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

(11) EP 3 960 899 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
02.03.2022 Bulletin 2022/09

(21) Application number: **21193393.2**

(22) Date of filing: **26.08.2021**

(51) International Patent Classification (IPC):
C23C 18/12 $^{(2006.01)}$ ***C25D 11/24*** $^{(2006.01)}$

(52) Cooperative Patent Classification (CPC):
C25D 11/246; C23C 18/122; C23C 18/1245

(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: **28.08.2020 IT 202000020590**

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(54) ANODIZED LAYERS RESISTANT TO ACID AND ALKALI

(57) The present invention relates to a process for coating an anodised aluminium or anodised aluminium alloy substrate in which a solution comprising at least one alkaline silicate, at least one silane and at least one siloxane and/or one polysiloxane is applied to the substrate and left to dry at a temperature comprised between 55°C and 80°C.

The invention also relates to an anodised aluminium or anodised aluminium alloy substrate coated with a protective layer obtained by the application of the solution comprising at least one alkaline silicate, at least one silane and at least one siloxane and/or one polysiloxane on the aluminium oxide layer. The coated substrate according to the invention resists at pHs from 1 to 13.5.

Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

[0001] The present invention relates to a surface treatment method for anodised aluminium or alloys thereof to make the anodised aluminium resistant to corrosion by acidic and/or alkaline agents, in particular for use in the automotive sector.

PRIOR ART

[0002] The automotive industry has recently imposed very high alkali resistance standards for the anodised aluminium used for automotive components, which can hardly be overcome by aluminium anodised and fixed in a conventional manner.

[0003] The electrochemical formation of oxide on aluminium or alloys thereof has long been used to produce protective and/or decorative layers on such metals for various uses and for different sectors.

[0004] The oxide layer is electrochemically formed on the metal by means of known processes in the sector. Once formed, the oxide layer has a porosity which can be useful if any colours are to be applied, but has the great disadvantage of not protecting the metal from corrosion. To overcome this problem, the anodised aluminium is usually subjected to a subsequent step of fixing the pores, for example by hot hydration or cold impregnation, which causes an expansion or swelling of the oxide layer and consequent closure of the pores.

[0005] The hot fixing of the pores is normally carried out with hot water in the presence of any additives, or with steam, while the cold fixing involves temperatures of 30°C and the presence of nickel fluoride.

[0006] These conventional fixing technologies allow the closure of the pores and resistance to corrosion and atmospheric agents.

[0007] However, such a treatment is not sufficient to allow the anodised aluminium to pass the tests required by the automotive industry, such as:

- Production standard 9.57448 (FIAT Group)
- Anorganische Schutzschicht Auf Aluminiumteilen - Oberflaechenschutzanforderung TL182 Volkswagen AG;
- GMW 14665, "Anodic Oxidation Coating on Aluminum" (General Motors Material Specification Finish - Worldwide Engineering Standards, January 2009).

[0008] The tests indicated above are similar and other well-known car manufacturers also apply similar tests.

[0009] The most critical test, as written in point 2.4.5 of the FCA specifications and similarly in the other specifications above, involves subjecting the anodised aluminium samples to the following test cycle:

- Immersion for 10 min. ± 30 sec. in acid solution at pH = 1 (1)
- Rinsing with running water and drying with compressed air.
- Time in stove for 1 h ± 5 min. at 40 °C ± 3 °C.
- Immersion for 10 min. ± 30 sec. in alkaline solution at pH = 13.5 (2)
- Rinsing with running water and drying with compressed air.

(1) 0.1 molar HCl solution
(2) Aqueous solution of 12.7 g/l NaOH + 4.64 g Na_3PO_4 + 0.33 g/l NaCl.

[0010] At the end of the test, the standard states that no aesthetic alterations must be observed with respect to an untreated sample.

[0011] It is true that all car manufacturers allow the use of a sol-gel technology on parts which must pass this test in order to further seal the pores of the aluminium oxide, but such application tends to "dull" a material requested as glossy and possibly coloured. A typical example of such parts can be windscreen wiper blades or the glossy, aluminium mouldings of many cars.

[0012] Maintaining the glossy appearance typical of polished, anodised and possibly coloured aluminium and passing the test indicated above is not at all simple, also because the use of sol-gel technology involves the use of silanes, which usually leave a polymer film on the treated surfaces which is not perfectly colourless or transparent.

[0013] The most complex aspects to overcome are as follows:

- Maintaining a glossy metallic appearance of the anodised aluminium even after a sol-gel type treatment;
- Resistance at pH = 13.5, i.e., at a pH greater than pH 12.5 to which the current finishes applied on anodised aluminium

already resist;

- Resistance at pH = 1 is certainly a critical point because hydrochloric acid attacks aluminium with a radical and exothermic reaction.

[0014] It is known to use an anodised aluminium finishing treatment for window frames which consists of a transparent (possibly glossy) electrophoretic coating of the type known as "E.D. coat" or, simply ED. This coating would allow anodised aluminium to pass the tests of car manufacturers, but the polymer layer of paint is visible to the naked eye and therefore may not be accepted in this sector.

[0015] To increase the corrosion resistance of anodised aluminium or alloys thereof, even when used in the automotive sector, surface treatments with silicate or silane solutions, possibly even in a mixture, are known.

[0016] For example, EP1873278 discloses an aluminium treatment, anodised and fixed, with a solution of alkaline silicates. The treatment serves to increase the corrosion resistance of the aluminium for uses in the automotive sector. According to this publication, the silane coating ensures a resistance up to pH 13.5.

[0017] JP2003183889 discloses a method for increasing the corrosion resistance of anodised aluminium. Such a method involves applying a silane solution to the surface of the aluminium.

[0018] US2015/0034487 relates to a method for improving the corrosion resistance of anodised and partially fixed aluminium up to pH 13.5 which consists in applying a solution containing an orthosilicate and a non-alkali silicate to the surface of the aluminium and then heating to 200°C for one hour. This treatment may result in the irreversible rupture of the oxide layer. Anodised aluminium treatments are also known in which a first layer of alkaline silicate is applied, followed by a second layer of silane.

[0019] This process is described in EP3245317 where it is indicated that the piece of aluminium thus treated withstands the automotive tests listed above, i.e., at pH 1 and pH 13.5.

[0020] However, the product obtained after treatment with silicates and silane in two steps exhibits a weight loss of at least 10 mg/dm^2 of surface when subjected to the alkali resistance test established by the rules of the car manufacturers. This result indicates that the treatment does not allow the product to pass the test without altering the functional and aesthetic properties thereof.

[0021] Therefore, the need remains in the sector to provide a surface treatment method of anodised aluminium (or alloys thereof) that allows to pass the tests at acidic and basic pHs (in particular at pH 1 and 13.5) established by car manufacturers without altering the aesthetic appearance and properties of the aluminium. This is in order to make such a substrate resistant to the atmospheric and chemical agents to which cars are subjected. In particular, the anodised aluminium components used for the construction of cars must withstand the products used in car washes which are solutions, foams, dispersions etc. which have a pH of about 13.5 or higher.

SUMMARY OF THE INVENTION

[0022] The present invention relates to a process for coating an anodised aluminium comprising treating anodised aluminium with a solution containing silicates, silanes and siloxanes and subsequently heating it to a temperature comprised between 55°C and 80°C.

[0023] The solution can also possibly comprise a surfactant.

[0024] Prior to the treatment according to the invention, the anodised aluminium substrate can be treated with conventional methods for pore closure (fixing).

[0025] In one embodiment the anodised aluminium substrate can be coloured by methods known in the sector.

[0026] The invention also relates to an anodised aluminium substrate or alloys thereof coated with a coating derived from the process according to the invention.

[0027] The aluminium substrate treated with the process of the invention passes, without alterations, the test established by the rules of car manufacturers, i.e., it resists unaltered at pHs from 1 to 13.5.

BRIEF DESCRIPTION OF THE FIGURES

[0028]

Figure 1 shows the initial step of a resistance test at pH 13.5 of two anodised aluminium substrates: left substrate (black coloured) not treated with the coating of the invention and right substrate (silver) treated with the coating of the invention.

Figure 2 shows the end of the immersion test of figure 1.

Figure 3 shows black-coloured anodised aluminium substrates after immersion in a solution at pH 13.5. Left substrate not coated with the coating of the invention; right substrate coated with the coating.

Figure 4 shows uncoloured anodised aluminium substrates subjected to immersion tests in basic solution at pH

13.5. Left substrate not coated with the coating of the invention; right substrates coated with the coating.

DETAILED DESCRIPTION OF THE INVENTION

[0029] The present invention relates to a process for coating an anodised aluminium substrate or anodised aluminium alloys, comprising:

a) Applying to the substrate a solution comprising at least one alkaline silicate, at least one silane and at least one siloxane;
b) Drying the substrate at a temperature comprised between 55°C e 80°C.

[0030] The anodised aluminium substrate (or alloys thereof) is preferably a component used for the construction of vehicles, in particular cars, such as windscreen wiper blades, body parts such as doors and hoods, wheels and other components which have an aesthetic value. These substrates can be subjected to extreme pH conditions especially when placed in contact with washing solutions which normally reach pHs even above 13.5.

[0031] The anodised aluminium substrate (or alloys thereof) can also be a furnishing component, a frame for a window, a door, a floor, a wall, a shower enclosure, or other furnishing items. The aluminium substrate (or alloys thereof) is subjected to a conventional anodising process. Such a process can comprise some preliminary steps of preparing the substrate selected from:

- Substrate cleaning;
- Mechanical polishing, if necessary for aesthetic purposes; often the components of cars are glossy;
- Chemical brightening, if necessary for aesthetic purposes; usually the brightening is performed with chemical rather than electrochemical treatments, as the substrates are small in size;
- Acid pickling.

[0032] Before and after the acid pickling, it is possible to wash the substrate.

[0033] After the application of one or more of the preliminary treatments indicated above, the substrate is anodised by immersing the piece in an acid bath, preferably of sulphuric acid, and applying a current having a density usually comprised between 1.0 and 3.0 A/dm^2, preferably between 1.5 and 2.0 A/dm^2. The acid bath is maintained at a temperature comprised between 15°C and 23°C, preferably between 18°C and 21 °C, thermostated ± 0.5 with respect to the chosen temperature.

[0034] The treatment time is comprised between 30 and 60 minutes, preferably between 40 and 50 minutes.

[0035] After anodising, a colour can be applied, if necessary, for the desired applications. In this case an organic colour is used which is absorbed by the oxide or an electrolytic colouring is performed.

[0036] If the colour is applied by immersing the substrate in the dye, the colour must be pre-fixed by immersing the coloured substrate in a solution containing nickel acetate. The nickel ion binds to the dye molecule and forms nickel hydroxide within the pore of the aluminium oxide, preventing the dye from bleeding with the consequent discolouration of the dyed substrate. Preferably, a solution of 5-10 g/L of nickel acetate is used. Preferably, the solution is heated at a temperature comprised between 60° and 75°C.

[0037] This is a known technique, established by the Qualanod Specifications.

[0038] The aluminium oxide thickness which forms can vary from 5 to 25 μm.

[0039] Before applying the coating according to the present invention, it is preferable to proceed with the total or partial closure of the pores of the aluminium oxide with a fixing process.

[0040] The fixing can be done by hydration with boiling water, optionally in the presence of additives, or by means of steam or by impregnation with a solution containing nickel ions and fluoride ions. The latter is particularly useful if a colour is applied to the anodised substrate. Preferably, the fixing used for the present invention is a fixing with nickel fluoride at a temperature comprised between 25°C and 30°C.

[0041] Alternatively, a treatment with nickel acetate can be carried out at a temperature between 70°C and 90°C.

[0042] Alternatively, the pores can be fixed by immersion in hot water, optionally with appropriate additives, at a temperature between 90°C and 100°C.

[0043] The fixing takes place for a time comprised between 1 to 3 min/μm of oxide thickness.

[0044] Once the pores have been closed, a solution comprising at least one alkaline silicate, at least one siloxane and at least one silane is applied.

[0045] Alkaline silicate is also known as soluble glass because it is an amorphous material and has the appearance of a transparent glass. It is soluble in water and forms viscous and alkaline solutions. Chemically, it is alkaline metal silicate with general formula $M_2O \times nSiO_2$ (M = Na, K, Li), wherein n is comprised between 1.5 and 4. Preferably, the alkaline silicate is a sodium silicate. Alkaline silicate is normally a concentrated solution, obtained by dissolving glassy silicates in water, or by directly dissolving siliceous sand in NaOH.

[0046] The alkaline silicate is present in the solution in an amount comprised between 0.5 and 10 g/l, preferably between 1 -4 g/l.

[0047] The silanes have a general formula:

$$R'(CH_2)_nSi(OR)_3$$

wherein:

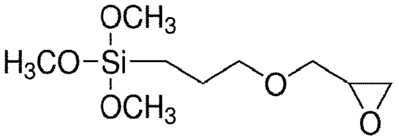
n is comprised between 2 and 4;
R' is a functional group selected from: vinyl, epoxy, glycidyloxy, methacrylate, primary amine, diamine, mercapto.
OR is a hydrolysable alkoxy group, such as methoxy (OCH_3), ethoxy (OC_2H_5) or acetoxy ($OCOCH_3$).

[0048] In a preferred embodiment, n is equal to 3 or 4, R' is vinyl, epoxy or glycidyloxy, OR is a methoxy group (OCH_3).

[0049] In a more preferred embodiment, the silane is selected from:

$$CH_2{=}CHSi(OCH_3)_3$$

$$CH_2{=}CHSi(OC_2H_5)_3$$



[0050] Preferably, the silane used in the solution of the invention is 3-glycidyloxypropyltrimethoxysilane having the formula given above.

[0051] Silane is present in the solution of the invention in an amount comprised between 0.5 g/L and 4 g/L, preferably between 1 g/L and 3 g/L.

[0052] Siloxanes are a class of chemical compounds in the structure of which the functional group R_2SiO is repeated, wherein R is a hydrogen or an alkyl or aryl group. The name "siloxane" comes from the combination of silicon, oxygen and alkane. They are considered part of the class of organo-siliceous compounds.

[0053] Siloxanes have a main, linear or branched chain, in which silicon and oxygen atoms -Si-O-Si-O- alternate with the R side chains bound to the silicon atoms.

[0054] Polymers of siloxanes wherein R is an alkyl group are commonly known as silicones or "polysiloxanes". The most representative examples of these polymers are $[SiO(CH_3)_2]_n$ (polydimethylsiloxane) and $[SiO(C_6H_5)_2]_n$ (polydiphenylsiloxane).

[0055] The synthesis of silicones generally begins with the hydrolysis of methyl chlorosilanes forming cyclosiloxanes: tetramethylchlorosilane, hexamethylchlorosilane, usually referred to as D4, D6 respectively. Cyclosiloxanes can be considered the "monomers" of silicone polymerisation. The polymerisation takes place in the presence of highly basic catalysts in a particular synthesis process which allows other siloxanes with alkyl, phenyl and vinyl terminations to be inserted into the polymer chain. With these introductions, the characteristics of the final polymer change considerably and, above all, can be modulated according to the needs of use with appropriate dosages.

[0056] The siloxane used in the solution of the invention is a siloxane and/or a polysiloxane.

[0057] The siloxane is preferably selected from:

alkoxymethylsiloxane,
polyvinyltrimethoxysiloxane,
polymethylvinylsiloxane,
hexamethylcyclotrisiloxane,
hexamethyldisiloxane,
polydimethylsiloxane, and
decamethylcyclopentasiloxane;

[0058] The polysiloxane is preferably selected from polyether siloxane and polyetheredimethylsiloxane.

[0059] Preferably, the solution comprises a siloxane preferably selected from: hexamethyldisiloxane and polydimethylsiloxane and a polysiloxane preferably selected from: polyether siloxane and polyetheredimethylsiloxane.

[0060] Siloxane is comprised in the solution in an amount from 0.1 to 1g/L, preferably 0.2 to 0.5 g/L. The polysiloxane is comprised in the solution in an amount from 0.1 to 1g/L, preferably 0.2 to 0.5 g/L.

[0061] The solution can comprise an anionic surfactant, preferably a disulphonate. If present, the surfactant is added in an amount comprised between 0.1 and 1% with respect to the volume of the solution, preferably between 0.2% and 0.5%.

[0062] The surfactant has the function of homogenising and making the solution clear and is particularly useful if anodised substrates with a glossy aesthetic effect are to be prepared, while if the substrates are frosted, the surfactant can also not be added, as on frosted surfaces (i.e., opaque and non-reflective), any aesthetic alterations are not visible.

[0063] The solution of the invention is applied to the substrate by immersing the same in the solution. The application time is comprised between 5 and 20 minutes, preferably between 7 and 15 minutes.

[0064] The solution is heated at a temperature comprised between 40°C and 85°C, preferably between 50°C and 80°C.

[0065] After immersion of the anodised substrate in the solution, the piece is dried, preferably without rinsing, at a temperature comprised between 55°C and 80°C, preferably between 60°C and 70°C.

[0066] The drying is preferably carried out with hot air.

[0067] The thickness of the layer obtained is comprised between 0.5 and 3 μm.

[0068] The process is self-limiting, as the thickness which is formed is not directly proportional to the immersion time; i.e., when a certain value is reached which depends on the operating conditions, the layer no longer increases.

[0069] The anodised substrate treated with the solution of the invention has been shown to pass the tests required by the FCA specifications, which envisage subjecting the anodised aluminium samples to the following test cycle:

- Immersion for 10 min. ± 30 sec. in acid solution at pH = 1 - (1)
- Rinsing with running water and drying with compressed air.
- Time in stove for 1 h ± 5 min. at 40 °C ± 3 °C.
- Immersion for 10 min. ± 30 sec. in alkaline solution at pH = 13.5 - (2)
- Rinsing with running water and drying with compressed air.

(1) 0.1 molar HCl solution
(2) Aqueous solution of 12.7 g/l NaOH + 4.64 g Na_3PO_4 + 0.33 g/l NaCl.

[0070] At the end of the test, the substrate does not have and must not have aesthetic alterations.

[0071] The invention also relates to an anodised aluminium substrate (or alloys thereof) coated with a coating layer obtainable by the application of the process according to the present invention.

[0072] Such a substrate is characterised in that it passes, without aesthetic alterations, the test established by the car manufacturers of resistance to acidic pHs equal to 1 and to basic pHs up to 13.5.

[0073] The anodised aluminium substrate (or alloys thereof) has an aluminium oxide thickness from 0.3 μm to 30 μm.

[0074] The thickness of the coating layer according to the present invention can vary from 0.5 to 3 μm.

[0075] The total thickness of the anodised aluminium substrate coated with the coating according to the present invention is comprised between 3 and 35 μm.

EXAMPLES

Solutions according to the invention

EXAMPLE 1

[0076]

4 g/L sodium silicate
0.9 g/L glycidyltrimethoxysilane
0.1 g/L alkoxymethylsiloxane
0.1 g/L polydimethylsiloxane
0.1% anionic surfactant (Dowfax 2 A 1) with respect to the volume of the solution

EXAMPLE 2

[0077]

5 g/l lithium silicate
1.5 g/l glycidyltrimethoxysilane
0.2 g/l alkoxymethylsiloxane
0.2 g/l anionic surfactant

EXAMPLE 3

[0078]

3.5 g/l potassium silicate
2 g/l glycidyltrimethoxysilane
0.15 g/l polyvinylsiloxane
0.15 g/l anionic surfactant

EXAMPLE 4

[0079]

6 g/l sodium silicate
2.5 g/l glycidyltrimethoxysilane
0.45 g/l hexamethylcyclotrisiloxane

SOLUTION PREPARATION EXAMPLE

(final volume, 1 litre)

[0080] Place approximately 500 ml of demineralised water in a container of suitable capacity.

[0081] Add, under stirring, the silicate solution (sodium, lithium or potassium silicate).

[0082] Mix for a few minutes, add the silane and wait until completely homogenised.

[0083] Add the siloxane/polysiloxane and leave under mechanical stirring for a few minutes.

[0084] Bring to the final volume (1 litre) with demineralised water and, if necessary, add the surfactant.

[0085] Heat the solution to operating temperature.

TREATMENT EXAMPLE ON ALUMINIUM ALLOY SERIES 1050

[0086] With the treatment described below, a glossy silver finish (possibly coloured) is obtained. Mechanical cleaning of an aluminium alloy substrate with suitable polishing pastes and cloth. Degreasing at 65°C for 5 minutes.

[0087] Chemical brightening at 96°C for 5 minutes.

[0088] Rinsing.

[0089] De-coating.

[0090] Oxidation at 12.5 V for t = 40 minutes at T= 20°C, to form an oxide layer of about 10 microns. Rinsing.

[0091] Fixing by impregnation t= 1 min/μm T = 28°C

[0092] Immersion in one of the solutions according to the examples 1-4 t= 10 min T= 60°C.

[0093] Final drying t= 10 min T= 65°C.

[0094] Preliminary treatments were carried out using commercial products and performed according to the Qualanod specifications.

[0095] To obtain a coloured and glossy substrate, it is necessary to carry out a 15 min step in colour (for example, red; blue, orange, turquoise, green, black) at the temperature recommended by the dye producer.

[0096] Rinsing.

[0097] Immerse in pre-fixing for 10 min at T= 65°C.

[0098] Rinsing.

[0099] Fixing by impregnation t= 1 min/μm T = 28°C

[0100] Immersion in one of the solutions according to the examples 1-4 t= 10 min T= 60°C.

[0101] Final drying t= 10 min T= 65°C.

TREATMENT EXAMPLE ON ALUMINIUM ALLOY SERIES 6060

[0102] With the treatment described below, a frosted silver finish (possibly coloured) is obtained.

[0103] Degreasing of the aluminium alloy substrate at 65°C for 5 minutes

[0104] Frosting at 65°C for 15 minutes.

[0105] Rinsing.

[0106] De-coating.

[0107] Oxidation at 14.5 V for t = 45 minutes T= 20°C, to form an oxide layer of approximately 15 microns.

[0108] Rinsing.

[0109] Fixing by impregnation t= 1 min/μm T = 28°C

[0110] Immersion in one of the solutions of the examples 1-4, t= 10 min T= 60°C.

[0111] Final drying t= 10 min T= 65°C.

[0112] To obtain the frosted colour, simply perform:
a passage of 15 min in colour (e.g., orange, blue, turquoise, etc.) at the temperature recommended by the dye producer.

[0113] Rinsing.

[0114] Pre-fixing for 10 min at T= 65°C.

[0115] Fixing by impregnation t= 1 min/μm T = 28°C

[0116] Immersion in one of the solutions of the examples 1-4, t= 10 min T= 60°C.

[0117] Final drying t= 10 min T= 65°C.

ALKALI RESISTANCE TESTS

[0118] To verify the alkali resistance of the anodised aluminium substrates coated with the coating of the invention, comparison tests were performed with uncoated substrates, performing a visual evaluation after immersion in a solution at pH 13.5.

[0119] Figure 1 shows the initial step of a resistance test at pH 13.5 of two anodised aluminium substrates: left substrate (black coloured) not treated with the coating of the invention and right substrate (silver) treated with the coating of the invention.

[0120] In the following figures, the part of the substrate immersed in the alkaline solution is delimited by a mark with a black marker.

[0121] Figure 2 shows the end of the immersion test of figure 1. It is clear that the untreated coloured substrate has completely lost colour and the aluminium oxide layer has been dissolved by the high alkalinity; instead the silver substrate treated with the coating of the invention has not been affected at all. In fact, the basic solution has remained clear and colourless.

[0122] If there had been a basic attack, and therefore aluminium dissolution, the solution would have become milky.

[0123] Figure 3 shows black-coloured anodised aluminium substrates after immersion in a solution at pH 13.5. The left substrate was not coated with the coating of the invention: the right substrate was coated with the coating. As can be seen in the figure, the substrate on the left has a total dissolution of the colour and of the oxide layer, while the substrate on the right is intact for both the colour and the oxide layer.

[0124] Figure 4 shows uncoloured anodised aluminium substrates subjected to immersion tests in basic solution at pH 13.5. The left substrate was not coated with the coating of the invention while two right substrates were coated. As can be seen from the figure, the aluminium oxide layer of the left substrate has been completely dissolved from the basic solution, while the right substrates are intact.

Claims

1. A process for coating an anodised aluminium or anodised aluminium alloy substrate, comprising:

   a) Applying to the substrate a solution comprising at least one alkaline silicate, at least one silane and at least one siloxane and/or one polysiloxane;
   b) Drying the substrate at a temperature comprised between 55°C and 80°C.

2. The process according to claim 1, wherein the at least one alkaline silicate is an alkaline metal silicate with the general formula $M_2O \times nSiO_2$, wherein M = Na, K, Li and n is comprised between 1.5 and 4.

3. The process according to claim 1 or 2, wherein the at least one silane has the general formula:

$$R'(CH_2)_nSi(OR)_3$$

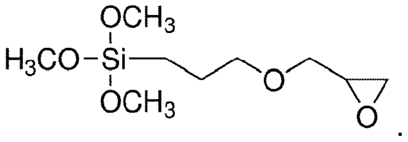
   wherein:

n is comprised between 2 and 4;
R' is a functional group selected from: vinyl, epoxy, glycidyloxy, methacrylate, primary amine, diamine and mercapto;
OR is a hydrolysable alkoxy group such as, for example, methoxy (OCH_3), ethoxy (OC_2H_5) or acetoxy ($OCOCH_3$), preferably
n is equal to 3 or 4, R' is vinyl, epoxy or glycidyloxy, OR is a methoxy group (OCH_3).

4. The process according to claim 3, wherein the at least one silane is selected from:

$CH_2{=}CHSi(OCH_3)_3$

$CH_2{=}CHSi(OC_2H_5)_3$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5. The process according to any one of claims 1 to 4, wherein at least one siloxane is selected from:

alkoxymethylsiloxane,
polyvinyltrimethoxysiloxane,
polymethylvinylsiloxane,
hexamethylcyclotrisiloxane,
hexamethyldisiloxane,
polydimethylsiloxane, and
decamethylcyclopentasiloxane.

6. The process according to any one of claims 1 to 4, wherein the at least one polysiloxane is selected from polyether siloxane and polyetherdimethylsiloxane.

7. The process according to any one of claims 1 to 6, wherein the solution of step a) comprises a siloxane, preferably selected from: hexamethyldisiloxane and polydimethylsiloxane and a polysiloxane preferably selected from: polyether siloxane and polyetherdimethylsiloxane.

8. The process according to any one of claims 1 to 7, wherein the solution of step a) comprises an anionic surfactant, preferably a disulphonate.

9. The process according to any one of claims 1 to 8, wherein the solution of step a) is applied to the substrate for a time comprised between 5 and 20 minutes, preferably between 7 and 15 minutes.

10. The process according to any one of claims 1 to 9, comprising a step of applying a colour before step a).

11. The process according to any one of claims 1 to 10, comprising a step of fixing the pores, prior to application of the solution of step a), preferably by hydration with boiling water, optionally in the presence of additives, or by means of steam or by impregnation with a solution containing nickel ions and fluoride ions.

12. An anodised aluminium or anodised aluminium alloy substrate coated with a coating layer obtainable by applying to the anodised substrate the process according to any one of claims 1 to 11.

13. The substrate according to claim 12, wherein the thickness of the coating layer is comprised between 0.5 and 3 μm.

14. The substrate according to claim 12 or 13, wherein the anodised aluminium substrate has an aluminium oxide thickness of 0.3 μm to 30 μm.

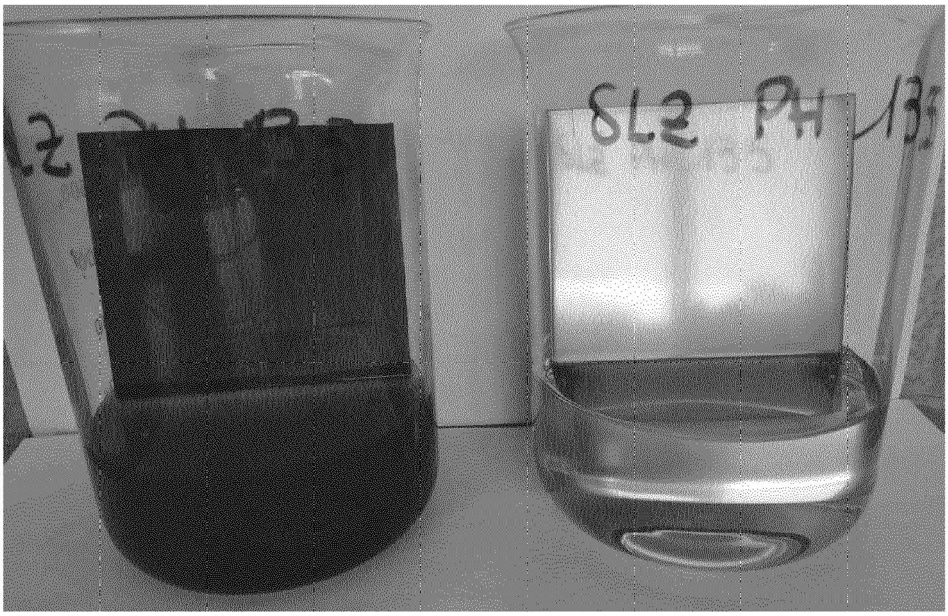

Fig. 1

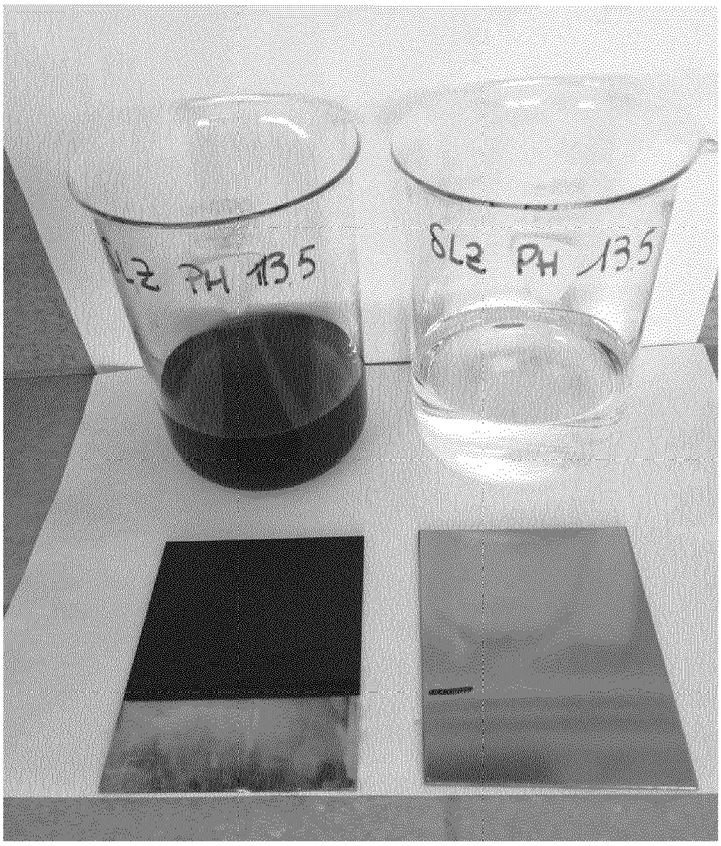

Fig. 2

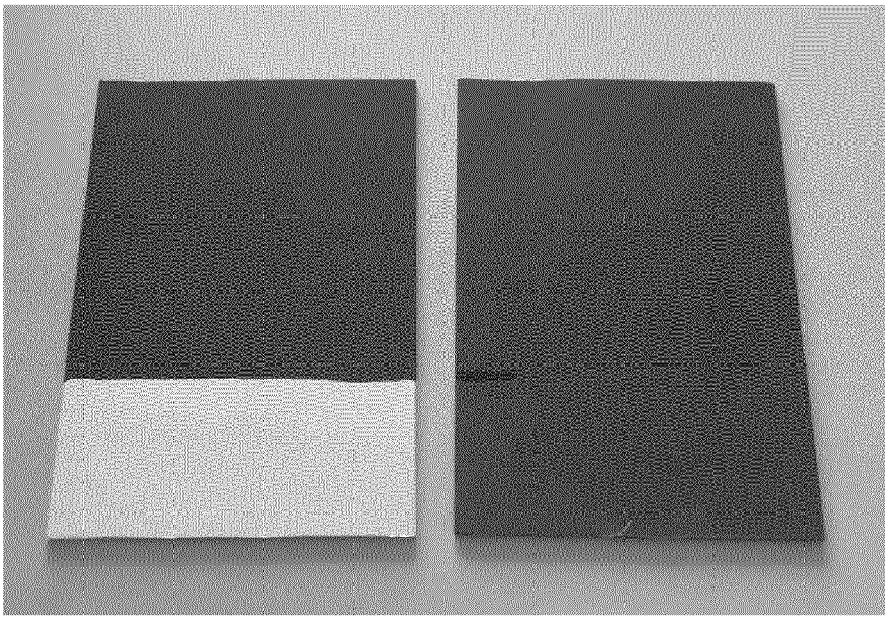

Fig. 3

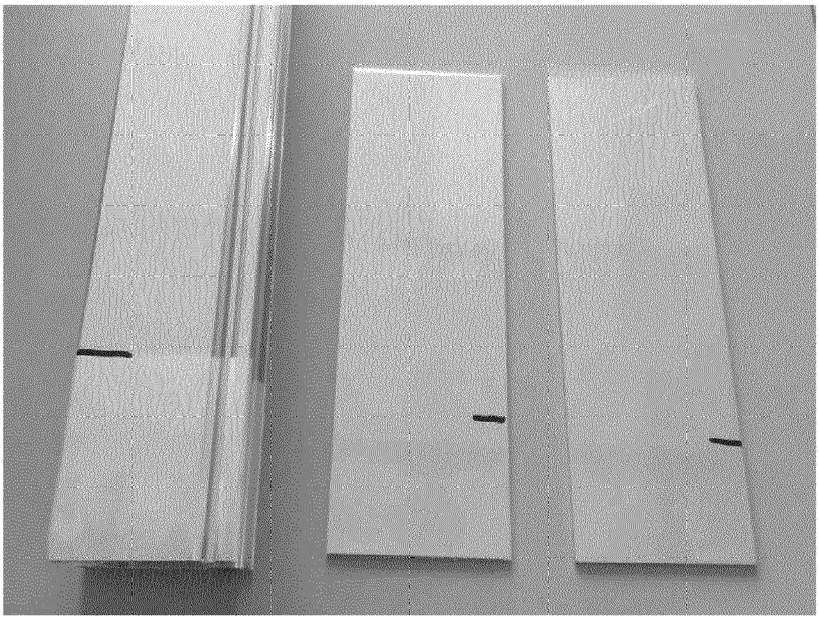

Fig. 4

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EUROPEAN SEARCH REPORT

Application Number
EP 21 19 3393

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1 The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	20 December 2021	Suárez Ramón, C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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