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(54) COMPOSITION AND PROCESS FOR TREATING METAL

ZUSAMMENSETZUNG UND VERFAHREN ZUR BEHANDLUNG VON METALL

COMPOSITIONS POUR LE TRAITEMENT DE METAUX ET PROCEDE CORRESPONDANT

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• **PATENT ABSTRACTS OF JAPAN vol. 011, no.**
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Description

[0001] This invention relates to processes of treating metal surfaces with aqueous acidic compositions to increase the resistance to corrosion of the treated metal surfaces, either as thus treated or after subsequent overcoating with some conventional organic based protective layer. A major object of the invention is to provide a storage stable, preferably single package, treatment that can be substantially free from hexavalent chromium but can protect metals substantially as well as hexavalent chromium containing treatments of the prior art, or can improve the stability of treatment solutions that do contain hexavalent chromium. This invention also relates to reaction of fluorometallic acids with other metal or metalloid containing materials to produce compositions or intermediates for compositions useful for such treatments.

[0002] A very wide variety of materials have been taught in the prior art for the general purposes of the present invention, but most of them contain hexavalent chromium or other inorganic oxidising agents which are environmentally undesirable. Also, many of the prior art treatment compositions include components that are chemically or physically unstable when mixed, so that single package concentrates for such treatment compositions are not practical.

[0003] Compositions comprising water-soluble or -dispersible polyvinyl alcohol and/or polymers and copolymers of acrylic and/or methacrylic acids are known, for example from European Publications Nos. EP 0,450,437 and EP 0,645,428, British Publication No. GB 2,090,603, United States Publication No. US 3,133,865, and Japanese Publications Nos. JP 62,001,882 and JP 62,010,280 (Patent Abstracts of Japan vol. 011, no. 176 (C-426) and no. 185 (C-428).)

[0004] Except in the claims and the operating examples, or where otherwise expressly indicated, all numerical quantities in this description indicating amounts of material or conditions of reaction and/or use are to be understood as modified by the word "about" in describing the broadest scope of the invention. Practice within the numerical limits stated is generally preferred. Also, unless expressly stated to the contrary:

percent, "parts of", and ratio values are by weight; the term "polymer" includes oligomer; the description of a group or class of materials as suitable or preferred for a given purpose in connection with the invention implies that mixtures of any two or more of the members of the group or class are equally suitable or preferred; description of constituents in chemical terms refers to the constituents at the time of addition to any combination specified in the description, and does not necessarily preclude chemical interactions among the constituents of a mixture once mixed; specification of materials in ionic form implies the presence of sufficient counterions to produce electrical neutrality for the composition as a whole (any counterions thus implicitly specified should preferably be selected from among other constituents explicitly specified in ionic form, to the extent possible; otherwise such counterions may be freely selected, except for avoiding counterions that act adversely to the stated objects of the invention); and the term "mole" and its variations may be applied to elemental, ionic, and any other chemical species defined by number and type of atoms present, as well as to compounds with well defined molecules.

[0005] The present invention provides a composition and process for coating surfaces of aluminium and alloys thereof, wherein the composition comprises preferably consists essentially of, or more preferably consists of, water and a mixture of:

(A') a water soluble or dispersible polyvinyl alcohol present in a concentration range of from 0.5 to 50 g/l;

(B') one or a mixture of more than one of the following, namely polymers and copolymers of acrylic and methacrylic acid and their salts present in a total concentration of from 0.5 to 50 g/l;
and

(C') a component selected from the fluorometallic acids of titanium, zirconium, hafnium, aluminium, silicon, germanium, tin and/or boron, and mixtures thereof, present in a total concentration of from 0.01 to 7 M;

and optionally one or more of the following:

(D') a component selected from the water-insoluble oxides, water-insoluble hydroxides, water-insoluble carbonates and/or water-insoluble elemental forms of titanium, zirconium, hafnium, boron, aluminium, silicon, germanium and/or tin; and

(E') a component of water soluble oxides, carbonates and/or hydroxides of at least one of Ti, Zr, Hf, B, Al, Si, Ge and/or Sn.

[0006] It should be understood that the descriptions of compositions above do not preclude the possibility of unspecified chemical interactions among the components listed, but instead describes the components of a composition according to the invention in the form in which they are generally used as ingredients to prepare such a composition. In fact, a chemical interaction, most probably to produce oxyfluoro complexes of the metal or metalloid elements or their compounds heated in contact with fluorometallic acids, is believed to occur, but the invention is not limited by any such theory.

[0007] The resulting compositions are suitable for treating metal surfaces to achieve excellent resistance to corrosion, particularly after subsequent conventional coating with an organic binder containing protective coating. The compositions are particularly useful on iron and steel, galvanised iron and steel, zinc and those of its alloys that contain at least 50 atomic percent zinc, and, most preferably, aluminium and its alloys that contain at least 50 atomic percent aluminium. The treating may consist either of coating the metal with a liquid film of the composition and then drying this liquid film in place on the surface of the metal, or simply contacting the metal with the composition for a sufficient time to produce an improvement in the resistance of the surface to corrosion, and subsequently rinsing before drying. Such contact may be achieved by spraying, immersion, and the like as known *per se* in the art.

[0008] The invention also provides a process for effectively coating the above-stated metallic surfaces in the absence of an intermediate rinsing step. The process comprises the steps of (i) cleaning the metal surface to be coated, (ii) rinsing the cleaned metal surface with water so as to remove any excess cleaning solution, (iii) contacting the metallic surface with the above-described coating composition, and (iv) drying the coated metallic surface.

[0009] The major type of coating used in the invention, employing a coating composition including necessary components (A'), (B') and (C') as already described above, has been found to be especially useful for treating metallic surfaces that are exposed to alkali metal ions, particularly sodium such as often occurs in detergents and other cleaners, after the treatment with a composition according to this invention has been completed.

(Protective coatings applied to metallic surfaces, particularly aluminium preferably are water insoluble and inhibit corrosion. However, metallic surfaces bearing a protective coating are often exposed to sodium ions later. It is believed that, upon exposure of some prior art coatings to sodium ions, the sodium ions often at least partially replace the aluminium in the formed coatings, much as in an ion-exchange resin; such replacement in turn causes the film coating to be water sensitive, by increasing its solubility in water.)

[0010] In an effort to decrease adverse effects of alkali metal ions on the treated surfaces, it has been found that by combining (i) polymers and copolymers of acrylic and methacrylic acids and their salts having an average molecular weight of about 50,000 with (ii) a water soluble or dispersible polymer having at least one -OH group per polymer molecule, adverse effects from exposure of the treated surface to alkali metal ions can be reduced. Possibly this occurs because the alcohol functionally cross-links by esterification with the acid functions. In a particularly preferred embodiment of this invention, the composition contacted with a metallic surface comprises water and: (A') from 0.5 to 50 g/l and (B') from 0.5 to 50, and more preferably from 0.5 to 16g/l of polyvinyl alcohol. The polyvinyl alcohol used in the invention preferably is a low molecular weight polyvinyl alcohol which is 75 - 99+ mole % hydrolysed, and has an average degree of polymerisation ranging from 100-600.

[0011] While any water soluble or dispersible polymer having at least one -OH group per polymer molecule may be employed without departing from the spirit of the invention, preferred polymers and amounts thereof include the above-stated polyvinyl alcohol; from 0.3 to 16g/l, preferably from 0.3 to 1.2g/l, of polyethylene glycol having a molecular weight of from 90,000 to 900,000; from 0.5 to 16g/l, and preferably from 0.5 to 10 g/l of dextrin, cyclodextrin, or a modified starch.

[0012] The term "modified starch" is one commonly known in the art. It refers to any of several water-soluble polymers derived from a starch by acetylation, chlorination, acid hydrolysis, or enzymatic action. These reactions yield starch acetates, esters, and ethers in the form of stable and fluid solutions and films. These starch derivatives useful herein are well known.

[0013] The hydroxyalkyl starch ethers and starch esters can be obtained by known etherification and esterification processes. These starch ethers and esters should have a degree of substitutions (hereinafter often abbreviated "D.S.") of 0.01 to 0.5, and preferably 0.1 to 0.5. As used herein D.S. means the average degree of substitution of starch hydroxyl groups per anhydroglucose unit of the chemical modifying substituent, as for example a hydroxyalkyl or carbonyl group.

[0014] Oxidised starch can be obtained by known processes involving oxidation of starch with a suitable oxidising agent, as for example sodium hypochlorite, potassium dichromate, and sodium permanganate. The starch can be oxidised under acid, alkaline or neutral conditions, and the resulting product can contain carboxyl and carbonyl groups. Preferably the oxidised starch has a "D.O." value of 0.01 to 1.0, where "D.O." refers to the number of carboxyl groups introduced per anhydroglucose unit.

These starch derivatives and methods for obtaining them are discussed in Whistler and Paschall (eds.), *Starch: Chemistry and Technology*, vol. I, (Academic Press, 1965), pp. 458-78.

[0015] Dextrins and cyclodextrins are polysaccharide products of a complex nature resulting from the partial degradation of starch, such as corn starch, potato starch, wheat starch, and the like, with heat, as for example, by roasting with acid or alkaline catalysts. Linear and branched dextrins are classified in three types. The particular type obtained depends on the heating time, temperature, and catalyst employed in the treatment of the starch. These types are classified as white dextrins, yellow or canary dextrins, and British gums, and all such dextrins are suitable herein. White and canary dextrins are preferred in that British gums are brown in colour. White dextrins are preferably pregelatinised (made water soluble during manufacture), if necessary, to render them more readily mixed with other water soluble

components. Dextrins and methods for obtaining them are well known. See, for example, Whistler and Paschall *op. cit.* Vol. I, p. 421 ff and vol. II, p. 253 ff.

[0016] The starch hydrolysates useful in the compositions of this invention are a relatively new class of starch materials. These starch hydrolysates are made by subjecting a source of starch, such as hereinbefore mentioned, to enzyme or acid treatment or a combination of both. It is important that the starch hydrolysate have a relatively low dextrose equivalent (hereinafter often abbreviated "D.E."). The starch hydrolysate should have a D.E. of from 2 to 35, and preferably have a D.E. of from 5 to 25. The most preferred materials have a D.E. within the range of 5 to 15. (The term D.E. is used herein to refer to the reducing sugars content of the dissolved solids in a starch hydrolysate expressed as percent dextrose as measured by the Luff-Schoorl method [NBS Circular C-40, p. 195; also appearing in *Polarimetry, Saccharimetry, and the Sugars* published by Frederick J. Bates and Associates].)

[0017] Particularly preferred modified starches include cyclodextrins, which are macrocyclic non-reducing D-glucosyl polymers containing six or more D-glucosyl residues bonded by α -(1,4) links. A more detailed description of cyclodextrins can be found in Whistler and Paschall, *op. cit.*, Vol. 1, pp. 209-224.

[0018] The pH of a composition according to this invention that contains components (A'), (B'), and (C') as necessary components preferably is in the range from 1.0 to 5.0, and more preferably from 1.0 to 3.5.

[0019] In a preferred embodiment of the invention utilising necessary components (A'), (B'), and (C'), the treating composition also includes 0.2 to 19.0, and more preferably from 0.2 to 8.0 g/l, of fluoroacids component (C') admixed therein. Component (C') is preferably selected from the group consisting of H_2TiF_6 , H_2ZrF_6 , and H_2SiF_6 , and more preferably is H_2TiF_6 and/or H_2ZrF_6 .

[0020] Another embodiment of the invention is a process of treating a metal with a composition prepared as described above. In one embodiment of the invention, it is preferred that the aqueous composition as described above be applied to the metal surface and dried in place thereon. For example, coating the metal with a liquid film may be accomplished by immersing the surface in a container of the liquid composition, spraying the composition on the surface, coating the surface by passing it between upper and lower rollers with the lower roller immersed in a container of the liquid composition, and the like, or by a mixture of methods. Excessive amounts of the liquid composition that might otherwise remain on the surface prior to drying may be removed before drying by any convenient method, such as drainage under the influence of gravity, squeegees, passing between rolls, and the like.

[0021] If the surface to be coated is a continuous flat sheet or coil and precisely controllable coating techniques such as gravure roll coaters are used, a relatively small volume per unit area of a concentrated composition may effectively be used for direct application. On the other hand, if the coating equipment used does not readily permit precise coating at low coating add-on liquid volume levels, it is equally effective to use a more dilute acidic aqueous composition to apply a thicker liquid coating that contains the same amount of active ingredients.

[0022] Drying may be accomplished by any convenient method, of which many are known *per se* in the art; examples are hot air and infrared radiative drying. Independently, it is preferred that the maximum temperature of the metal reached during drying fall within the range from 30 to 200, more preferably from 30 to 150, still more preferably from 30 to 75, °C. Also independently, it is often preferred that the drying be completed within a time ranging from 0.5 to 300, more preferably from 2 to 50, still more preferably from 2 to 10, seconds (hereinafter abbreviated "sec") after coating is completed.

[0023] According to an alternative embodiment of the invention, the metal to be treated preferably is contacted with a composition prepared as described above at a temperature within the range from 25 to 90, more preferably from 30 to 85, still more preferably from 30 to 60, °C for a time ranging from 1 to 1800, more preferably from 1 to 300, still more preferably from 3 to 30, sec, and the metal surface thus treated is subsequently rinsed with water in one or more stages before being dried. In this embodiment, at least one rinse after treatment with a composition according to this invention preferably is with demineralised, distilled, or otherwise purified water. Also in this embodiment, it is preferred that the maximum temperature of the metal reached during drying fall within the range from 30 to 200, more preferably from 30 to 150, or still more preferably from 30 to 75, °C and that, independently, drying be completed within a time ranging from 0.5 to 300, more preferably from 2 to 50, still more preferably from 2 to 10, sec after the last contact of the treated metal with a liquid before drying is completed.

[0024] A process according to the invention as generally described in its essential features above may be, and usually preferably is, continued by coating the dried metal surface produced by the treatment as described above with a siccativ coating or other protective coating, relatively thick as compared with the coating formed by the earlier stages of a process according to the invention as described above. Such protective coatings may generally, in connection with this invention, be selected and applied as known *per se* in the art. Surfaces thus coated have been found to have excellent resistance to subsequent corrosion, as illustrated in the examples below. Particularly preferred types of protective coatings for use in conjunction with this invention include acrylic and polyester based paints, enamels, lacquers, and the like.

[0025] In a process according to the invention that includes other steps after the formation of a treated layer on the surface of a metal as described above and that operates in an environment in which the discharge of hexavalent

chromium is either legally restricted or economically handicapped, it is generally preferred that none of these other steps include contacting the surfaces with any composition that contains more than, with increasing preference in the order given, 1.0, 0.35, 0.10, 0.08, 0.04, 0.02, 0.01, 0.003, 0.001, or 0.0002 % of hexavalent chromium. Examples of suitable and preferred chromium free treatments are described in U. S. Patent 4,963,596. However, in certain specialized instances, hexavalent chromium may impart sufficient additional corrosion protection to the treated metal surfaces to justify the increased cost of using and lawfully disposing of it.

[0026] Preferably, the metal surface to be treated according to the invention is first cleaned of any contaminants, particularly organic contaminants and foreign metal fines and/or inclusions. Such cleaning may be accomplished by methods known to those skilled in the art and adapted to the particular type of metal substrate to be treated. For example, for galvanized steel surfaces, the substrate is most preferably cleaned with a conventional hot alkaline cleaner, then rinsed with hot water, squeegeed, and dried. For aluminum, the surface to be treated most preferably is first contacted with either an aqueous alkaline cleaning solution in accordance with that disclosed in U.S. Patent No. 4,762,638, incorporated herein by reference, or an aqueous acidic cleaning solution as disclosed in U.S. Pat. No. 4,370,173, also incorporated herein by reference. With respect to the aqueous acidic cleaning solution, it should also be noted that a source of fluoride such as HF may also be employed to even further enhance the cleaning process. Irrespective of the type of cleaning solution employed, the aluminum is then subjected to a water rinse, after which a composition in accordance with the present invention may then be coated onto the aluminum in accordance with the processes disclosed herein.

[0027] The practice of this invention may be further appreciated by consideration of the following, non-limiting, working examples, and the benefits of the invention may be further appreciated by reference to the comparison examples.

GROUP I COMPONENTS (A) AND (B), WITH DRY IN PLACE TREATMENTS)

Test Methods and Other General Conditions

[0028] Test pieces of Type 3105 aluminum were spray cleaned for 15 seconds at 54.4° C with an aqueous cleaner containing 28 g/L of PARCO® Cleaner 305 (commercially available from the Parker+Amchem Division of Henkel Corp., Madison Heights, Michigan, USA). After cleaning, the panels were rinsed with hot water, squeegeed, and dried before roll coating with an acidic aqueous composition as described for the individual examples and comparison examples below.

[0029] For this first group of examples and comparison examples, the applied liquid composition according to the invention was flash dried in an infrared oven that produces approximately 49° C peak metal temperature. Samples thus treated were subsequently coated, according to the recommendations of the suppliers, with various commercial paints as specified further below.

[0030] T-Bend tests were according to American Society for Testing materials (hereinafter "ASTM") Method D4145-83; Impact tests were according to ASTM Method D2794-84E1; Salt Spray tests were according to ASTM Method B-117-90 Standard; Acetic Acid Salt Spray tests were according to ASTM Method B-287-74 Standard; and Humidity tests were according to ASTM D2247-8 Standard. The Boiling water immersion test was performed as follows: A 2T bend and a reverse impact deformation were performed on the treated and painted panel. The panel was then immersed for 10 minutes in boiling water at normal atmospheric pressure, and areas of the panel most affected by the T-bend and reverse impact deformations were examined to determine the percent of the paint film originally on these areas that had not been exfoliated. The rating is reported as a number that is one tenth of the percentage of paint not exfoliated. Thus, the best possible rating is 10, indicating no exfoliation; a rating of 5 indicates 50 % exfoliation; etc.

Specific Compositions

Example 1:

[0031]

5.6	parts of amorphous fumed silicon dioxide
396.2	parts of deionized water
56.6	parts of aqueous 60 % fluotitanic acid (i.e., H ₂ TiF ₆)
325.4	parts of deionized water
216.2	parts of an aqueous solution containing a mixture of 4.1 g/l polyacrylic acid and 4.0 g/l polyvinyl alcohol

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Example 2:

[0032]

5	58.8	parts of aqueous 60 % fluotitanic acid
	646.0	parts of deionized water
	5.9	parts of amorphous fumed silicon dioxide
	10.5	parts of zirconium hydroxide
10	278.8	parts of the 10 % solution of water soluble polymer as used in Example 1.

Example 3

[0033]

15	62.9	parts of aqueous 60 % fluotitanic acid
	330.5	parts of deionized water
	6.2	parts of amorphous fumed silicon dioxide
	358.9	parts of deionized water
20	241.5	parts of the 10 % water soluble polymer solution as used in Example 1

Example 4

[0034]

25	56.4	parts of aqueous 60 % fluotitanic acid
	56.4	parts of deionized water
	2.1	parts of Aerosil™ R-972 (a surface treated dispersed silica)
30	667.0	parts of deionized water
	218.1	parts of the 10 % water soluble polymer solution as used in Example 1

Example 5

[0035]

35	58.8	parts of aqueous 60 % fluotitanic acid
	3.7	parts of amorphous fumed silicon dioxide
	10.3	parts of zirconium basic carbonate
40	647.7	parts of deionized water
	279.5	parts of the 10 % solution of water soluble polymer as used in Example 1

Example 6

[0036]

45	52.0	parts of aqueous 60 % fluotitanic acid
	297.2	parts of deionized water
50	3.3	parts of amorphous fumed silicon dioxide
	9.1	parts of zirconium basic carbonate
	273.6	parts of deionized water
	364.8	parts of the 10 % solution of water soluble polymer as used in Example 1

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Example 7**[0037]**

11.0	parts of fumed amorphous silicon dioxide
241.0	parts of deionized water
114.2	parts of 60 % aqueous fluotitanic acid
633.8	parts of an aqueous composition prepared from the following ingredients:
5.41	% of CrO ₃
0.59	% of pearled corn starch
94	% of water

Example 8**[0038]**

666.0	parts of deionized water
83.9	parts of 60 % aqueous fluotitanic acid
5.3	parts of Cab-O-Sil™ M-5 fumed amorphous silicon dioxide
14.8	parts of zirconium basic carbonate
230.0	parts of RDX 68654™ (also known as RIX 95928™) epoxyl resin dispersion commercially available from Rhône-Poulenc, containing 40 % solids of polymers of predominantly diglycidyl ethers of bisphenol-A, in which some of the epoxide groups have been converted to hydroxy groups and the polymer molecules are phosphate capped

Example 9**[0039]**

656.0	parts of deionized water
183.9	parts of 60 % aqueous fluotitanic acid
5.3	parts of Cab-O-Sil™ M-5 fumed amorphous silicon dioxide
14.8	parts of zirconium basic carbonate
240.0	parts of Accumer™ 1510, a commercially available product from Rohm & Haas containing 25 % solids of polymers of acrylic acid with a molecular weight of 60,000

Example 10**[0040]**

636.2	parts of deionized water
83.7	parts of 60 % aqueous fluotitanic acid
5.3	parts of Cab-O-Sil™ M-5 fumed amorphous silicon dioxide
14.6	parts of zirconium basic carbonate
37.6	parts of the 10 % solution of water soluble polymer as used in Example 1 .
222.6	parts of Accumer™ 1510, a commercially available product from Rohm & Haas containing 25 % solids of polymers of acrylic acid with a molecular weight of 60,000

[0041] For each of Examples 1 - 6 and 8 - 10, the ingredients were added in the order indicated to a container provided with stirring. (Glass containers are susceptible to chemical attack by the compositions and generally should not be used, even on a laboratory scale; containers of austenitic stainless steels such as Type 316 and containers made of or fully lined with resistant plastics such as polymers of tetrafluoroethene or chlorotrifluoroethene have proved to be satisfactory.) In each of these Examples except Example 4, after the addition of the silica component and before

the addition of the subsequently listed components, the mixture was heated to a temperature in the range from 38 - 43 ° C and maintained within that range of temperatures for a time of 20 - 30 minutes. Then the mixture was cooled to a temperature below 30° C, and the remaining ingredients were stirred in without additional heating, until a clear solution was obtained after each addition.

[0042] For Example 4, the SiO₂ used was surface modified with a silane, and because of its hydrophobic nature, the mixture containing this form of silica was heated for 1.5 hours at 70° C to achieve transparency. The remaining steps of the process were the same as for Example 1.

[0043] For Example 7, the first three ingredients listed were mixed together and maintained at 40 ± 5 ° C for 20 - 30 minutes with stirring and then cooled. In a separate container, the CrO₃ was dissolved in about fifteen times its own weight of water, and to this solution was added a slurry of the corn starch in twenty-four times its own weight of water. The mixture was then maintained for 90 minutes with gentle stirring at 88±6 ° C to reduce part of the hexavalent chromium content to trivalent chromium. Finally, this mixture was cooled with stirring and then added to the previously prepared heated mixture of fluotitanic acid, silicon dioxide, and water. This composition is used in the manner known in the art for compositions containing hexavalent and trivalent chromium and dispersed silica, but it is much more stable to storage without phase separation.

Comparative Example 1

[0044]

18.9	parts of aqueous 60 % fluotitanic acid
363.6	parts of the 10 % solution of water soluble polymer as used in Example 1
617.5	parts of deionized water

Comparative Example 2

[0045]

18.9	parts of aqueous 60 % fluotitanic acid
71.8	parts of the 10 % solution of water soluble polymer as used in Example 1
909.3	parts of deionized water

[0046] For Comparative Examples 1 and 2 the components were added together with agitation in the order indicated, with no heating before use in treating metal surfaces.

[0047] Add-on mass levels, specific paints used, and test results with some of the compositions described above are shown in Tables 1 - 5 below.

TABLE 1:

Panels Painted with PPG Duracron™ 1000 White Single Coat Acrylic Paint					
Treatment	Boiling Water		Coating Weight	HAc Salt Spray 504 Hours	Humidity 1008 Hrs.
	2T Bend	Impact			
Example 1	9	10	65 mg/m ² as Ti	e 0-1 ^s s 0-1 ^s	Vf9
"	9	10	43 mg/m ² as Ti	e 0-1 ^s s 0-1 ^s	Vf9
Comparative Example 1	5	7	39 mg/m ² as Ti	e 0-1 ^s s 0-2 ^s	D9
"	0	0	27 mg/m ² as Ti	e 0-1 ^s s 0-2 ^s	D9

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TABLE 1: (continued)

Panels Painted with PPG Duracron™ 1000 White Single Coat Acrylic Paint					
Treatment	Boiling Water		Coating Weight	HAc Salt Spray 504 Hours	Humidity 1008 Hrs.
	2T Bend	Impact			
Comparative Example 2	7	8	65 mg/m ² as Ti	e 0-1 ^s s 0-1 ^s	Vf ⁹
"	4	6	29 mg/m ² as Ti	e 0-1 ^s s 0-1 ^s	Fm ⁹

TABLE 2:

Panels Painted with Lilly™ Black Single Coat Polyester						
Treatment	Boiling Water		Coating Weight	HAc Salt Spray 504 Hours	Salt Spray 1008 Hours	Humidity 1008 Hrs.
	2T Bend	Impact				
Example 2	10	10	54 mg/m ² as Ti	e 0-1 ^s s N	e N s N	Vf ⁹
Example 3	10	10	64 mg/m ² as Ti	e 0-2 ^s s 0-2 ^s	e 0-1 ^s s N	Vf ⁹

TABLE 3:

Panels Painted with Lilly™ Colonial White Single Coat Polyester						
Treatment	Boiling Water		Coating Weight	HAc Salt Spray 504 Hours	Salt Spray 1008 Hours	Humidity 1008 Hrs.
	2T Bend	Impact				
Example 4	5	8	65 mg/m ² as Ti	e N s N	e N s N	Vf ⁹
Example 5	10	10	22 mg/m ² as Ti	e N s N	e N s N	Vf ⁹
Example 5	10	10	54 mg/m ²	e N s N	e N s N	Vf ⁹
Example 6	10	10	22 mg/m ²	e 0-1 ^s s N	e N s N	Vf ⁹
Example 6	10	10	54 mg/m ²	e 0-1 ^s s N	e N s N	Vf ⁹
Example 8	9.8	10	12 mg/m ²	e N s 0-1 ^s	e N s N	N
Example 8	9.6	10	24 mg/m ²	e N s 0-1 ^s	e N s N	N
Example 9	10	10	11 mg/m ²	e N	e N	

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TABLE 3: (continued)

Panels Painted with Lilly™ Colonial White Single Coat Polyester						
Treatment	Boiling Water		Coating Weight	HAc Salt Spray 504 Hours	Salt Spray 1008 Hours	Humidity 1008 Hrs.
	2T Bend	Impact				
Example 9	9.8	10	24 mg/m ²	s 0-1 ^s e 0-1 ^s s 0-1 ^s	s 0-1 ^s e s 0-1	N N N
Example 10	9.8	9.8	17 mg/m ²	e 0-1 ^s s 0-1 ^s	e N s N	Vf ⁹
Example 10	9.9	10	25 mg/m ²	e 0-1 ^s s 0-1 ^s	e N s N	Vf ⁹
Example 10	9.9	10	33 mg/m ²	e 0-1 ^s s 0-1 ^s	e N s N	Vf ⁹

TABLE 4:

Panels Painted with Valspar/Desoto™ White Single Coat Polyester						
Treatment	Boiling Water		Coating Weight	HAc Salt Spray 1008 Hours	Salt Spray 1008 Hours	Humidity 1008 Hrs.
	2T Bend	Impact				
Example 2	10	10	39 mg/m ² as Ti	e 0-1 ^s s 0-1 ²	e N s N	Vf ⁹
Example 2	10	10	48 mg/m ² as Ti	e 0-1 ^s s 0-1 ^s	e N s N	Vf ⁹
Example 2	10	10	70 mg/m ² as Ti	e 0-2 ^s s 0-1 ^s	e N s N	Vf ⁹
Example 2	10	10	87 mg/m ² as Ti	e N s 0-1 ^s	e 0-1 ^s s N	Vf ⁹
Example 3	10	10	29 mg/m ² as Ti	e 0-2 ^s s 0-1 ^s	e N s N	Vf ⁹
Example 3	10	10	42 mg/m ² as Ti	e 0-1 ^s s 0-1 ^s	e N s N	Vf ⁹
Example 3	10	10	57 mg/m ² as Ti	e 0-1 s 0-1 ^s	e N s N	Vf ⁹
Example 3	10	10	82 mg/m ² as Ti	e 0-2 ^s s 0-2 ^s	e 0-1 ^s s N	Vf ⁹
Example 4	7	10	65 mg/m ²	e 0-1 ^s	e N	

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TABLE 4: (continued)

Panels Painted with Valspar/Desoto™ White Single Coat Polyester						
Treatment	Boiling Water		Coating Weight	HAc Salt Spray 1008 Hours	Salt Spray 1008 Hours	Humidity 1008 Hrs.
	2T Bend	Impact				
			as Ti	s 0-1 ^s	s N	Vf ⁹

TABLE 5:

Panels Painted with Valspar™ Colonial White Single Coat Polyester						
Treatment	Boiling	Water	Coating Weight	HAc Salt Spray 504 Hours	Salt Spray 1008 Hours	Humidity 1008 Hrs.
	2T Bend	Impact				
Example 2	10	10	54 mg/m ² as Ti	e N s N	e N s N	Fm ⁹
Example 3	10	10	64 mg/m ² as Ti	e 0-1 ^s s N	e 0-1 ^s s 0-1 ^s	Fm ⁹

[0048] The storage stability of the compositions according to all of the examples above except Example 2 was so good that no phase separation could be observed after at least 1500 hours of storage. For Example 2, some settling of a slight amount of apparent solid phase was observable after 150 hours.

GROUP II

COMPONENTS (A) AND (B), WITH SPRAY TREATMENT

[0049] To obtain the results reported below, an alternative process of treating the metal surfaces according to the invention and different aluminum alloys were used. Specifically, in part I of this Group, test pieces of Type 5352 or 5182 aluminum were spray cleaned for 10 seconds at 54.4° C with an aqueous cleaner containing 24 g/L of PARCO® Cleaner 305 (commercially available from the Parker+Amchem Division of Henkel Corp., Madison Heights, Michigan, USA). After cleaning, the panels were rinsed with hot water; then they were sprayed with the respective treatment solutions according to the invention, which were the same as those already described above with the same Example Number, except that they were further diluted with water to the concentration shown in the tables below, for 5 seconds; and then were rinsed successively with cold tap water and deionized water and dried, prior to painting.

[0050] The "OT Bend" column in the following tables reports the result of a test procedure as follows:

1. Perform a 0-T bend in accordance with ASTM Method D4145-83.
2. Firmly apply one piece of #610 Scotch® tape to the area of the test panel with the O-T bend and to the adjacent flat area.
3. Slowly pull the tape off from the bend and the adjacent flat area.
4. Repeat steps 2 and 3, using a fresh piece of tape for each repetition, until no additional paint is removed by the tape.
5. Report the maximum distance from the 0-T bend into the flat area from which paint removal is observed according to the scale below:

Paint loss in mm	Rating
0	5.0
0.20	4.9
0.30	4.8
0.8	4.5
1.6	4.0

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(continued)

Paint loss in mm	Rating
2.4	3.5
3.2	3.0
4.0	2.5
4.8	2.0
5.6	1.5
6.4	1.0
7.2	0.5
>7.2	0

[0051] The "Ninety Minute Steam Exposure" columns of the tables below report the results of tests performed as follows:

1. Expose the painted samples to steam at a temperature of 120° C steam for 90 minutes in a pressure cooker or autoclave.
2. Crosshatch the painted sample - two perpendicular cuts; a Gardner crosshatch tool with 11 knife edges spaced 1.5 mm apart was used.
3. Firmly apply #610 Scotch™ tape to the crosshatched area and remove tape.
4. Examine the crosshatched area for paint not removed by the tape and report a number representing one-tenth of the percentage of paint remaining.
5. Using a microscope at 10 - 80 times magnification, visually observe crosshatched area for blistering, and rate size and density of blisters.

[0052] The "15 Minute Boiling DOWFAX™ 2A1 Immersion" columns of the tables below report the results of tests performed after treatment as follows:

1. Prepare solution of 1 % by volume of DOWFAX™ 2A1 in deionized water and bring to boil.
- 2 Immerse painted test panels in the boiling solution prepared in step 1 and keep there for 15 minutes; then remove panels, rinse with water, and dry.

[0053] DOWFAX™ 2A1 is commercially available from Dow Chemical and is described by the supplier as 45 % active sodium dodecyl diphenyloxide disulfonate. The "Cross Hatch" test after this treatment was made in the same way as described above for steps 2 - 4 after "Ninety Minute Steam Exposure". The "Reverse Impact" test was made as described in ASTM D2794-84E1 (for 20 inch pounds impact), then proceeding in the same way as described above for steps 3 - 4 after "Ninety Minute Steam Exposure". The "Feathering" test was performed as follows: Using a utility knife, scribe a slightly curved "V" on the back side of the test panel. Using scissors, cut up about 12 millimeters from the bottom along the scribe. Bend the inside of the V away from side for testing. Place sample in a vise and, using pliers, pull from the folded section with a slow continuous motion. Ignore the part of the panel between the top edges nearest to the vertex and a line parallel to the top edge but 19 mm away from it. On the remainder of the panel, measure to edge of feathering in millimeters. Record the largest value observed.

[0054] The results of tests according to these procedures are shown in Tables 6 - 8 below.

TABLE 6:

5352 Alloy Panels Painted with Valspar™ S-9009-139 Paint						
Invention Composition	Concentration	pH	Coating Weight	OT Bend	Ninety Minute Steam Exposure	
					Cross Hatch	Blistering
Example 1	1%	2.7	4.0 mg/m ² as Ti	5	10	Very few, small-medium
Example 1	1%	3.2	11.4 mg/m ² as Ti	5	10	few, small
Example 1	3%	2.5	2.3 mg/m ² as Ti	5	10	very few, very small

TABLE 6: (continued)

5352 Alloy Panels Painted with Valspar™ S-9009-139 Paint						
Invention Composition	Concentration	pH	Coating Weight	OT Bend	Ninety Minute Steam Exposure	
					Cross Hatch	Blistering
Clean only (Comparison)	N/A			1.5	10	few, medium

TABLE 7:

5352 Alloy Panels Painted with Valspar™ S-9009-154 Paint						
Invention Composition	Concentration	pH	Coating Weight	OT Bend	Ninety Minute Steam Exposure	
					Cross Hatch	Blistering
Example 1	1%	2.9	4.2 mg/m ² as Ti	5	9-10	Very few, small
Example 1	3%	2.7	2.6 mg/m ² as Ti	5	9-10	very few, very small

TABLE 8:

5182 alloy panels Painted with Valspar™ S-9835002 Paint						
Invention Composition	Concentration	pH	Coating Weight	15 Minute Boiling DOWFAX™ 2A1 Immersion		
				Cross Hatch	Reverse Impact	Feathering
Example 1	1 % by weight	2.9	7.9 mg/m ² as Ti	10	10	0.35 mm

[0055] In part II of this Group, Type 5352 aluminum was used, and the process sequence used in part I, except for final drying, was used but was then followed by passing the test pieces, still wet from the deionized water rinse after contact with a composition according to this invention, through power driven squeegee rolls arranged so that the test pieces passed through the squeegee rolls in a horizontal position immediately after being sprayed liberally with the final treatment liquid composition at a temperature of 60° C before being dried. In Examples 11 and 13 the treatment liquid in this final stage was simply deionized water with a conductivity of not more than 4.0 μ Siemens/cm, while in Example 12 the treatment liquid in this final stage was obtained by mixing 35 ml of Parcolene™ 95AT and 2.0 ml of Parcolene™ 88B with 7 liters of deionized water and had a pH of 5.18 and a conductivity of 56 μ Siemens/cm. (Both Parcolene™ products noted are commercially available from the Parker+Amchem Div. of Henkel Corp., Madison Heights, Michigan.) This latter type of final treatment liquid is an example of one containing polymers and/or copolymers of one or more x-(N-R¹-N-R²-aminomethyl)-4-hydroxy-styrenes as already described above.

[0056] Concentrate II-II used in each of Examples 11 - 13 had the following composition:

1892.7	parts of deionized water
83.7	parts of 60 % aqueous fluotitanic acid
5.3	parts of Cab-O-Sil™ M-5 fumed amorphous silicon dioxide
18.3	parts of zirconium basic carbonate.

These ingredients were simply mixed together with mechanical agitation in the order shown, with a pause after each addition until the solution became optically clear. Although the partial mixture was not transparent immediately after addition of the silicon dioxide, it became clear after a few minutes of mixing, even without any heating.

[0057] The working solution for Examples 11 and 12 was prepared by diluting 200 grams of the concentrate II-II, along with sufficient sodium carbonate to result in a pH of 2.92 ± 0.2 , to form 6 liters of working composition. For Example 13, the working solution was made in the same way, except that it also contained 5 grams of a concentrated

polymer solution made according to the directions of column 11 lines 39 - 49 of U.S. Patent 4,963,596, except as follows: The preparation was carried out on a substantially larger scale; the proportions of ingredients were changed to the following: 241 parts of Propasol™ P, 109 parts of Resin M, 179 parts of N-methylglucamine, 73.5 parts of aqueous 37 % formaldehyde, and 398 parts of deionized water, of which 126 parts were reserved for a final addition not described in the noted patent, with the remainder used to slurry the N-methylglucamine as noted in the patent; and the temperature noted as 60 - 65 ° C in the patent was reduced to 57° C.

[0058] The dried test panels were then coated with Valspar™ 9009-157 paint according to the directions of the paint supplier, and the paint coated panels were tested as described for the tests of the same name in part I of Group II. Results are shown in Table 9.

TABLE 9

Example Number	mg of Ti/m ²	O-T Bend	90 Minute Steam Exposure	
			Cross Hatch	Blistering
11	3.6	4.5	10	4.5
12	4.6	4.9	10	4.5
13	5.4	4.8	10	4.0

GROUP III, WITH NECESSARY COMPONENTS (A') AND (B')

Example 14

[0059] A first concentrate was made by mixing 750 parts of tap water and 274 parts of Acrysol™ A-1, a commercially available product from Rohm and Haas containing 25.% solids of polymers of acrylic acid with a molecular weight of less than 50,000. A second concentrate was made by mixing, in a container separate from that used for the first concentrate 951.3 parts of tap water and 66.7 g/l of Gohsenol™ GLO-5, a commercially available product from Nippon Gohsei which is a low molecular weight polyvinyl alcohol; the latter was added to the tap water with stirring at a slow and controlled flow, after which the temperature was increased to 49 - 54 ° C for 30 minutes with slow stirring until all was dissolved.

[0060] An amount of these concentrates equal, for each concentrate separately, to 6 volume % of the final volume of composition ready for treating a metal surface according to this invention, was then added with stirring at ambient temperature to a large excess of water, and after addition of both concentrates, additional water was added to reach the final volume of treatment composition, which contained 4.1 g/l of polyacrylic acid and 4.0 g/l of polyvinyl alcohol.

[0061] This composition was then contacted with an aluminum surface by dipping or spraying for a time from 30 to 60 seconds, after which time the surfaces treated were removed from contact with the treating composition, allowed to dry in the ambient atmosphere without rinsing, and then baked in a warm air oven at 88° C for 5 minutes to simulate commercial operating conditions. The surfaces thus prepared were painted with conventional paints.

Examples 15 - 20

[0062] In each of these examples, the treating composition is prepared in the same general manner as in Example 14, by making separate concentrates of the hydroxyl group containing polymer and polyacrylic acid components, mixing an appropriate amount of these concentrates with a larger volume of water, adding any additional components used, and finally adjusting to the final desired volume or mass by the addition of more water. These compositions are then applied to aluminum surfaces in the same manner as described for Example 14. The specific active ingredients and concentrations or amounts thereof in the treatment composition for each example are as follows:

Example 15: 4.1 g/l of Acrysol™ A-1; 4.0 g/l of Gohsenol™ GLO-5; and 1.2 g/l of hexafluorozirconic acid.

Example 16: 4.1 g/l of Acrysol™ A-1 and 0.6 g/l of polyethylene glycol having a molecular weight of less than about 600,000.

Example 17: 4.1 g/l of Acrysol™ A-1; 0.6 g/l of polyethylene glycol having a molecular weight of less than about 600,000; and 1.2 g/l of hexafluorozirconic acid.

Example 18: 4.1 g/l of Acrysol™ A-1 and 0.8 g/l of dextrin.

Example 19: 4.1 g/l of Acrysol™ A-1; 0.8 g/l of dextrin; and 1.2 g/l of hexafluorotitanic acid.

Example 20: 651.4 parts of deionized water; 83.7 parts of 60 % aqueous fluotitanic acid; 5.3 parts of Cab-O-Sil™ M-5 fumed amorphous silicon dioxide; 14.6 parts of zirconium basic carbonate; 200.0 parts of Accumer™ 1510,

a commercially available product from Rohm and Haas containing 25 % solids of polymers of acrylic acid with a molecular weight of about 60,000; and 55.0 parts of Gohsenol™ GLO-5.

Claims

1. An aqueous liquid composition, which besides water consists essentially of the following components:

(A') a water-soluble or -dispersible polyvinyl alcohol, present in a concentration range of from 0.5 to 50 g/l;
 (B') one or a mixture of more than one of the following, namely polymers and copolymers of acrylic acid and methacrylic acid and their salts, present in a total concentration of from 0.5 to 50 g/l;
 (C') a component selected from H_2TiF_6 , H_2ZrF_6 , H_2HfF_6 , H_3AlF_6 , H_2SiF_6 , H_2GeF_6 , H_2SnF_4 , HF_4 and mixtures thereof, present in a total concentration of from 0.01 to 7 M;

and optionally, one or more of the following components:

(D') a component selected from the water-insoluble oxides, water-insoluble hydroxides, water-insoluble carbonates and/or water-insoluble elemental forms of titanium (Ti), zirconium (Zr), hafnium (Hf), boron (B), aluminium (Al), silicon (Si), germanium (Ge) and/or tin (Sn); and
 (E') a component of water-soluble oxides, water-soluble carbonates, and/or water-soluble hydroxides of Ti, Zr, Hf, B, Al, Si, Ge, and/or Sn.

2. An aqueous liquid composition as claimed in claim 1, in which component A' is or includes polyvinyl alcohol having a degree of polymerisation in the range of from 100 to 600.

3. An aqueous liquid composition as claimed in claim 2, in which said polyvinyl alcohol is present in a concentration in the range of from 0.5 to 16 g/l.

4. An aqueous liquid composition as claimed in any of the preceding claims, -in which component B' is or includes polyacrylic acid having an average molecular weight of the order of 50,000.

5. An aqueous liquid composition as claimed in any of the preceding claims in which component C' is H_2ZrF_6 and/or H_2TiF_6 .

6. An aqueous liquid composition as claimed in any of the preceding claims, having a pH value in the range of from 1.0 to 5.0.

7. An aqueous liquid composition as claimed in any of the preceding claims having a pH in the range of from 1.0 to 3.5.

8. A process for treating aluminium and aluminium alloys, in which the aluminium surface is brought into contact with an aqueous liquid composition as claimed in any of the preceding claims.

Patentansprüche

1. Wässrige, flüssige Zusammensetzung, die neben Wasser im wesentlichen aus den folgenden Komponenten besteht:

(A') einem wasserlöslichen oder wasserdispergierbaren Polyvinylalkohol, der in einem Konzentrationsbereich von 0,5 bis 50 g/l vorhanden ist;

(B') einem Stoff oder einer Mischung von mehr als einem der folgenden Stoffe, nämlich Polymere und Copolymere von Acrylsäure und Methacrylsäure und deren Salze, die in einer Gesamtkonzentration von 0,5 bis 50 g/l vorhanden sind;

(C') einer aus H_2TiF_6 , H_2ZrF_6 , H_2HfF_6 , H_3AlF_6 , H_2SiF_6 , H_2GeF_6 , H_2SnF_4 , HF_4 und Mischungen davon ausgewählte Komponente, die in einer Gesamtkonzentration von 0,01 bis 7 M vorhanden ist;

und gegebenenfalls einer oder mehrerer der folgenden Komponenten:

(D') einer Komponente, die ausgewählt ist aus den wasserunlöslichen Oxiden, wasserunlöslichen Hydroxiden, wasserunlöslichen Carbonaten und/oder wasserunlöslichen elementaren Formen von Titan (Ti), Zirkonium (Zr), Hafnium (Hf), Bor (B), Aluminium (Al), Silicium (Si), Germanium (Ge) und/oder Zinn (Sn); und

(E') einer Komponente aus wasserlöslichen Oxiden, wasserlöslichen Carbonaten und/oder wasserlöslichen Hydroxiden von Ti, Zr, Hf, B, Al, Si, Ge und/oder Sn.

2. Wässrige, flüssige Zusammensetzung nach Anspruch 1, wobei Komponente A¹ ein Polyvinylalkohol mit einem Polymerisationsgrad im Bereich von 100 bis 600 ist oder einen solchen umfasst.

3. Wässrige, flüssige Zusammensetzung nach Anspruch 2, wobei der Polyvinylalkohol in einer Konzentration im Bereich von 0,5 bis 16 g/l vorhanden ist.

4. Wässrige, flüssige Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei Komponente B' Polyacrylsäure mit einer mittleren Molmasse in der Größenordnung von 50 000 ist oder diese umfasst.

5. Wässrige, flüssige Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei Komponente C' H₂ZrF₆ und/oder H₂TiF₆ ist.

6. Wässrige, flüssige Zusammensetzung nach einem der vorhergehenden Ansprüche mit einem pH-Wert im Bereich von 1,0 bis 5,0.

7. Wässrige, flüssige Zusammensetzung nach einem der vorhergehenden Ansprüche mit einem pH-Wert im Bereich von 1,0 bis 3,5.

8. Verfahren zur Behandlung von Aluminium und Aluminiumlegierungen, wobei die Aluminiumoberfläche mit einer in einem der vorhergehenden Ansprüche beanspruchten wässrigen, flüssigen Zusammensetzung in Kontakt gebracht wird.

Revendications

1. Composition liquide aqueuse qui contient, hormis l'eau, essentiellement les composants suivants :

(A') un alcool polyvinylique soluble dispersible dans l'eau, présent dans une gamme de concentrations allant de 0,5 à 50 g/l;

(B') un ou un mélange de plus d'un des éléments suivants à savoir des polymères et des copolymères de l'acide acrylique et de l'acide méthacrylique et leurs sels, présent en une concentration totale comprise entre 0,5 et 50 g/l;

(C') un composé choisi parmi H₂TiF₆, H₂ZrF₆, H₂HfF₆, H₃AlF₆, H₂SiF₆, H₂GeF₆, H₂SnF₄, HBF₄ et des mélanges de ces derniers, présents en une concentration totale comprise entre 0,01 et 7 M;

et facultativement un ou plusieurs des constituants suivants :

(D') un constituant choisi parmi des oxydes insolubles dans l'eau, des hydroxydes insolubles dans l'eau, des carbonates insolubles dans l'eau et/ou des formes élémentaires, insolubles dans l'eau, du titane (Ti), du zirkonium (Zr), du hafnium (Hf), du bore (B), de l'aluminium (Al), du silicium (Si), du germanium (Ge) et/ou de l'étain (Sn); et

(E') un constituant d'oxydes solubles à l'eau, de carbonates solubles à l'eau et/ou d'hydroxydes solubles à l'eau de Ti, Zr, Hf, B, Al, Si, Ge et/ou Sn.

2. Composition liquide aqueuse selon la revendication 1, dans laquelle le constituant A' est ou inclut l'alcool polyvinylique possédant un degré de polymérisation dans la gamme comprise entre 100 et 600.

3. Composition liquide aqueuse selon la revendication 2, dans laquelle ledit alcool polyvinylique est présent en une concentration située dans la gamme comprise entre 0,5 et 16 g/l.

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4. Composition liquide aqueuse selon l'une quelconque des revendications précédentes, dans laquelle le constituant (B') est ou inclut de l'acide polyacrylique ayant un poids moléculaire moyen de l'ordre de 50 000.
- 5 5. Composition liquide aqueuse selon l'une quelconque des revendications précédentes, dans laquelle le constituant (C') est du H_2ZrF_6 et/ou du H_2TiF_6 .
6. Composition liquide aqueuse selon l'une quelconque des revendications précédentes, possédant une valeur du pH dans la gamme comprise entre 1,0 et 5,0.
- 10 7. Composition liquide aqueuse selon l'une quelconque des revendications précédentes, possédant une valeur du pH située dans la gamme comprise entre 1,0 et 3,5.
- 15 8. Procédé pour traiter l'aluminium et des alliages d'aluminium, selon lequel la surface de l'aluminium est placée en contact avec une composition liquide aqueuse telle que revendiquée dans l'une quelconque des revendications précédentes.

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