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(54) Silicate treatment of sealed anodised aluminum

(57) The present invention describes a method for the post-treatment of fully sealed anodised aluminum parts, especially for the automotive industry, characterised in that an aqueous silicate solution is applied to fully sealed anodised aluminum layers, where said fully sealed anodised aluminum layer has a film thickness of at least 5 μm and a film weight of at least 13 g/m^2, respectively. Said solution preferably contains an alkaline metal (M) silicate with not more than 2.0 wt.-% of SiO_2, in which the ratio of SiO_2: M_2O is preferably not more than 2. This treatment increases the alkaline stability according to the standardised corrosion tests in the automotive industry without any further treatment or organic coating applied to said treated aluminum surface.

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Description

[0001] The present invention describes a method for the post-treatment of fully sealed anodised aluminum parts, especially for the automotive industry, characterised in that an aqueous silicate solution is applied to fully sealed anodised aluminum layers, where said fully sealed anodised aluminum layer has a film thickness of at least 5 μm and a film weight of at least 13 g/m^2, respectively. Said solution preferably contains an alkaline metal (M) silicate with not more than 2.0 wt.-% of SiO_2, in which the ratio of SiO_2 : M_2O is preferably not more than 2. This treatment increases the alkaline stability according to the standardised corrosion tests in the automotive industry without any further treatment or organic coating applied to said treated aluminum surface.

[0002] The electrochemical formation of oxide layers on aluminum is a well-known and widely used industrial procedure to produce protective and/or decorative coatings on aluminum and/or aluminum alloys. Electrolytically produced aluminum oxide layers protect the base metal from corrosion and weathering and furthermore may increase the surface hardness and the abrasive resistance of the aluminum part.

[0003] The different processes of anodising are described briefly in Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Vol. 9 (1987), pp. 174 - 176. Anodising of the aluminum material can be accomplished by standardised methods in electrolytes such as sulfuric acid (Eloxal GS), chromic acid (Bengough-Stuart), phosphoric acid (Boeing) and oxalic acid (Eloxal GX). The Eloxal GS method applies dc current densities of 0.5 - 3 A/dm^2 at voltages between 18-21 V and a bath temperature of 10-25 °C. Through this treatment film thicknesses of the anodised aluminum oxide layer of approximately 45 μm can be obtained, which is a maximum film thickness determined by the equilibrium of the oxide formation rate and its dissolution rate in the sulfuric acid solution at the specific process parameters chosen.

Such anodised aluminum layers are comprised of a thin compact layer on top of the base metal that acts as a primal barrier coating against corrosive attack, which is only up to 2 % of the overall layer thickness, and a porous and amorphous oxide layer as the main constituent of the anodised layer. The porosity of the anodised layer might be favorable for the adhesion of further applied organic coatings, but exhibits a major drawback that is the lack in protection against corrosive media rendered by the anodised aluminum. Therefore and to impart maximum corrosion stability, the anodised aluminum layers have to be sealed in a subsequent process step. During the sealing, which might be a hot sealing and/or cold sealing process, the aluminum oxide becomes hydrated and is transformed from its amorphous, essentially water-free constitution to the boehmite structure. This transformation is accompanied by a volume expansion or swelling of the oxide that in turn procures the sealing of the porous structure. Hot sealing of the anodised layer is usually performed in hot water or in a water steam whereas the cold sealing process is operated at temperatures close to 30 °C in the presence of nickel fluoride. Sealing improves the corrosion resistance and resistance to weathering of anodised aluminum parts in a pH range from 5 - 8 (T.W. Jelinek, Oberflächenbehandlung von Aluminum, Eugen G. Leuze Verlag, 1997, ch. 6.1.3.1)

[0004] In prior art the treatment of aluminum surfaces with silicate solutions is well known and for example described for the sealing of porous anodised aluminum surfaces to increase the corrosion resistance (US 6,686,053) as well as for hydrophilising the aluminum surface in lithographic printing technologies (US 3,181,461, US 2,714,066). In these areas of application silicate treatment is favorable due to the strong affinity of aluminum and silicon to form a mixed oxide. Thus, aqueous silicate solutions support in sealing anodised aluminum by precipitating and forming mixed oxides within the pores of the coating and in hydrophilising aluminum oxide surfaces by the formation of thin layers comprising silicon dioxide on top of the aluminum oxide. To improve the corrosion resistance of sealed anodised aluminum surfaces metal complexes of zirconium- and/or titanium (EP 0193964) and dispersed particulate matter like silicon dioxide and/or aluminum oxide (EP 1064332) have been added to the aqueous silicate solution. Nevertheless, these post treatments can not prevent the anodic aluminum oxide film from being stripped away in corrosive environments with a high pH. This is especially the case when aluminum parts of car bodies are being exposed to detergent solutions in vehicle wash stations which might have a pH of 12.5 - 13.5. Since aluminum gathers more importance as a construction material in the automotive industry, manufacturers started to issue test standards (AUDI TL212, VOLVO TR31804674) to their suppliers in order to reject anodised aluminum parts with low alkaline resistance.

The post-treatment of sealed anodised aluminum with aqueous silicate solutions in order to hydrophilize the aluminum surface for lithographic printing is disclosed in US 5,811,218. Within this patent the corrosion resistance of the silicate treated anodised and sealed aluminum layer, which is a prerequisite for a metal to fulfill the standards of the automotive industry, is neither discussed nor revealed. Due to the fact that the subject matter of this document is not related to the use of aluminum parts in automotive industry, the aluminum oxide layers described therein are much thinner (1-8 g/m^2) and the sealing time per micron much shorter (65 seconds/μm) than needed to meet the specific requirements and quality standards of the automotive industry.

EP 1625944 characterizes a silicate treatment of sealed and non-sealed anodised aluminum plates for lithographic printing, which is first aimed to hydrophilize and/or seal the aluminum oxide surface and secondly to enhance the resistance of the lithographic printing plate against dissolution by the alkaline developer. Here, a sealing ratio (SR) of the anodised aluminum layer of at least 50% is postulated before the hydrophilising step including the silicate treatment can be performed. Again the treatment according to EP 1625944 is not sufficient to provide the alkaline and corrosion resistance that is mandatory in the field of automotive industry. EP 1625944 does not reveal the resistance of their layers exposed to an aqueous alkaline solution that contains corrosive agents such as halide ions.

[0005] Surprisingly, the present inventor found that the treatment of a sealed anodised aluminum layer with an aqueous silicate solution provides an alkaline stability of the aluminum material for at least 10 minutes, preferably for at least 14 minutes and most preferably for at least 16 minutes at a temperature of 23 ± 2 °C in a solution containing a mixture of 0.2 wt.-% sodium phosphate and 0.02 wt.-% sodium chloride and sodium hydroxide with a pH value of at least 11.5, preferably at least 12.5, but not higher than 13.5.

[0006] Within this invention, alkaline and corrosive stability of the aluminum material is defined on the basis of a standardised testing method introduced in the automotive industry whereupon the visual appearance of the aluminum material after a defined exposure to the aforesaid alkaline testing solution that contains a mixture of 0.2 wt.-% sodium phosphate and 0.02 wt.-% sodium chloride and sodium hydroxide with a pH value of at least 11.5 is evaluated. The classification system of the standardised corrosion tests AUDI TL212 and VOLVO TR31804674 covers the following specifications of the visual appearance of the aluminum material after exposure to a testing solution in the order of increasing corrosive damage:

Grade 0: no visible change in appearance
Grade 1: slight dulling of luster
Grade 2: light etch
Grade 3: etch of substrate
Grade 4: heavy etch
Grade 5: very heavy etch of substrate

Quality results of at most Grade 2 after 16 minutes of exposure to a solution with a pH of 12.5 are considered to be sufficiently alkaline stable according to the guidelines of AUDI TL212 and VOLVO TR31804674.

[0007] As a part of the invention the treatment of the sealed anodised aluminum layer with an aqueous silicate solution is applied within a sequential process of surface finishing of an aluminum material that is comprised of

a) cleaning and/or electro-polishing and/or desmutting;
b) anodising of the aluminum material up to a film thickness of at least 5 μm;
c) cold sealing or hot sealing of the anodised aluminum material up to a sealing ratio (SR) of at least 90 %, preferably 95 % and most preferably 99 %;
d) treatment of the sealed anodised aluminum material with an aqueous silicate solution

with or without rinsing and/or drying in between the listed process steps and with or without applying an organic coating to the aluminum after the process step d) has been accomplished.

[0008] The scope of the invention also includes an aluminum material produced by treating the surface thereof sequentially by the following process steps

a) anodising of the aluminum material up to a film thickness of at least 5 μm;
b) sealing of the anodised aluminum material up to a sealing ratio (SR) of at least 90 %, preferably 95 % and most preferably 99 %;
c) treatment of the sealed anodised aluminum material with an aqueous silicate solution

whereupon the aluminum material treated in that way shows at most a light etch (Grade 2) in the appearance after exposure to an alkaline testing solution with a pH value of at least 11.5, preferably at least 12.5, but not higher than 13.5 for at least 10 minutes, preferably at least 14 minutes and most preferably at least 16 minutes at a temperature of 23 ± 2 °C. The aluminum material according to this invention may be used in exterior applications such as a building material for window frames, doors and claddings, and preferably used in the automotive industry as a member of vehicle bodies and/or vehicle wheels.

[0009] The aluminum material used for the said silicate treatment and/or within the said process of aluminum surface finishing according to this invention is selected from pure aluminum containing at least 99 wt.-% aluminum or aluminum alloyed with copper, manganese, titanium, silicon, zinc and preferably magnesium where the magnesium content is preferably not more than 5 wt.-% and most preferably not more than 1 wt.-%.

[0010] Preferably, the aqueous silicate solution used according to the present invention contains not more than 2.0 wt.-% of SiO_2, more preferably not more than 1.0 wt.- %, and most preferably not more than 0.5 wt.-%, but not less than 0.05 wt.-% SiO_2 and more preferably not less than 0.1 wt.-%.

[0011] Furthermore, the silicate solution is preferably comprised of an alkaline metal (M) silicate such as potassium silicate, lithium silicate and more preferably sodium silicate, where said aqueous solution preferably exhibits a molar ratio of $SiO_2 : M_2O$, that is not more than 2, more preferably not more than 1.5, but not less than 0.5 and most preferably equals 1.

The pH value does not need to be adjusted and thus may be left at the value provided by the dissolved silicate.

[0012] Optimised conditions for the silicate treatment are maintained, when said treatment is performed at a temperature of at least 40 °C, preferably at least 50 °C, but not higher than 90 °C and preferably not higher than 70 °C, and most preferably at 60 °C, and said treatment is performed for at least 10 seconds, preferably at least 80 seconds, but not more than 300 seconds, preferably not more than 160 seconds and most preferably for 120 seconds.

[0013] Furthermore, it is beneficial to the appearance of the aluminum part after the treatment according to this invention that the silicate treatment solution contains a wetting agent, preferably anionic and/or nonionic surfactants in a concentration of preferably at least 50 ppm, more preferably at least 200 ppm, but preferably not more than 1000 ppm and more preferably not more than 600 ppm.

The nonionic surfactant can be one or more selected from the group of alkoxylated, preferably ethoxylated or propoxylated, branched or straight alkyl alcohols or branched or straight arylalkyl alcohols or branched or straight fluoroalkyl alcohols or branched or straight alkyl amines or from the group of alkylpolyglycosides. The alkyl moiety of the selected nonionic surfactant consists preferably of at most 18, more preferably of at most 12, but at least 6 carbon atoms, such as those ones sold under the trade names Triton®, Tergitol®, Merpol® and Zonyl®.

The anionic surfactant can be one or more selected from the group of branched or straight alkyl or alkylaryl or alkylpolyether sulfates and/or sulfonates and/or phosphonates preferably with not more than 12 carbon atoms in the alkyl chain.

[0014] In a preferred embodiment of this invention an aluminum part (AIMg1, AlMg0.5) was anodised under constant current conditions in a sulfuric acid medium at a dc current density of 1-2 A/dm^2 (dc voltage approx. 12-20 V) and was subjected thereupon to a cold sealing and a subsequent hot sealing procedure. The cold sealing was performed for 800 seconds followed by a hot rinse / sealing step for another 800 seconds. According to this sealing process a sealing ratio of the anodised aluminum surface of at least 90% was attained, which accounts for a total sealing rate of approx. 200 seconds/μm or 67 seconds/gm^{-2}, respectively.

[0015] The testing of the sealed anodised aluminum surfaces is performed with the dye absorption test according to Scott described within the British Standard BS1615:1972 (Anodic oxidation coatings on aluminum). This standard test allows to quantify the degree of surface sealing by measuring the colouring of the aluminum surface photometrically. For that purpose, one drop of a 4.6 wt.-% sulfuric acid solution, which contains additionally 1 wt.-% potassium fluoride, is applied to the cleaned anodised aluminum surface for one minute. After this treatment the aluminum surface is cleaned and thereupon exposed at the same spot for one further minute to an aqueous colouring solution of the specific dye Aluminum Fast Red B3LW. The colouring of the anodised aluminum surface can be quantified by measuring the residual optical reflectivity with a reflection photometer. The residual optical reflectivity is given by the ratio of the reflective light intensity measured with the probe head of the photometer at the dyed surface spot to the reflective light intensity of the untreated anodised aluminum surface. The capability of the aluminum oxide surface to absorb the specific dye is directly related to the free surface that is provided by the amorphous aluminum oxide layer. Thus, the free surface and the photometrically measured reflective light intensity are closely related to each other, in a way that the sealing ratio (SR) can be expressed as follows:

$$SR=\left(1-\frac{S_{seal}-S_{geom}}{S_{anod}-S_{geom}}\right)\times 100\% \cong \left(1-\frac{R_{seal}}{R_{anod}}\right)\times 100\% \qquad \text{Eq.1}$$

with S_{anod}, R_{anod} being the surface area and reflective light intensity, respectively, after anodising the aluminum material, and S_{seal}, R_{seal} being the surface area and reflective light intensity, respectively, after sealing the anodised aluminum material, and S_{geom} being the geometric surface area of the aluminum material.

From a technical point of view, anodised aluminum layers are considered to be "fully" sealed when a sealing ratio of at least 90% is realised as defined by Eq.1.

[0016] In the preferred embodiment the film thickness of the sealed anodised aluminum part with a sealing ratio of at least 90% is about 8 μm, which corresponds to a film weight of approximately 21 g/m^2 considering a density of the sealed aluminum oxide layer of $\rho = 2.6\ g/cm^3$ according to the British Standard BS1615:1972 (Anodic oxidation coatings on aluminum). The film thickness of the sealed anodised aluminum oxide layer was determined by using an eddy current instrument (Isoscope® MP30, Fischer GmbH) calibrated with a reference sample of the same material.

[0017] Anodised aluminum parts sealed in such a way were immersed for 120 seconds at 60 °C in aqueous sodium metasilicate solutions with varying SiO_2 content and afterwards rinsed with deionised water and dried at ambient room temperature.

[0018] The quality of the aluminum parts prepared according to this preferred embodiment of the invention with respect to their visual appearance directly after the silicate treatment and to their alkaline stability after immersing the aluminum part for 16 minutes in a chloride containing aqueous solution at pH 12.5 is listed in Example 1.

Example 1:

Appearance of sealed anodised aluminum (AIMg1, AlMg0.5) treated for 120 seconds at 60°C with a sodium metasilicate solution and appearance of said treated aluminum after 16 minutes of immersion in standard test solution at pH 12.5 containing NaOH, 0.2 wt.-% Na_3PO_4 and 0.02 wt.-% NaCl according to the specification (grade 0-5) of the standardised corrosion test (AUDI TL212 /VOLVO TR31804674)

SiO_2 /wt.-%	grade 0 - 5	appearance
0	3-4	O
0.05	2-3	+
0.25	0	++
0.5	0	-

O neutral / + good / ++ very good / - worse

[0019] The results in Example 1 reveal that the preferred embodiment of the invention contains 0.25 wt.-% SiO_2 in the form of an aqueous sodium metasilicate solution. Even for an aqueous solution containing 0.5 wt.-% SiO_2 an optimum alkaline and corrosive stability results, but the optical appearance of the treated aluminum part after rinsing with deionised water and drying at ambient room temperature is inferior to the one obtained from more diluted sodium metasilicate solutions. Example 2 shows the effect of surfactants added to the silicate treatment solution on the appearance of the sealed anodised aluminum part treated accordingly to this invention. The appearance is evaluated by means of brightness and stainlessness of the surface directly after this treatment as compared to a reference treatment which is denoted in the table of Example 2 for providing a neutral (o) appearance (refers also to Example 1). In a specific embodiment of the invention, where a combination of anionic (A) and non-ionic (B) surfactants is added to the silicate treatment solution, an improved wettability, cleaning and rinse-off behaviour of the aluminum surface without any deterioration of the performance of said treated aluminum part in the standardised corrosion test can be achieved.

Example 2:

Appearance of sealed anodised aluminum (AIMg1, AlMg0.5) treated for 120 seconds at 60 °C with a sodium metasilicate solution (0.5 wt.-%) containing disodium lauryl diphenylether disulfonate (A) and tetraethylene glycol monooctylether (B) as well as appearance according to the specifications of the standardised corrosion test (see Example 1).

A / ppm	B / ppm	grade 0 - 5	appearance
50	10	0	O
100	20	0	+
200	40	0	++
500	100	0	++
1000	200	1	+

O neutral / + good / ++ very good

[0020] According to these embodiments of the invention a process for the treatment of an anodised aluminum material is hereby disclosed which complies with the high quality standards of the automotive industry without any further treatment or organic coating applied to said treated aluminum surface. These standards are especially introduced to avoid corrosive damages of the aluminum parts of car bodies during cleaning procedures especially in assembly lines and car-wash plants and during hand-guided cleaning. Thus, the advantage of the silicate treatment of fully sealed anodised aluminum is demonstrated in an excellent alkaline and corrosive stability of the aluminum material treated according to this invention even in a highly corrosive environment, e.g. in the presence of chloride ions. Moreover, the treatment can be easily adopted in state-of-the-art processes of aluminum surface finishing.

Claims

1. A method for the treatment of a sealed anodised aluminum material, where the film thickness of the anodising layer is at least 5 μm and the sealing ratio (SR) is at least 90 %, **characterised in that** an aqueous silicate solution is applied to said sealed anodised aluminum material.

2. The method according to claim 1 **characterised in that** the aqueous silicate solution contains not more than 2.0 wt.-% of SiO_2, preferably not more than 1.0 wt.-%, and most preferably not more than 0.5 wt.-%, but not less than 0.05 wt.- % SiO_2 and preferably not less than 0.1 wt.-%.

3. The method according to one of the preceding claims **characterised in that** the aqueous silicate solution contains an alkaline metal (M) silicate, where said aqueous solution exhibits a molar ratio of SiO_2: M_2O, that is not more than 2, preferably not more than 1.5, but not less than 0.5 and most preferably equals to 1.

4. The method according to one of the preceding claims **characterised in that** said treatment is performed at a temperature of at least 40 °C, preferably at least 50 °C, but not higher than 90 °C and preferably not higher than 70 °C, and most preferably at 60 °C.

5. The method according to one of the preceding claims **characterised in that** said treatment is performed for at least 10 seconds, preferably at least 80 seconds, but not more than 300 seconds, preferably not more than 160 seconds and most preferably for 120 seconds.

6. The method according to one of the preceding claims **characterised in that** said treatment solution contains a wetting agent, preferably anionic and/or nonionic surfactants, in a concentration of at least 20 ppm, preferably at least 100 ppm, but not more than 1000 ppm and preferably not more than 500 ppm.

7. A process of surface finishing of an aluminum material in or for the automotive industry, which imparts to the aluminum material an alkaline stability such that said material shows at most a light etch (Grade 2) in the appearance after exposure to an alkaline testing solution, which optionally contains corrosive agents such as halide ions and especially chloride ions, with a pH value of at least 11.5, preferably at least 12.5, but not higher than 13.5 for at least 10 minutes, preferably at least 14 minutes and most preferably at least 16 minutes at a temperature of 23 ± 2 °C, **characterised in that** the aluminum material is subjected to sequential treatment steps comprised of

    a) cleaning and/or electro-polishing and/or desmutting;
    b) anodising of the aluminum material up to a film thickness of the anodised layer of at least 5 μm;
    c) cold sealing or hot sealing of the anodised aluminum material up to a sealing ratio (SR) of at least 90 %, preferably 95 % and most preferably 99 %;
    d) treatment of the sealed anodised aluminum material according to one of the preceding claims.

8. An aluminum material produced by treating the surface thereof sequentially by the following process steps

    a) anodising of the aluminum material up to a film thickness of the anodised layer of at least 5 μm;
    b) sealing of the anodised aluminum material up to a sealing ratio (SR) of at least 90 %, preferably 95 % and most preferably 99 %;
    c) treatment of the sealed anodised aluminum material according to one of the claims 1-6.

9. The aluminum material according to claim 8 **characterised in that** said material shows at most a light etch (Grade 2) in the appearance after exposure to an alkaline testing solution with a pH value of at least 11.5, preferably at least 12.5, but not higher than 13.5 for at least 10 minutes, preferably at least 14 minutes and most preferably at least 16 minutes at a temperature of 23 ± 2 °C.

10. The aluminum material according to claim 9 **characterised in that** said material shows at most a light etch (Grade 2) after exposure to an alkaline testing solution, which also contains corrosive agents such as halide ions and especially chloride ions.

11. Use of an aluminum material according to claims 8 to 10 as a member in the construction of vehicle bodies and/or vehicle wheels.

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EUROPEAN SEARCH REPORT

Application Number
EP 06 01 3572

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	GB 926 418 A (RUDOLPH SIMON) 15 May 1963 (1963-05-15) * page 1, lines 25-43 * * page 1, line 67 - page 2, line 2 * * page 2, lines 19-71 * * page 2, line 118 - page 3, line 10 * * claims 1,4,6,8 * -----	1,2,4-11	INV. C25D11/24
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X	US 3 374 155 A (WEBER LUDWIG J) 19 March 1968 (1968-03-19) * claims 13,21 * * column 5, lines 10-17 * * column 16, lines 57-63; table 15 * * example 13 * -----	1-5,7-11	TECHNICAL FIELDS SEARCHED (IPC)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	4 December 2006	Gault, Nathalie

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 06 01 3572

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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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