ₂ O	30 g/l

Samples so electrocoloured showed, compared to controls obtained with electrolytic colouring baths according to prior art, colour stabilization in the shades of green-grey, homogeneity of distribution of said colouring and high reproducibility of the colour shade.

EXAMPLE 3

In this case, samples have been pickled, neutralized, anodized and then modified and conditioned according to the already described process.

The electrocolouring treatment has been carried out in a bath having a capacity of 52 l, utilizing the same electrolytic bath composition as described in example 1.

The aluminium treated had a surface of 25 dm², the temperature at which electrocolouring has been carried out was of 23 °C, operating voltage was 12-13V; colouring times have been varied according to the following scheme:

TIME	COLOUR OBTAINED
4 minutes	blue
8 minutes	middle blue-grey
15 minutes	light blue-grey

The comparison has been made on samples treated in the same conditions but electrocoloured with a Carmiol-type conventional bath.

Also in this case, the samples submitted to electrocolouring utilizing the composition of example 1 produced more permanent, homogeneous and reproducible colours compared to those obtained by electrocolouring according to prior art.

Some of electrocolouring samples have been exposed to the accelerated test of exposure to U.V. light lamp, obtaining evaluation indexes over grade 8 of the blue scale.

All of the samples have been fixed after electrocolouring according to techniques known, such as: hot-fixing in AS salt or cold plus hot-fixing according to Qualanod standard.

Claims

1. A process for electrocolouring by optical interference aluminium and its alloys, comprising the following stages: anodic oxidation; modification through electrolysis in phosphoric acid solution; electrocolouring by utilizing a solution comprising at least a salt of a colouring metal and a support electrolyte; a final fixing, which process is characterized in that said electrocolouring stage is carried out by utilizing an electrolytic solution in which the concentration of colouring metal is comprised between 0.018 and 0.1 moles/l.
2. A process for electrocolouring according to claim 1, characterized in that said colouring metal is nickel or cobalt.
3. An electrocolouring process according to claim 1, characterized in that between said stage of modification with phosphoric acid and said stage of electrocolouring, a stage of conditioning of the oxide layer is inserted, which stage is carried out by treatment with an aqueous diluted solution of an acid chosen among the group comprising sulphuric acid, perchloric acid, hydrochloric acid, hydrobromic acid, oxalic acid, sulphamic acid and trifluoroacetic acid.
4. A process according to claim 1, characterized in that said support electrolyte comprises magnesium sulphate.
5. An electrolytic solution for electrocolouring according to claims 1 and 3, characterized in that it comprises the following constituents:

- Colouring metal	0.018 to 0.1 moles/l
- Electrolytic support salts	55 to 75 g/l
- pH regulators, acids and various known additives	30 to 100 g/l

6. An electrolytic solution according to claim 5, characterized in that said electrolytic support salts are constituted by a mixture of magnesium sulphate and ammonium sulphate.



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EUROPEAN SEARCH REPORT

Application Number

EP 93 10 1547

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	CHEMICAL ABSTRACTS, vol. 90, no. 12, March 1979, Columbus, Ohio, US; abstract no. 94398u, TSUTOMU 'electrolytic coloring aluminium and its alloys' page 441 ; & JP-A-53 128 547 (FUJISASH INDUSTRIES LTD) 9 November 1978 ---	1,2,3	C25D11/22
X	CHEMICAL ABSTRACTS, vol. 96, no. 10, March 1982, Columbus, Ohio, US; abstract no. 76532c, KATSUO 'ELECTROLYTIC COLORING OF ALUMINIUM' page 520 ; * abstract * & JP-A-53 147 635 (SANKYO ALUMINIUM INDUSTRIES CO) 22 December 1978 ---	1,2	
A	US-A-4 152 222 (SHEASBY) -----		TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C25D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 11 JUNE 1993	Examiner NGUYEN THE NGHIEP N.
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			