(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 597 795 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
22.01.2020 Bulletin 2020/04

(21) Application number: **19187128.4**

(22) Date of filing: **18.07.2019**

(51) Int Cl.:
C25D 11/08 *(2006.01)* ***C25D 11/10*** *(2006.01)*
C25D 11/24 *(2006.01)*

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **18.07.2018 IT 201800007314**

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(54) ANODIZATION METHOD FOR CORROSION PROTECTION OF ALUMINIUM OR ALUMINIUM ALLOY ELEMENTS USED IN AN AIRCRAFT STRUCTURE

(57) An anodization method for corrosion protection of an aluminium or aluminium alloy element used in an aircraft structure, **comprising** the following steps: a) subjecting the element to a degreasing step by means of an alkaline bath (block 100) for removing contaminating elements; b) subjecting the element to a subsequent first washing in water (block 110); c) subjecting the element to an acid pickling step (120) by dipping the element in an acid solution and then extracting the element from the acid solution and subjecting the element to a subsequent washing in water; (d) subjecting the washed element to a subsequent electrochemical treatment step in a tank (140) by dipping the element in a solution of tartaric acid ($C_4H_6O_6$) and sulphuric acid (H_2SO_4); e) subjecting the element to a subsequent washing in water (150); f) dipping (block 170) the element in a bath in which a solution of chromium, with an oxidation number of +3, and zirconium ions and fluorides is present, in order to carry out a first post-anodization sealing step; g) extracting the element from the bath of step f) and subjecting it to a subsequent final washing and a subsequent dipping in a tank of boiling water (second sealing step), and then drying the element (block 180).

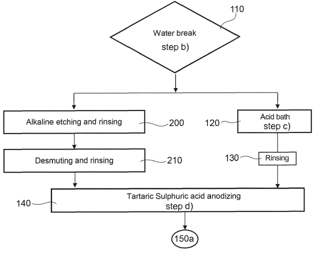

FIG. 1

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Printed by Jouve, 75001 PARIS (FR)

Description

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This patent application claims priority from Italian patent application no. 102018000007314 filed on July 18, 2018.

TECHNICAL FIELD

[0002] The present invention relates to an anodization method for corrosion protection of aluminium or aluminium alloy elements used in an aircraft structure.

BACKGROUND OF THE INVENTION

[0003] As is known, in order to protect aluminium or aluminium alloy elements used in an aircraft structure, anodization methods have been developed to provide a thin (a few microns) protective layer of metal oxide, which protects the underlying aluminium/aluminium alloy from corrosion. This layer of metal oxide also facilitates the subsequent painting of the aircraft structures and also increases the surface electrical resistance of the aircraft structure.

[0004] Typically, the known anodization processes comprise a plurality of steps, including:

a) subjecting the element to a degreasing step by means of an alkaline bath for removing contaminating elements, such as for example oils, fats, lubricants, protective layers, dusts and residues in general - then subjecting it to a first washing in water;
b) subjecting the element to an acid pickling step. Then extracting the element from the acid solution and subjecting the element to a subsequent washing in water. This step contributes to the removal of natural oxide, thermal oxides, traces of materials deposited as a result of mechanical processing, scratches, discolourations, mild corrosion;
c) subjecting the washed element to a subsequent electrochemical treatment step by dipping the element in a chromic acid solution (using chromium with an oxidation number of +6 - hexavalent chromium) and applying an electric potential to this element;
d) subjecting the element to a subsequent second washing in water;
e) dipping the element in a bath in which a solution of a chromium compound with an oxidation number of +6 (hexavalent chromium) is present, in order to carry out a post-anodization sealing step;
f) extracting the element from the bath of step e) and subjecting it to a third final washing.

[0005] This method uses very dangerous compounds, such as H_2CrO_4, commonly called chromic acid where the chromium has an oxidation number of +6; it is a highly oxidizing species.

[0006] The chemical reaction that occurs is the following: Electrochemical reaction at the anode:

$$\mathbf{2Al + 3H_2O = Al_2O_3 + 6H^+ + 6e^-}$$

[0007] Electrochemical reaction at the cathode:

$$\mathbf{6H^+ + 6e^- = 3H_2}$$

[0008] Resulting anodization reaction:

$$\mathbf{2Al + 3H_2O => Al_2O_3 + 3H_2}$$

[0009] Aluminium chromate will also be formed according to the following mechanism:

chromic anhydride -> chromic acid -> aluminium chromate CrO_3 -> H_2CrO_4 -> $Al_2(CrO_4)_3$

[0010] Furthermore, on the basis of experimental and epidemiological evidence, chromium with an oxidation number of +6 (hexavalent chromium) has been classified by IARC as a human carcinogen (Class I).

[0011] With regard to the effects on health, several studies have demonstrated that exposure to hexavalent chromium is one of the possible causes of lung cancer, as it is mutagenic and carcinogenic. In fact, the respiratory system is the main target of the toxic and carcinogenic action, and acute and chronic occupational exposure occurs above all by absorption through inhalation. The toxicity of the hexavalent form at the intracellular level appears above all with the numerous molecular and structural alterations caused by the unstable [Cr(V) and Cr(IV)] and stable [Cr(III)] forms resulting from the reduction process.

[0012] US2015020925 describes a method for the surface treatment of an aluminum, magnesium or one of its alloys, to protect the part from corrosion. The method consists in consecutively immersing the part in the following two baths:

- first aqueous bath at low temperatures containing a corrosion inhibiting metal salt and an oxidizing compound to form a conversion coating on the surface of the part containing oxides, hydroxides and fluorides based on Zirconium / Chromium;
- a second aqueous bath, kept at a temperature below 80 ° C and containing an oxidizing compound and a rare earth salt corrosion inhibitor. Through the presence of hydrogen peroxide, the oxidation of chromium is obtained from the trivalent to the hexavalent form and the formation of chromates.

[0013] The method can be performed for the chemical conversion of aluminum or its alloys and magnesium or its alloys, on parts that have not been previously treated or after anodizing the piece to seal the anodic layer.

[0014] Therefore, there is a need to develop a method which does not use toxic/carcinogenic materials and allows the formation of an oxide layer that provides good protection to the underlying aluminium/aluminium alloy.

SUMMARY OF THE INVENTION

[0015] The above object is achieved by the present invention in so far as it relates to an anodization method for corrosion protection of an aluminium or aluminium alloy element used in an aircraft structure, **comprising** the following steps:

a) subjecting the element to a degreasing step by means of an alkaline bath (block 100) for removing contaminating elements;
b) subjecting the element to a subsequent first washing in water (block 110);
c) subjecting the element to an acid pickling step (120) by dipping the element in an acid solution and then extracting the element from the acid solution and subjecting the element to a subsequent washing in water;
d) subjecting the washed element to a subsequent electrochemical treatment step in a tank (140) by dipping the element in a solution of tartaric acid ($C_4H_6O_6$) and sulphuric acid (H_2SO_4) and applying an electric potential to said element;
e) subjecting the element to a subsequent second washing in water (150);
f) dipping (block 170) the element in a bath in which a solution of chromium, with an oxidation number of +3, and zirconium ions and fluorides is present, in order to carry out a post-anodization sealing step;
g) extracting the element from the bath of step f) and subjecting it to a third final washing in water and a subsequent dipping in a tank of boiling water, which provides a second sealing step, and then drying the element (block 180) .

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] The invention will now be illustrated with reference to the accompanying figures wherein:

Figure 1 represents a non-limiting embodiment showing the main steps of the method according to the present invention; and
Figure 2 specifies one step of the method of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0017] With reference to Figure 1, the anodization method for corrosion protection of an aluminium or aluminium alloy element used in an aircraft structure **comprises** the following steps:

a) subjecting the element to a degreasing step by means of an alkaline bath (block 100) for removing contaminating elements, such as for example oils, fats, lubricants, protective layers, dusts and residues in general. Typically, step a) is carried out by dipping the element in the alkaline bath for a time interval of 10 - 20 minutes. Typically, the alkaline bath has a temperature of approximately 55 ± 5 degrees Celsius.
b) subjecting the element to a subsequent first washing in water (block 110). Typically, step b) is carried out with water for a time ranging from 2 to 5 minutes at a temperature below 35 degrees Celsius.
c) subjecting the element to an acid pickling step (block 120) by dipping the element for approximately 5-10 minutes in an acidic solution based on ferric sulphate and a mixture of acids maintained at a temperature comprised between 20°C and 40°C and then extracting the element from the acidic solution and subjecting the element to a subsequent

washing in water (block 130 following block 120) for 4 - 10 minutes at room temperature and assessing the film of water. Checking by assessing the film of water on the surface of the part during the rinsing ensures the effectiveness of the pretreatment. Step c) contributes to the removal of natural oxide, thermal oxides, traces of materials deposited as a result of mechanical processing, scratches, discolourations, mild corrosion;

d) subjecting the washed element to a subsequent electrochemical treatment step in a tank (block 140) by dipping the element in a solution of tartaric acid ($C_4H_6O_6$) and sulphuric acid (H_2SO_4) and applying an electric potential, wherein the aluminium/aluminium alloy element behaves as the anode (positive pole) whereas the negative electrode (or cathode) is represented by the tank. Step d) is carried out with a solution having a temperature comprised between 36 and 39 degrees Celsius. The typical concentration of tartaric acid is 72-88 g/l and that of sulphuric acid is 36-44 g/l.

The chemical reaction occurring in step d) is the following:

Electrochemical reaction at the anode:

$$\mathbf{2Al + 3H_2O = Al_2O_3 + 6H^+ + 6e^-}$$

Electrochemical reaction at the cathode:

$$\mathbf{6H^+} + \mathbf{6e^- = 3H_2}$$

Resulting anodization reaction:

$$\mathbf{2Al + 3H_2O => Al_2O_3 + 3H_2}$$

Aluminium sulphate, which contributes to the protection of the underlying metal/metal alloy, will also be formed according to the following mechanism:

$$\mathbf{3H_2SO_4 + 2Al \longleftrightarrow Al_2 (SO_4)_3 + 3H_2}$$

Step d) is typically performed using the following parameters (see Figure 2):

- applying on the element the voltage within one minute from the dipping of the element in the solution;
- subsequently and without interruption applying on the element an increasing voltage with a ramp not exceeding 3 volts per minute;
- subsequently and without interruption applying on the element a constant voltage (approximately 14 Volts) for approximately 20 minutes, and thereafter;
- gradually reducing the applied voltage to a null value in approximately one minute;
- removing the element from the solution within 3 minutes from the switching off of the voltage

e) subjecting the element to a subsequent second washing in water (block 150). Typically, step e) **comprises** an optional rinsing step by dipping in industrial water (block 150a) at room temperature and a subsequent rinsing step by dipping in purified water at room temperature (block 150b).

Subsequently, the washed element is subjected to visual inspection by an operator (block 160) and, if this step is fulfilled, the following step is carried out:

f) dipping (block 170) the element in a bath in which chromium, with an oxidation number of +3, zirconium ions and fluorides (resulting from salts and fluorozirconates/silicates) are present, in order to carry out a first post-anodization sealing step;

The chemical reaction that occurs is the following:

$$\mathbf{4Al2O3 + 24F^- + 3Zr^{+4} + 4Cr^{+3} \rightarrow 8AlF3 + 3ZrO2 + 2Cr2O3}$$

Typically, the dipping time in step f) is comprised between 2 and 20 minutes. It is suggested a time comprised between 2 and 3 minutes.

g) extracting the element from the bath of step f) and subjecting it to a third final washing and a subsequent dipping in a tank of boiling water (temperature comprised between 95 and 100 degrees Celsius, pH ranging from 4.5 to 7, for approximately 30 minutes), which provides a second sealing step, according to the following reaction:

$$\mathbf{Al_2O_3 + H_2O \text{ -> } 2\ AlO\ (OH)\ \text{(an aluminium oxide hydroxide-böhmite)}}$$

Which results in a volume increase, which is responsible for the "filling" of the pores of the anodic oxide. The reduction in porosity resulting from alumina hydration drastically reduces the adsorption capacity, making the surface insensitive to fingerprints, colour and grease stains, and giving the oxide a greater resistance to corrosion. To achieve the above reaction and to obtain AlO (OH) (aluminum hydroxide oxide), the temperature has a fundamental influence. If in fact the temperature were lower than the one highlighted above, a layer of aluminum hydroxide [Al (OH) 3] would be created with different characteristics and with a percentage of hydration of the oxide that would not guarantee the same resistance to corrosion.

[0018] Drying the element (block 180). Typically, the drying can be carried out in a dust-free environment, for example an oven that reaches a temperature between 45 and 65 degrees Celsius for at least 20 minutes.

[0019] Between step b) and step d) the following further steps may also be carried out, optional to step c), which is carried out anyway:

rapid alkaline chemical etching (block 200) with a caustic soda based solution in order to prepare/activate the aluminium/aluminium alloy surfaces for the electrochemical treatment in step d). Typically, this step is carried out by dipping the element in an alkaline solution having a temperature of approximately 60 degrees for 30-60 seconds; and

[0020] Aluminium desmutting and rinsing (block 210). Typically, this step of clearing the blackening due to the preceding alkaline bath is performed by dipping the element in a clearing solution (based on ferric sulphate and a mixture of acids) at room temperature (approximately 25 degrees) for 5-10 minutes.

[0021] From the above description it appears that the method of the present invention, in particular the sealing (step f), does not use highly toxic, and in particular carcinogenic compounds, such as chromium with an oxidation number of +6. The sealed oxide layer has a sensibly constant thickness of a few microns (typically from 2 to 7 microns) and good adhesion characteristics. The elements are therefore effectively protected from corrosion.

[0022] The Applicant performed a series of mechanical fatigue tests on samples subjected to the method of the present invention. The tests were carried out on cylindrical specimens treated according to the method of the present invention in accordance with standard EN6072 provided in the aeronautical field. Results were plotted in a Wohler curve at various load levels.

[0023] By comparing the data, the treatment according to the present method was thus shown not to alter the fatigue resistance of the sample, which complies with the CS 25.571 aeronautical directives. Corrosion tests, which were carried out in a salt spray chamber for ASTM B 117, also performed well. In this case, a salt spray chamber was used, which was capable of providing a controlled saline environment fed by a 5% NaCl salt solution. Tests for permanence in the salt spray for 336 hours were brilliantly passed.

[0024] Tests for adhesion of the paint to the elements treated according to the method of the present invention were also carried out. These tests were carried out in accordance with ISO 2409 standard after dipping in demineralized water at 23 degrees Celsius for 14 days. The test consists in squaring off, after the dipping in water, the paint layer with a six-blade cutter, arranging and pressing a layer of tape against the squared paint and then tearing off the tape quickly. The tests gave a positive result, with a detachment of the coating paint of less than 5%.

Claims

1. An anodization method for corrosion protection of an aluminium or aluminium alloy element used in an aircraft structure,
comprising the following steps:

a) subjecting the element to a degreasing step by means of an alkaline bath (block 100) for removing contaminating elements;
b) subjecting the element to a subsequent first washing in water (block 110);
c) subjecting the element to an acid pickling step (120) by dipping the element in an acid solution and then extracting the element from the acid solution and subjecting the element to a subsequent washing in water;
d) subjecting the washed element to a subsequent anodization step in a tank (140) by dipping the element in a solution of tartaric acid ($C_4H_6O_6$) and sulphuric acid (H_2SO_4) and applying an electric potential to said element that acts as anode;
e) subjecting the element to a subsequent second washing in water (150);
f) dipping (block 170) the element in a bath in which a solution of chromium, with an oxidation number of +3, and zirconium ions and fluorides is present, in order to carry out a post-anodization sealing step;
g) extracting the element from the bath of step f) and subjecting it to a third final washing in water and a subsequent dipping in a tank of water having a temperature comprised between 95° and 100°, which provides a second sealing step, and then drying the element (block 180).

2. The anodization method as defined in claim 1, wherein step c) is carried out by dipping the element in an acid bath for a time interval of 5 to 10 minutes.

3. The anodization method as defined in claim 1 or 2, wherein step c) is carried out by dipping the element in an acid bath having a temperature of 20°C to 40°C.

4. The anodization method as defined in any one of the preceding claims, wherein step d) is configured to perform the following chemical reactions:

Electrochemical reaction at the anode:

$$2Al + 3H_2O = Al_2O_3 + 6H^+ + 6e^-$$

Electrochemical reaction at the cathode:

$$6H^+ + 6e^- = 3H_2$$

Resulting anodization reaction:

$$2Al + 3H_2O => Al_2O_3 + 3H_2$$

5. The anodization method as defined in any one of the preceding claims, wherein step d) is carried out using the following parameters:

applying to the element the voltage within one minute from the dipping of the element in the solution;
applying to the element an increasing voltage with a ramp not exceeding 3 volts per minute;
subsequently and without interruption applying to the element a constant voltage for approximately 20 minutes, and thereafter;
gradually reducing the applied voltage to a null value;
removing the element from the solution within 3 minutes from the switching off of the voltage.

6. The anodization method as defined in any one of the preceding claims, wherein step d) is carried out using a solution having a temperature ranging between 36°C and 39°C.

7. The anodization method as defined in any one of the preceding claims, wherein step g) is carried out in a tank of boiling water with a temperature higher than 95°C and a pH ranging between 4.5 and 7 for approximately 30 minutes.

8. The anodization method as defined in any one of the preceding claims, wherein in step d) the concentration of tartaric acid is 72-88 g/l and the concentration of sulphuric acid is 36-44 g/l.

9. The anodization method as defined in any one of the preceding claims, wherein step f) performs the following chemical reactions:

$$4Al2O3 + 24F^- + 3Zr^{+4} + 4Cr^{+3} \rightarrow 8AlF3 + 3ZrO2 + 2Cr2O3$$

10. The anodization method as defined in any one of the preceding claims, wherein between step b) and step d) the following further steps are also carried out:

alkaline chemical etching (200) in order to prepare/activate the aluminium/aluminium alloy surfaces for the electrochemical treatment in step d); and
aluminium/aluminium alloy desmutting and rinsing (210).

11. The anodization method as defined in any one of the preceding claims, wherein said boiling water has a pH ranging between 4.5 and 7.

12. The anodization method as defined in any one of the preceding claims, wherein said fluorides result from salts and fluorozirconates/silicates.

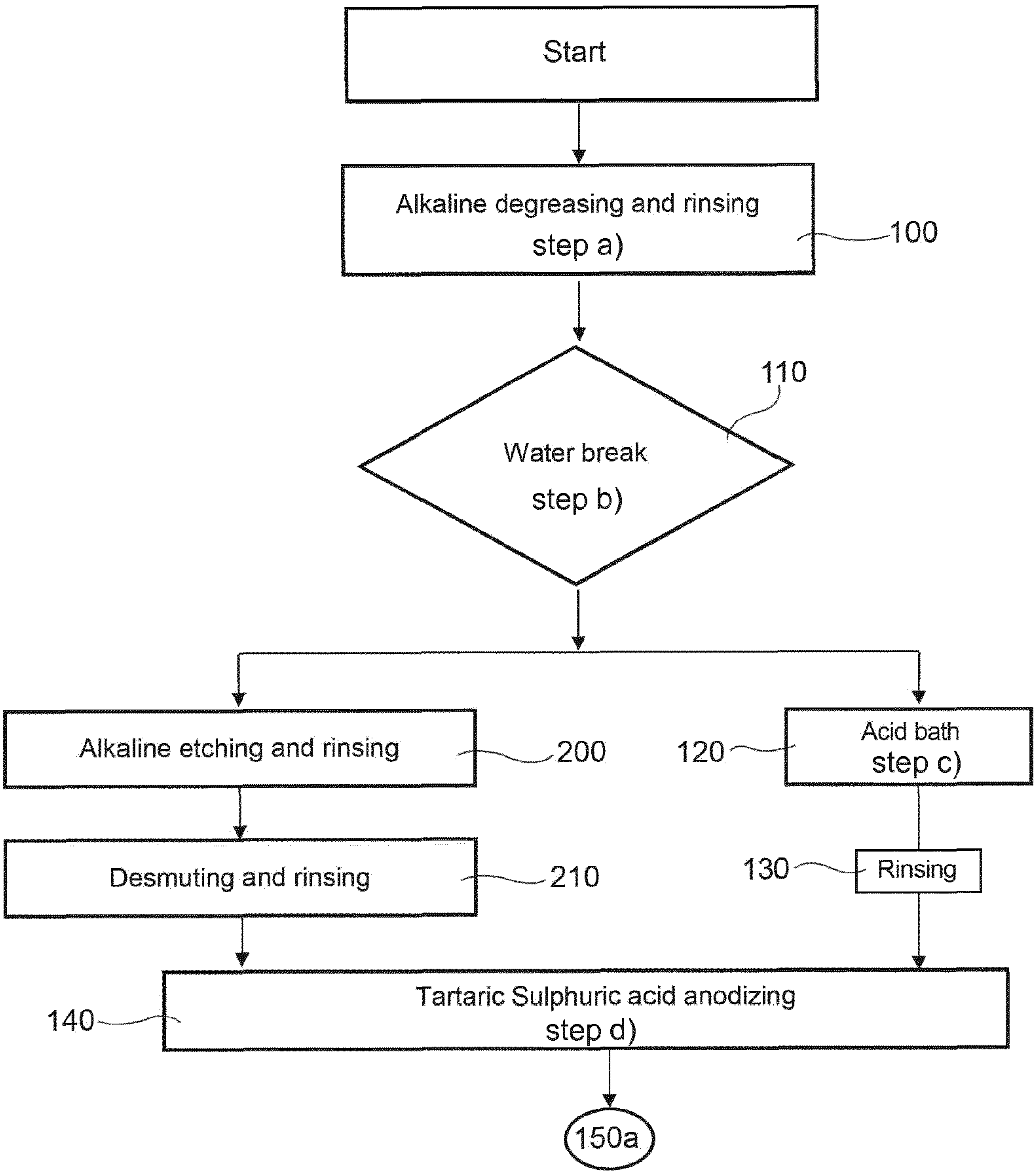

Start
Alkaline degreasing and rinsing
step a)
100
110
Water break
step b)
Alkaline etching and rinsing
200
120
Acid bath
step c)
Desmuting and rinsing
210
130
Rinsing
140
Tartaric Sulphuric acid anodizing
step d)
150a

FIG. 1

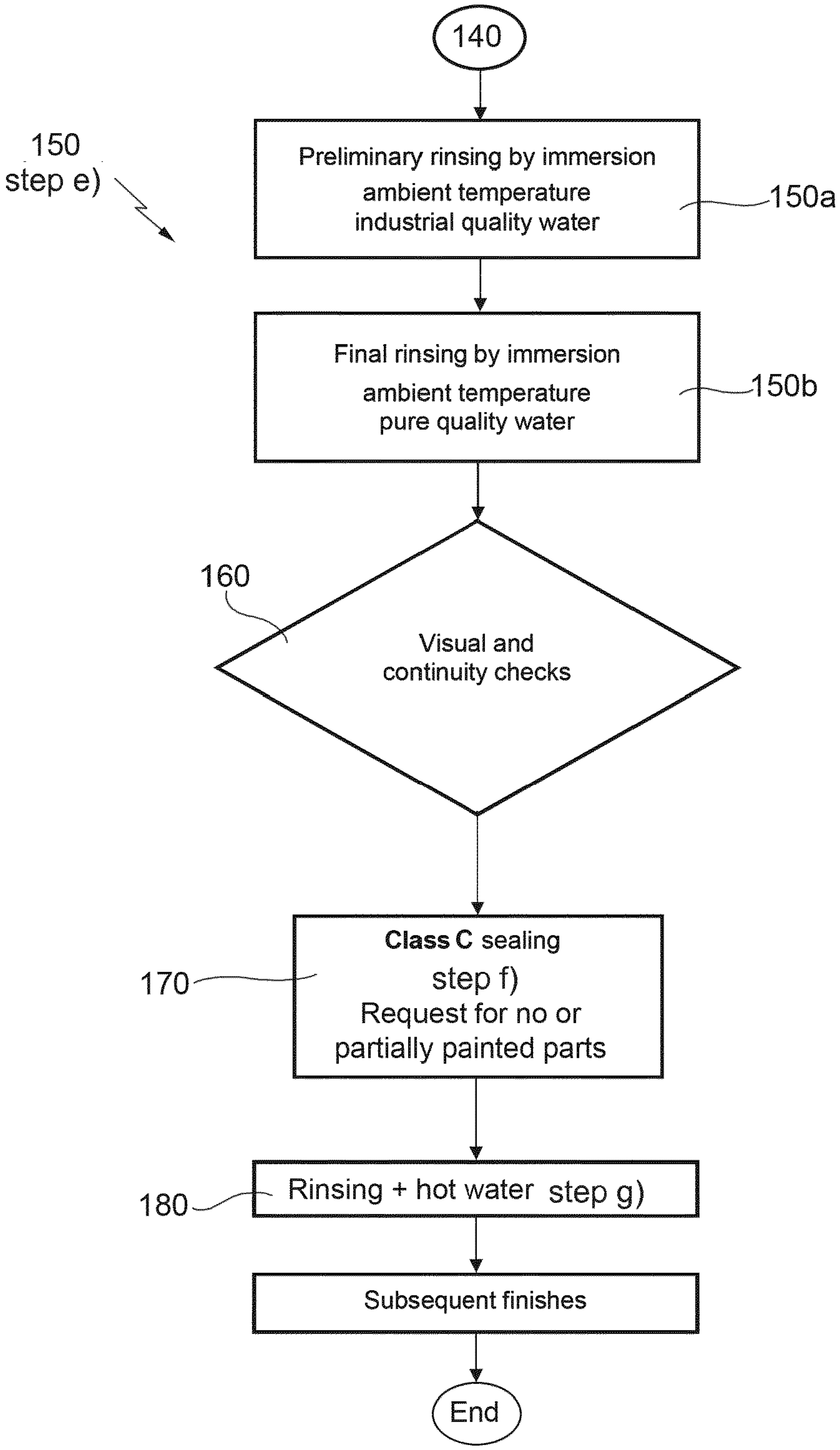
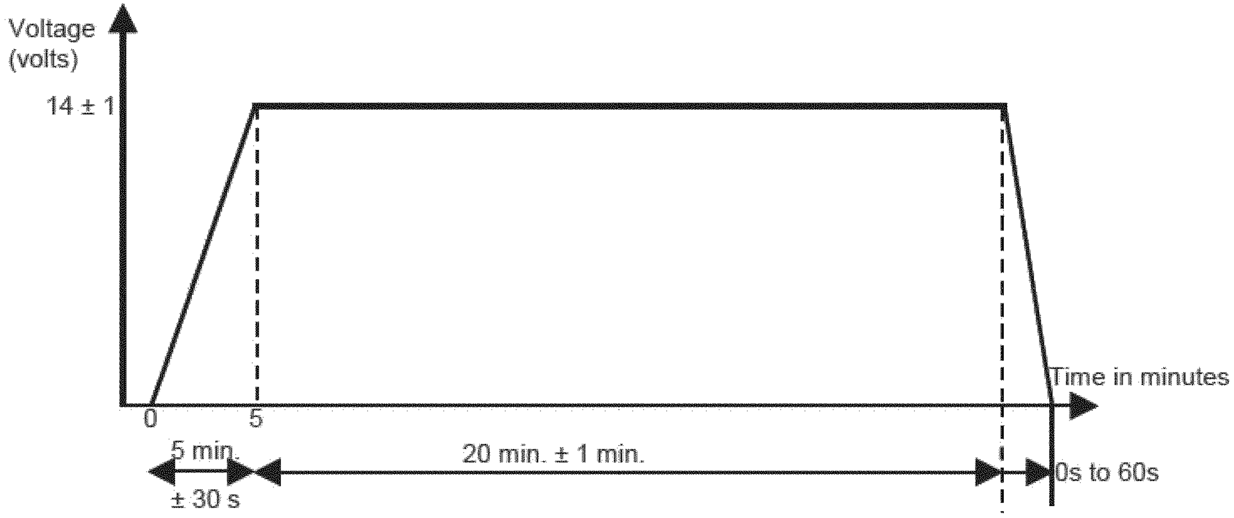

140
150
step e)
Preliminary rinsing by immersion
ambient temperature
industrial quality water
150a
Final rinsing by immersion
ambient temperature
pure quality water
150b
160
Visual and
continuity checks
170
Class C sealing
step f)
Request for no or
partially painted parts
180
Rinsing + hot water step g)
Subsequent finishes
End

FIG. 1



Graph: Anodizing electrolytic cycle

FIG. 2

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EUROPEAN SEARCH REPORT

Application Number
EP 19 18 7128

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	US 2015/020925 A1 (BARES PIERRE [FR] ET AL) 22 January 2015 (2015-01-22) * column 3, lines 24-50 * * column 5, lines 47-60 * * column 3, line 61 - column 4, line 22 * * column 6, line 64 - column 7, line 9; examples 1, 4 * * column 7, lines 13-17; example 4; tables 8,12 * -----	1-12	INV. C25D11/08 C25D11/10 C25D11/24
Y	WO 03/040437 A1 (US NAVY [US]; MATZDORF CRAIG A [US]; KANE MICHAEL J [US]; GREEN JAMES) 15 May 2003 (2003-05-15) * page 7, lines 13-34; claims 6,7; table 1 * * page 6, lines 23-31 * -----	1-12	
A	US 2006/226020 A1 (OHTANI TOMOHIRO [JP] ET AL) 12 October 2006 (2006-10-12) * table 1 * -----	10	

TECHNICAL FIELDS SEARCHED (IPC)
C25D C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	31 July 2019	Suárez Ramón, C

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

1

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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