The invention is related to chemical treatment applied to products made of aluminum or aluminum alloys, that have been first submitted to anodic oxidation and pore sealing according to known prior technics, the invention comprising two additional steps:

- a treatment with an alkali-silicate solution;
- a treatment with silanes solutions.

The products according to the invention are showing improved resistance to corrosion tests to acid and alkalis.
Anodized aluminum has low resistance to alkalis and to acids. In domains such as automotive and building there is a pressing need for anodized articles the surface of which, while preserving their characteristic appearance, can withstand contact with strong alkaline solutions, and possibly also with strong acid solutions.

In the present application when speaking of aluminum, this also encompasses usual aluminum alloys.

The automotive industry recently imposed for anodized aluminum parts used in cars, tests resistance to alkalis that, in practice, cannot be passed by aluminum that has been anodized, even when "sealed" conventionally. Anodized articles are known to exhibit porous surfaces. These pores made the surface more easily attacked notably by alkaline or acid solutions. It is usual to have these porous surfaces sealed to improve their resistance.

Treatments to improve this resistance are notably the subject of standards, such as those of the European Aluminum Anodisers Association, these are referred as "Qualanod" standards. But products treated in accordance to these standards, mainly directed to buildings material, prove not to pass the tests of the automotive industry. These tests, that are not yet unified, present in common the same goal that is to resist with success, after a first acid contact, a strong alkali solution the pH of which is as high as 13.5.

Among the tests stipulated by the automotive industry may be mentioned:

- FIAT production standard 9.57448
- Volkswagen AG “Anorganische Schutzschicht Auf Aluminiumteilen-Oberflaeschenschutzanforderung TL 182
- General Motors GMW 14665 "Anodic Oxidation Coating on Aluminum” (General Motors Material Specification Finish-Worldwide Engineering Standards, January 2009)
- Volvo TR 31804674.

Example of the content such a standard appears in the FIAT documentation. Articles are subject to the test cycle including:

- Immersion for 10 minutes in an acid solution at pH 1 (0.1 molar solution of HCl)
- Standing in a stove for 6 minutes at 40°C
- Immersion for 10 minutes in alkaline solution at pH 13.5 (aqueous solution of 12.7 g/l of NaOH+4.64g/l Na₃PO₄)
- Rinsing with running water and drying with compressed air.

At the end of the test there must not be any aesthetic change, relative to material that has not been exposed.

Several attempts are reported in prior art to meet the requirements of automotive industry. They are all failing in one or more criteria notably concerning the appearance of the products. This is the case where electrophoretic coating is used. This may allow passing the resistance tests but the coating is visible, and the required aesthetic quality is not fully satisfied. When using sol-gel including silanes, another way trying to reach the proper resistance, the resulting polymer film is not colorless and the transparency may be altered.

Taking into account the deficiencies of prior art there is still a need for improved anodized aluminum products, that allow to pass the very specific requirements recalled above. The present invention aims at solving this problem. If in the first place the products for automotive industry are concerned, the invention also applies to any type of anodized product including those intended for building or domestic appliances.

Surprisingly the inventors have shown that such a goal could be reached according to the invention, through specific treatments of these anodized products, part of these treatments pertaining to prior art. More precisely according to the invention, treatment of anodized aluminum products is carried out as claimed in the first appending claim.

The anodized aluminum product treated first is one obtained that presents no prior defects, to that effect the anodization must follow the best known practices.

Usual anodization is carried out in electrolytic solution that includes an inorganic acid. Among those acids, most common is sulfuric acid. Other acids are also of interest notably those that are less susceptible to dissolve the anodic oxide film created. The anodization conditions such as voltage, temperature are well known from prior art that gives products free of any defects but need a precise control especially when using sulfuric acid solution. For example to low temperature corresponds a slow rate forming of the oxide layer, but if the temperature is too high the dissolution rate is increased. The temperature is usually not above 24°C.

At the end of the anodization step the anodic solution is immediately removed and the product washed to prevent further dissolution of the oxide film.

The usual thickness selected must be sufficient to allow for the necessary resistance, chemical and mechanical. This is normally above 5μm, and preferably above 10μm. The thickness is preferably not above 50μm to prevent possible defect formation such as cracks.
Anodization leads to an oxide layer the structure resulting in a porous system that has poor resistance notably to acids or alkaline solutions. It is common to prevent these corrosive chemicals to penetrate the porous structure by sealing the pores. The usual sealing is made by hydration of the aluminum oxide that swells and obstructs the pores. Hydration may be made by way of hot water or steam. ("hot sealing"). This is done at temperature above 95°C. Another possibility called "cold sealing" is starting with an impregnation step that includes contact with a first solution e.g. of nickel fluoride used for its properties to form insoluble complexes with aluminium and plug the pores, producing a good sealing. Other metallic salts notably of chromium may substitute to those of nickel. In this cold impregnation the temperature is not above 30°C. The impregnation is followed by ageing in a hot water treatment. Impregnation needs also careful control notably of nickel and fluoride respective concentrations.

Whatever the care taken to seal the pores of the oxide layer, the corrosion resistance to strong acid and alkali solution is not enough to meet the levels required by the automotive industry. Further treatments are necessary that are the subject of the invention.

According to the invention a first post treatment is using a solution of silicates in which the products are immersed under conditions that result in a further sealing or coating with "silicates polymers". A second treatment is following that includes using specific silanes solutions that adds another coating.

Treatment by silicates have been proposed in the prior art, and the products treated supposed, at least, to present an increased resistance to corrosion without the need for anything else. A treatment of this kind appears e.g. in EP1873278 that contains restrictive conditions regarding the ratio SiO₂/Na₂O. But this treatment is not supposed to result in products that may resist solution the pH of which is higher than 12.5. When having this sole additional treatment, even if the products exhibit better resistance to high pH, they do not allow simultaneously resistance to strong acid solution as needed to pass the tests stipulated by automotive industry.

According to the invention this type of treatment using silicate, is still to be improved. In sub-claims the invention provides for conditions to carry out this step, that makes both more efficient control and prevent possible defects.

First before starting contact with a silicate solution the treated products must be free of any powder deposit at the surface of the material that could alter the final aesthetic appearance.

The products are thus immersed in the silicates solution. The silicate solution used is preferably one of alkaline metal, sodium, potassium or lithium or mixture thereof. These, notably sodium and potassium, are readily available in commerce and extensively used in many industrial sectors, notably as thickening agents. The solutions are containing an amount of silicate that depends on the stability. When increasing the concentration there is a limit above which the solution turns a gel. The concentration that allows remaining stable for long period of time are also depending on the nature of the silicate including the molar ratio SiO₂/M₂O (M standing for Na, K or Li). The higher this ratio, the lower the possible amount of silicate when trying to prevent the gel formation.

According to the invention having a relatively high SiO₂/M₂O ratio is preferable as it leads to product that present a better resistance. The ratio is at least of 2.5, and preferably at least of 3.

The silicate solution is preferably at pH above 5 and preferably above 6.

To make the coating fast enough the concentration of the solution is as high as the solubility permits. This concentration for sodium silicate is preferably higher than Ig/l and preferably from 10 to 30g/l.

The coating also depends on temperature of the solution. Faster deposition of silicates is obtained with the highest temperature. For easiness of control over the process, the temperature is preferably higher than 40°C and does not exceed 95°C. The best temperature range according to the invention is from 60 to 80°C.

The processing time depends on the previous parameters and is most usually between 5 and 50 minutes.

Between each step of the process the articles are thoroughly washed and dried so as not to disturb the composition of the following baths. The next step according to the invention is a treatment with a solution of one or more silanes or silanols that result from hydrolysis of these silanes.

The silanes used according to the invention are alkoxy-silanes that may be hydrolyzed to give in silanols that may react with hydroxyl groups leading to covalent bonds according to the known general mechanism:

\[
\text{Al-OH} + \text{R-SiOH} \rightarrow \text{Al-O-Si-R + H₂O}
\]

The presence of aluminum oxides, partly hydrated by the sealing process, partly complexed by reaction with the silicate solution, makes the surface very amenable to reaction with silanols.

The silanols are seldom available as such for reason that, to be stable, they need to be in greatly diluted solutions. For this reason it is most often necessary to have the silanols prepared when needed.

The silanes used according to the invention are preferably of the general formula:

\[ \text{R'(CH₂)nSi(OR)₃} \]

with \( n \) at most equal to 4
where -OR is one of:

- \(-\text{OCH}_3\)
- \(-\text{OC}_2\text{H}_5\)
- \(-\text{OCOCH}_3\)

and \(R'\) is a radical from: vinyl, epoxy, methacrylate, primary amine, di-amine, mercapto. Among those silanes the most preferred ones of the formulas:

\[
\text{CH}_2=\text{CHSi(OCH}_3\text{)}_3
\]
\[
\text{CH}_2=\text{CHSi(OC}_2\text{H}_5\text{)}_3
\]
\[
\text{CH}_2\text{CH-C}_2\text{H}_2\text{-O-(CH}_2\text{)}_3\text{Si(OCH}_3\text{)}_3
\]
\[
\text{CH}_2=\text{C(CH}_3\text{)-COO-(CH}_2\text{)}_3\text{Si(OCH}_3\text{)}_3
\]
\[
\text{H}_2\text{N(CH}_2\text{)}_2\text{Si(OCH}_3\text{)}_3
\]
\[
\text{H}_2\text{N(CH}_2\text{)}_2\text{NH(CH}_2\text{)}_3\text{Si(OCH}_3\text{)}_3
\]
\[
\text{N}_2\text{HNC(O)H(CH}_2\text{)}_3\text{Si}
\]
\[
\text{HS(CH}_2\text{)}_3\text{Si(OCH}_3\text{)}_3
\]

The silanes that are used may also be bis-silanes of the general formula:

\[(\text{RO})_3\text{Si(CH}_2\text{nR} (\text{CH}_2\text{n-Si(OR)}_3\]

with \(R\), \(R'\) and \(n\) having the same significance as indicated above. Among the bis-silanes preferred ones are:

\[(\text{C}_2\text{H}_5\text{O})_3\text{Si(CH}_2\text{)Si(OC}_2\text{H}_5\text{)}_3\]
\[(\text{C}_2\text{H}_5\text{O})_3\text{Si(CH}_2\text{)}_3\text{-S}_4\text{-Si(OC}_2\text{H}_5\text{)}_3\]
\[(\text{C}_2\text{H}_5\text{O})_3\text{Si(CH}_2\text{)}_3\text{-NH-(CH}_2\text{)}_3\text{Si(OC}_2\text{H}_5\text{)}_3\]

[0031] As said above to allow reaction with hydroxyl groups of the substrate the silanes are first to be hydrolysed in silanols following typical reactions:

\[\text{R'}\text{-Si(OR)}_3 + \text{H}_2\text{O} \leftrightarrow \text{R'}\text{-Si(OR)}_2\text{OH} + \text{ROH}\]
\[\text{R'}\text{-Si(OR)}_2\text{OH} + \text{H}_2\text{O} \leftrightarrow \text{R'}\text{-Si(OR)(OH)}_2 + \text{ROH}\]
\[\text{R'}\text{-Si(OR)(OH)}_2 + \text{H}_2\text{O} \leftrightarrow \text{R'}\text{-Si(OH)}_3 + \text{ROH}\]

These reactions are both ways and thus the equilibrium must be shifted on the right side. Reaction with hydroxyl groups of the substrate is in competition with selfcondensation of the silanols producing oligomer siloxanols. To prevent excess of this possible reaction the silanes solutions are necessarily diluted.

[0032] Preferably the concentration in silanes is less than 8% by weight of the solution, and most preferably less than 5% by weight. At these concentrations the hydrolysis tends to get to completion. To limit the processing time the concentration is preferably no less than 0.1% by weight.

[0033] Most of organo-silanes that are useful have a limited solubility as such in water. Using a water alcohol mixture enhance the solubility to the necessary concentration. The presence of alcohol may also regulate the hydrolysis of the silanes, and possibly makes the final drying easier. Depending on the silanes the content of alcohol may be up to 15% by weight of the mixture.

[0034] The hydrolysis of silanes needs time and depends on various factors notably the type of organo-silanes, the medium of the reaction and the pH. Hydrolysis in water proceeds more quickly than in mixture of water and organic
solvent such as ethanol, and tends to completion. Playing with pH may catalyze the hydrolysis and enhance its speed.

[0035] The hydrolysis is faster with the smallest alkoxy group of the silanes, e.g. hydrolysis of methoxy-silanes is 6 to 10 times faster than ethoxy-silanes of the same structure.

[0036] The treatment may be started when the concentration of silanols is sufficient, this corresponding to the solution becoming clear showing a true solution where before it was mostly a suspension.

[0037] Application on the surface may be e.g. by dipping or by spraying. The necessary contact time depends notably on the temperature. For example, at a temperature of 15 to 35°C, this contact may be from 0.5 to 5 minutes.

[0038] Silanols reacts with hydroxyl groups linked to the metal, but may also give rise to condensation reactions of the silanols themselves to forms silanes films. The former are increasing the adhesion to the substrate when the silanols condensates are promoting formation of a film the thickness of which depends on the concentration of the silanes solutions. Typical thickness may be up to 400nm. The structure of the film is possibly cross-linked depending on the specific silanes used (or mixture of silanes). The cross-linking is normally high with bis-silanes and better protection is obtained.

[0039] When the necessary contact is over, the aluminum article is dried at temperature that may be from ambient to as high as 120°C, preferably from 40 to 120°C. The above mentioned reactions are going n during the drying step.

[0040] Anodized aluminum and aluminum alloys according to the invention exhibit specific resistance to the corrosive action that are the subject of the tests specified by the automotive industry. They notably have a weight loss at most of 10mg/dm² surface and preferably at most 5 mg/dm², and most preferably at most 1mg/dm² when submitted to acid followed by alkaline test according to the specifications of the corrosion test 9.57448 from Fiat group. This weight loss is notably obtained for corrosion tests in which the acid is at a pH 1 and the alkali solution is at pH 13.5.

[0041] The product according to the invention, their surface having been polished so that, before being subject to these corrosion tests mentioned above, they exhibit a high gloss measured with a "glossmeter". Their loss of gloss after these tests is less than 10% and preferably less than 5%

[0042] The invention is further disclosed in details in the following examples.

[0043] Samples of aluminum profile are prepared prior to anodic oxidation by cleaning the pieces and polishing up to a surface roughness $R_{a}$ of 0.6μm.

[0044] Chemical pickling or electrochemical treatment of surface may be preferred to confer another appearance, notably etched appearance to other samples.

[0045] Before anodic treatment, the pieces are thoroughly washed with running water.

[0046] The anodization bath is containing 200 ±10g/l sulfuric acid. This solution is maintained at about 15°C. The current density is about 1.8 A/dm².

[0047] The anodization is carried out till the oxide layer is 20μ. At the indicated current density this needs about 45 minutes. The anodized article is thoroughly washed in deionized water to remove any adhering solution.

[0048] A sealing process is then made to close the pore of the oxide layer. The sealing is of the "cold sealing" type including an impregnation with nickel ions.

[0049] The example is made with Ni2+ at 1.2g/l and fluoride ions at 0.250g/l.

[0050] The temperature selected is 28°C and treatment is maintained for 20 minutes.

[0051] To prevent possible deposit of powdery material that alters the surface appearance, the solution is continuously filtered to remove any precipitate.

[0052] These sealing are the usual treatments proposed by the standard "QUALANOD" published by European Anodisers Association, standard followed for pieces that are intended to be used in less corrosive conditions such as the ones prevailing for buildings. These are not sufficient to pass successfully tests as such required by automotive industry whatever the sealing ratio of the pores.

[0053] When the sealing is completed and the samples properly washed and dried, they are ready to the silicate treatment.

[0054] According to this treatment, the anodized samples are immersed in an aqueous solution of sodium silicate. The solution is prepared by diluting to 11, 10ml of a sodium silicate solution containing by weight:

- \( \text{Na}_2\text{O} \) 9%
- \( \text{SiO}_2 \) 29%

The molar ratio \( \text{SiO}_2/\text{Na}_2\text{O} \) is thus 3.2.

[0055] The pH is 8.0.

[0056] Treatment of the samples is by immersion at a temperature of 70°C. The immersion time is 10 minutes.

[0057] The various parameters are selected so that no precipitation occurs during the treatment. In addition continuous filtration of the solution is carried out.

[0058] The samples are washed in tap water then in demineralized water and dried.

[0059] Careful examination of the product is done to control that no defects such as spots or powdery appearance of
the surface may be detected.

[0060] The conditions recited in table 1 for anodization and sealing and silicate treatment are other possible examples substitutes to the ones indicated above.

Table 1. It includes various conditions relating to the steps: anodization, sealing and treatment with silicates.

<table>
<thead>
<tr>
<th>Preliminary treatment</th>
<th>Anodizing parameters</th>
<th>Coloring</th>
<th>Sealing</th>
<th>Additional treatment</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Chemical polishing</td>
<td>H₂SO₄ 200g/l A1 dissolved 7g/l 20±1°C 1.5 A/dm² 45 minutes</td>
<td>Organic dying &quot;Black MLW&quot;¹ 10g/l 45°C 10 minutes</td>
<td>Impregnation Sealing Ni²⁺ 1.2 g/l F⁻ 0.250g/l 28°C 20 minutes</td>
<td>Sodium silicate sol. (waterglass) 10ml/l 70 °C 20min</td>
</tr>
<tr>
<td>B</td>
<td>Chemical polishing</td>
<td>H₂SO₄ 200g/l A1 dissolved 7g/l 20±1°C 1.5 A/dm² 45 minutes</td>
<td>None</td>
<td>Medium Temp. sealing. Commercial specialty²</td>
<td>Sodium silicate sol. (waterglass) 10ml/l 70 °C 20min</td>
</tr>
<tr>
<td>C</td>
<td>Chemical polishing</td>
<td>H₂SO₄ 200g/l A1 dissolved 7g/l 20±1°C 1.5 A/dm² 45 minutes</td>
<td>None</td>
<td>Hot. sealing. Commercial specialty³</td>
<td>Sodium silicate sol. (waterglass) 10ml/l 70 °C 20min</td>
</tr>
<tr>
<td>D</td>
<td>Chemical polishing</td>
<td>H₂SO₄ 200g/l A1 dissolved 7g/l 20±1°C 1.5 A/dm² 45 minutes</td>
<td>Electrocolouring SnSO₄ 16g/l H₂SO₄ 20g/l Additives⁴ 10g/l 10 minutes</td>
<td>Hot. sealing. Commercial specialty³</td>
<td>Sodium silicate sol. (waterglass) 10ml/l 70 °C 20min</td>
</tr>
<tr>
<td>E</td>
<td>Chemical polishing</td>
<td>H₂SO₄ 150g/l A1 dissolved 7g/l 15±1 °C 2.5 A/dm² 20 minutes</td>
<td>Organic &quot;Black MLW&quot; 10g/l 45°C 20 minutes</td>
<td>Ni²⁺ 1.2 g/l F 0.250g/l 28°C 20 minutes</td>
<td>Sodium silicate sol. (waterglass) 10ml/l 70 °C 20min</td>
</tr>
</tbody>
</table>

1 - Black MLW from Clariant.
2 - Medium Temperature sealing chemical specialties available on the market are based on a solution of about 10 g/nickel acetate and 0.2-05 g/l of a surfactant acting as a "bloom preventer" (i.e. it avoid the formation of powder on the anodic layer surface). Temperature 85-90 °C, dipping time 1 minute / micron (i.e. 20 min)
3 - Hot sealing chemical specialties available on the market contains essentially a mixture of surfactant used at a concentration of 1-2 ml/l acting as a "bloom preventer" (i.e. it avoid the formation of powder on the anodic layer surface). Temperature > 95 °C, dipping time 2 minute / micron (i.e. 40 min)
4 - Additives known to stabilize the tin ions solution, hampering its oxidation and/or precipitation.

[0061] To go on with the samples having been anodized, sealed and treated with silicates solutions, these are subject to a silane treatment. In this case the selected silanes composition is the one sold by the company CHEMETAL under the name "OXILAN MM 0706". The solution contains 3% by weight of this composition of silanes in water with addition of ethanol (5% by weight).

[0062] The samples are immersed in the solution at room temperature during 2 minutes. After this the samples are removed from the tank and without washing directly dried in a hot air flow at 60°C for 20 minutes.

[0063] These samples are then tested according to the specification recalled above. As a result it is found that the weight loss measured at each stage of the preparation is:

- anodized samples prior to other treatment 692mg/dm²
- after sealing 97,2mg/dm²
- after silicate treatment 11,5mg/dm²
The product made according to the invention was analyzed at each stage of the preparation. This allows to confirm that the product in itself may be the subject of identification without having recourse to the process for making it. A possible investigation includes an X-ray photoelectron spectrometry (XPS). This method allows for identification of the elements entering in the surface layer of the product. The method permit analysis of very thin layers (around 20-30Å) preventing a possible confusion with elements from under-layers. Nevertheless when the layers considered exhibit average thicknesses that are less than these figures, and/or the roughness of the surface is noticeable, part of the measurements may indicate a limited amount of elements from under-layers.

The results are included in the following table.

<table>
<thead>
<tr>
<th>n°</th>
<th>Compound preparation</th>
<th>Solution operating parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A bis[triethoxysilyl]ethane (BTSE) added directly and mixed</td>
<td>BTSE 30g/l, ethanol 50ml/l 24°C 4 minutes</td>
</tr>
<tr>
<td>2</td>
<td>γ-aminopropyl-trimethoxysilane (AMPTS) added directly and mixed</td>
<td>AMPTS 30g/l ethanol 70ml/l 24°C 4 minutes</td>
</tr>
<tr>
<td>3</td>
<td>D bis[triethoxysilyl]propyl]-tetrathionate (bis-sulphosilane) added directly and mixed</td>
<td>...bis-sulphosilane 30g/l ethanol 70ml/l 24°C 4 minutes</td>
</tr>
<tr>
<td>4</td>
<td>E Composition 4: 3 parts γ-aminotriethoxysilane (in water) 1 part vinyl-triethoxysilane 24 °C mixing 1 hour</td>
<td>Composition 4 50g/l ethanol 50ml/l 24°C 4 minutes</td>
</tr>
<tr>
<td>5</td>
<td>B Composition 5 : 5 parts &quot;Dynasylan HS 2776&quot; 1 part &quot;Dynasylan D-VTEO&quot; 24 °C mixing 1 hour</td>
<td>Composition 5 50g/l from Degussa-Evonik</td>
</tr>
<tr>
<td>6</td>
<td>C &quot;Dynasylan HS 2627&quot;</td>
<td>&quot;Dynasylan HS 2627&quot; 30g/l ethanol 50ml/l 24°C 4 minutes</td>
</tr>
<tr>
<td>7</td>
<td>A &quot;Oxsilan MM 0706&quot;</td>
<td>&quot;Oxsilan MM 0706&quot; ethanol 50ml/l 24°C 4 minutes</td>
</tr>
</tbody>
</table>
Silanes of 4-7 above are sold pre-hydrolyzed and thus directly water soluble.

**Claims**

1. Chemical treatment applied to products made of aluminum or aluminum alloys, that have been first subjected to anodic oxidation and pore sealing according to known prior techniques, comprising two additional steps:
   - a treatment with an alkali-silicate solution;
   - a treatment with silanes solutions.

2. Treatment according to claim 1 wherein the thickness of the anodic oxide layer is not less 5μ.

3. Treatment according to claim 1 wherein the treatment in alkaline solution is carried out in a stable aqueous solution containing one or more silicates of sodium, potassium or lithium, or mixtures thereof.

4. Treatment according to claim 3 wherein the molar ratio of SiO₂/M₂O is such that the solution is at a pH above 6, preferably above 8, M standing for either Na, K or Li.

5. Treatment according to claim 4 wherein the alkali-silicate is sodium silicate, the molar ratio SiO₂/Na₂O being at least 3.

6. Treatment according to one of the preceding claims the solution containing from 1.0 g/l, up to the solubility limit, preferably from 10 to 30g/l, of alkali silicate.

7. Treatment according to one of the preceding claims wherein the alkali-silicate treatment is carried out at a temperature from 40 to 95 °C, preferably from 60 to 80°C.

8. Treatment according to one of the preceding claims wherein the product is maintained in the alkali silicate solution from 5 to 50 minutes.

9. Treatment according to any of the preceding claims wherein the product is treated in an aqueous or aqueous-alcoholic solution of a silane or a mixture of silanes.

10. Treatment according to claim 9 wherein the silanes are mono-silanes of the general formula:

\[ R'(CH₂)nSi(OR)₃ \]

with n at most equal to 4

where -OR is one of:

- -OCH₃, -OC₂H₅, -OCOCH₃

and R' is a radical from: vinyl, epoxy, methacrylate, primary amine, di-amine, mercapto.

11. Treatment according to claim 10 wherein the silanes are one or several of:
12. Treatment according to claim 9 wherein silanes are bis-silanes of the general formula:

$\text{(RO)ₙSi(\text{CH₂})ₙR'CH₂Si(OCH₃)₃} \quad \text{with R, R'} \text{ and n, having the same significance as in claim 10.}$

13. Treatment according to claim 12 wherein the bis-silanes are one of:

- $(C₂H₅O)₃Si(\text{CH₂})₃-S₄-(\text{CH₂})₃Si(OCH₃)₃$
- $(C₂H₅O)₃Si(\text{CH₂})₃-NH-(\text{CH₂})₃Si(OCH₃)₃$
- $N₂HCN(O)H(\text{CH₂})₃Si$
- $\text{HS(\text{CH₂})₃Si(OCH₃)₃}$

14. Treatment according to one of claims 9 to 13 wherein the solution contains from 0.1 to 5 weight % of silanes.

15. Treatment according to one of claims 9 to 14 wherein the solution contains from 0.1 to 15 weight % of an aliphatic alcohol.

16. Treatment according to one of the claims 9 to 15 wherein the contact time with the solution is from 0.5 an 5mn, and the temperature from 15 to 35°C.

17. Treatment according to one of the claims 9 to 16 wherein the product is dried at a temperature from ambient to 120°C.

18. Anodized aluminium or aluminium alloy product, the surface of which having been sealed and further treated in silicates solutions, and silanes solutions, exhibiting a weight loss of at most 10mg/dm² surface, and preferably at most 5mg/dm² when submitted to acid followed by alkaline test according to the specifications of the corrosion test.

19. Product according to claim 18 in which the acid is at a pH 1 and the alkali solution is at pH 13.5.

20. Product according to claim 18 or 19 the surface of it is polished prior to the full treatment, including anodic oxidation, such that its loss of gloss when subjected to the corrosion test of claim 19 or 20 is less than 10% and preferably less than 5%.
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (IPC)</th>
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<tbody>
<tr>
<td></td>
<td>* abstract *</td>
<td></td>
<td>ADD. C25D11/16</td>
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<td></td>
<td>* page 5, line 6 - page 7, line 7 *</td>
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<td></td>
<td>* claims 1-4,9-13 *</td>
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<td>Y,D</td>
<td>EP 1 873 278 A1 (HENKEL KGAA [DE])</td>
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<td>2 January 2008 (2008-01-02)</td>
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<tr>
<td></td>
<td>* abstract *</td>
<td></td>
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<tr>
<td></td>
<td>* claims 1-11 *</td>
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<td>US 2008032121 A1</td>
<td>07-02-2008</td>
</tr>
<tr>
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<td></td>
<td>GB 1422050 A</td>
<td>21-01-1976</td>
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<td>JP 549100129 A</td>
<td>21-09-1974</td>
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<td>US 3935349 A</td>
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Patent documents cited in the description

- EP 1873278 A [0017]

Non-patent literature cited in the description

- Anodic Oxidation Coating on Aluminum, General Motors GMW 14665, January 2009 [0005]
- QUALANOD. European Anodisers Association [0052]