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(54) **PROCESS AND COMPOSITION FOR SEALING POROUS COATINGS CONTAINING METAL AND OXYGEN ATOMS**

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(57) **ABSTRACT**

Anodized aluminum surfaces are sealed using a process in which one step involves bringing the anodized aluminum surface into contact for a relatively brief period of time at a relatively low temperature with a liquid sealing composition. The liquid sealing composition contains water, lithium cations, fluoride anions and at least one high capacity buffering agent such as boric acid.

PROCESS AND COMPOSITION FOR SEALING POROUS COATINGS CONTAINING METAL AND OXYGEN ATOMS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from provisional U.S. application Ser. No. 60/271,502, filed Feb. 26, 2001.

BACKGROUND OF THE INVENTION

[0002] It is well known that valuable protective coatings that contain both metal atoms and oxygen atoms can be formed on many metal surfaces, particularly those of aluminum and its alloys, by passing a current in an anodizing direction through the surface while it is in contact with a suitable electrolyte. See, e.g., S. Wernick, R. Pinner, and P. G. Sheasby, *The Surface Treatment and Finishing of Aluminum and Its Alloys* (ASM International, Metals Park, Ohio, U. S. A., 1987), pp. 289-661. Similar coatings, generally less commercially valuable, can be produced by chemical treatment of metal surfaces with appropriate oxidizing agents. *Op. cit.*, pp. 220-288.

[0003] Coatings formed by anodization on aluminum substrates in suitable electrolytes can be grown to almost any desired thickness. The outer parts of such coatings, when they have a thickness that provides good corrosion resistance for architectural uses, are initially formed with pores that extend from their exterior surface nearly to the substrate metal, the pores being separated from the substrate metal by an at least relatively pore-free "barrier layer". The thickness of the barrier layer depends almost solely on the electrolyte and the anodizing voltage and, unlike the outer porous part of the coating, normally can not, after the first few seconds of electrolysis, be increased in thickness without increasing the voltage, no matter how long anodization is continued. In order to achieve good corrosion resistance, at least the exterior zone of the pores that are initially formed as an inherent characteristic of the anodization process must be closed before the substrate and its protective coating are exposed to corrosive environments after anodization is completed. The process of closing the at least the outer zone of the pores in an initially formed coating is known as "sealing". Traditionally, sealing has been accomplished by exposure of the surface of the coated substrate to steam or very hot water. The high energy cost of this process has motivated earlier developments of liquid compositions for sealing that contain solutes in addition to water and can accomplish effective sealing at lower temperatures in a reasonable time. Most if not all of such low temperature sealing compositions with commercially demonstrated success to date, however, contain cations of at least one of the heavy metals nickel, cobalt, iron, and manganese. The presence of these metal cations increases waste disposal costs under the pollution laws of most jurisdictions.

[0004] WO 99/10567 discloses an invention that can overcome this and some other problems of the prior art. In a process according to this disclosure, a surface to be sealed is first treated at a temperature of not more than 75° C. with an aqueous composition that contains at least lithium and fluoride ions. This is followed by a second stage of sealing with hot water or steam that can be much shorter and can be completed in a reasonable time at a lower temperature than

traditional single step sealing with water. This invention is an improvement of that disclosed in WO 99/10567, specifically by achieving at least one of the following benefits:

[0005] increasing the ability of the first stage treatment composition to resist pH changes as a result of the unavoidable drag-into it of some acid, which is almost always used as the electrolyte for anodizing and can not practically be removed completely from the pores formed during anodization before the anodized substrate is transferred into the sealing composition, and/or as a result of the deliberate additions of alkaline materials that are normally made to the first treatment composition in order to neutralize the unavoidable drag-in of acid;

[0006] reducing the tendency of clear and bronze colored anodized coatings to develop smut during sealing;

[0007] permitting the removal of any smut that does form by gentle abrasion without greatly reducing the corrosion protection achieved by the sealing treatment;

[0008] making the corrosion protection achieved by the sealing treatment less susceptible to damage by contact with other solid surfaces; and

[0009] improving the corrosion resistance achieved in the sealed coating, as measured by one or more standard accelerated corrosion tests.

[0010] 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, however. Also, throughout the description, unless expressly stated to the contrary: percent, "parts of", and ratio values are by weight or mass; the term "polymer" includes "oligomer", "copolymer", "terpolymer" and the like; 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 or of generation in situ within the composition by chemical reaction(s) noted in the specification between one or more newly added constituents and one or more constituents already present in the composition when the other constituent(s) are added, and does not preclude unspecified chemical interactions among the constituents of a mixture once mixed; specification of constituents in ionic form additionally implies the presence of sufficient counterions to produce electrical neutrality for the composition as a whole and for any substance added to the composition; any counterions thus implicitly specified preferably are 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 an object of the invention; the word "mole" means "gram mole", and the word itself and all of its grammatical variations may be used for any chemical species defined by all of the types and

numbers of atoms present in it, irrespective of whether the species is ionic, neutral, unstable, hypothetical, or in fact a stable neutral substance with well defined molecules; the terms "solution", "soluble", "homogeneous", and the like are to be understood as including not only true equilibrium solutions or homogeneity but also dispersions that show no visually detectable tendency toward phase separation over a period of observation of at least 100, or preferably at least 1000, hours during which the material is mechanically undisturbed and the temperature of the material is maintained within the range of 18-25° C.; the first definition of an acronym or other abbreviation applies to all subsequent uses of the same acronym or other abbreviation; and the term "paint" and its grammatical variations includes all similar types of coatings that may be described by more specialized names such as "lacquer", "varnish", "primer coat", "top coat", or the like. Except where otherwise noted, all materials, the names of which appear in all capitals and/or are designated by "®" or "TM" are commercial products of the Surface Technologies Division of Henkel Corporation (Madison Heights, Mich.).

BRIEF SUMMARY OF THE INVENTION

[0011] In WO 99/10567 it was taught that effective sealing can be achieved by a two step process in which the first step is exposure of the anodized surface to be sealed to an aqueous solution containing lithium cations and fluoride anions at a relatively low temperature, followed by a short treatment with a different treatment composition at a higher temperature than the second step. The pH and silicon content of the aqueous solution used for the first treatment step are carefully controlled to achieve consistently satisfactory results. It has now been found that the presence of a high capacity buffering component together with lithium and fluoride ions in the first sealing composition achieves at least one of the alternative objects of the inventions as set forth above, without diminishing its effectiveness as a sealing composition. Compositions for use according to process embodiments of the invention, concentrate compositions from which such compositions for use can be made by mixing and dilution with water, and articles of manufacture treated by a process according to the invention are also within the scope of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0012] A process according to the invention for sealing an anodized aluminum surface comprises at least the following operations:

[0013] (I) bringing the anodized aluminum surface into contact for not more than 30 min at a temperature not greater than 75° C. with a liquid first sealing composition as described below; and

[0014] (II) after completion of operation (I), bringing the anodized aluminum surface as modified by operation (I) into contact at a temperature of at least 82° C. with a second sealing composition comprising steam or liquid water.

[0015] Compositions for use in operation (I) of sealing according to the invention as described above have a pH value from 7.0 to 10.0 (more preferably, from 7.5 to 9.5), this pH value being sufficiently well buffered that at least,

with increasing preference in the order given, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65 milliequivalent of strong alkali per liter of sealing composition is required to raise the pH of the sealing composition by 0.50 pH unit and at least, with increasing preference in the order given, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65 milliequivalent of strong acid per liter of sealing composition is required to lower the pH of the sealing composition by 0.50 pH unit. A first sealing composition to be used in a first sealing operation according to this invention also comprises, preferably consists essentially of, or more preferably consists of, water and the following components:

[0016] (A) a component of dissolved lithium cations;

[0017] (B) a component of dissolved fluoride anions. Optionally, one or more of the following components may also be present in the first sealing composition:

[0018] (C) a component of one or more dissolved, dispersed, or both dissolved and dispersed surfactants;

[0019] (D) a component of dissolved pH controlling agent that is not part of any of components (A) through (C);

[0020] (E) a component of preservative material that is not part of any of components (A) through (D);

[0021] (F) not more than 50 parts of silicon per million parts by weight of the total composition, a concentration unit which may be applied to other constituents as well as silicon and is hereinafter usually abbreviated as "ppm", in any dissolved or suspended chemical form;

[0022] (G) up to 2000 ppm of complex transition metal containing anions, said anions not being part of any of components (A) through (F) as recited above and being selected from the group consisting of simple and condensed molybdates, tungstates, and vanadates; and

[0023] (H) up to 1000 ppm of polymers that are not part of any of components (A) through (G), said polymers being selected from the group consisting of homo- and co-polymers of at least one of acrylic acid, methacrylic acid, and maleic acid, all optionally bearing phosphonic acid substituents.

[0024] Component (A) may be derived from any sufficiently water soluble lithium salt, including the fluoride, which would also supply component (B). However, the preferred concentrations of components (A) and (B) are such that if lithium fluoride, with a water solubility of only about 1 part per thousand by weight, is used as the source of component (A), only slight dilution of a saturated solution is possible without reducing the concentration of at least one of components (A) and (B) below the most preferred level. Furthermore, if solid lithium fluoride is used as a source of components (A) and (B), it may be slow to dissolve, and the relatively small amounts of it needed may be difficult to measure and control accurately enough at the point of use. Still further, the most preferred ratio between fluoride and lithium concentrations is lower than that in lithium fluoride salt. For all of these reasons, the normally preferred source of component (A) is lithium acetate, which is relatively inexpensive and very soluble in water, so that concentrates can easily be prepared, and/or lithium hydroxide, which is also relatively inexpensive and sufficiently soluble in water to make useful concentrates, even though it is much less soluble than lithium acetate.

[0025] A concentrate composition according to the invention preferably contains at least, with increasing preference in the order given, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, or 24 times the concentration of at least one of the ingredients, other than water, that is specified as preferred for one of the necessary components of a working sealing composition to be used in a first sealing step in a process according to the invention. Thus at least two concentrates of preferred strength are needed for making a preferred working sealing composition to be used in a first sealing step in a process according to this invention. Preferably one of them contains lithium acetate and, optionally and preferably, additional acetic acid, while another contains the principal fluoride source. At least one of the two preferred concentrates preferably also contains any other ingredient desired in the working composition to be made from the two concentrates, so that each may be used as a replenisher for a volume of working composition to be operated for a long time, without depleting the content of any desired ingredient by drag-out of the sealing composition on surfaces treated with it.

[0026] Irrespective of its source, the concentration of lithium cations in a liquid composition used in a first sealing step according to the invention preferably is at least, with increasing preference in the order given, 0.07, 0.14, 0.23, 0.31, 0.37, 0.42, 0.46, 0.49, 0.52, 0.55, 0.58, 0.61, 0.63, or 0.65 grams of lithium cations per liter of solution, a unit which may be applied to any other material as well as to lithium and is hereinafter usually abbreviated as "g/l", and independently, primarily for reasons of economy and/or stability against precipitation of lithium fluoride, preferably is not more than, with increasing preference in the order given, 5.0, 4.0, 3.0, 2.0, 1.0, 0.80, 0.77, 0.74, 0.71, 0.69, or 0.67 g/l.

[0027] Any sufficiently water soluble fluoride salt and/or hydrofluoric acid may be used as the source of component (B). It has been found that the presence of relatively small amounts of silicon, in any chemical form found in many commercially sourced fluoride salts that have not been particularly carefully kept free of silicon, in a composition used in a first sealing step according to this invention can be highly detrimental to the corrosion resistance of the resulting sealed coating, so that one aspect of the preferred source of component (B) is a low silicon content. Sodium and potassium fluorides have both been found satisfactory and are generally preferred, with sodium more preferred. The fluoride also may be supplied in complexed form, for example as hexafluorozirconate, hexafluorotitanate, tetrafluoroborate, or hexafluoro-silicate, or as an acid fluoride, but normally these sources are more expensive and are less preferred at least for that reason.

[0028] Irrespective of its source, the concentration of component (B) in a liquid composition used for a first sealing step according to this invention preferably is at least, with increasing preference in the order given, 0.08, 0.12, 0.16, 0.20, 0.25, 0.30, 0.35, 0.39, 0.43, 0.47, 0.49, or 0.51 g/l and independently, primarily for reasons of economy, preferably is not more than, with increasing preference in the order given, 6.0, 4.0, 2.0, 1.5, 1.3, 1.1, 0.90, 0.80, 0.70, 0.65, 0.60, 0.55, or 0.53 g/l.

[0029] Irrespective of the actual concentrations of fluoride anions and lithium cations in a composition to be used in a first sealing step according to this invention, the ratio of the

mass of fluoride anions to the mass of lithium cations preferably is at least, with increasing preference in the order given, 0.20:1.00, 0.30:1.00, 0.40:1.00, 0.50:1.00, 0.56:1.00, 0.59:1.00, 0.62:1.00, 0.65:1.00, 0.68:1.00, 0.71:1.00, 0.74:1.00, 0.76:1.00, or 0.78:1.00 and independently preferably is not more than, with increasing preference in the order given, 3.0:1.00, 2.0:1.00, 1.5:1.00, 1.30:1.00, 1.20:1.00, 1.10:1.00, 1.05:1.00, 1.00:1.00, 0.95:1.00, 0.85:1.00, 0.81:1.00, or 0.79:1.00.

[0030] Buffering of the pH as required may be achieved by including in a first sealing composition to be used in a first sealing operation according to this invention any combination of materials with sufficient buffering capacity that do not otherwise interfere with forming a good seal. Boric acid, which is readily available in a grade sufficiently free of known disadvantageous components such as silicon and phosphate, has been found to be particularly effective in buffering in the most preferred pH range and may have other benefits that have not been elucidated, so that its inclusion in a first sealing composition to be used in a first sealing operation according to this invention is preferred. Salts of boric acid (borates) may also be utilized, as may mixtures of boric acid and borates. (As already noted above, acetate and/or acetic acid are also normally preferred contributors to the buffering capacity.) When boric acid and/or a borate is included as a buffering agent, the boron concentration preferably is at least, with increasing preference in the order given, 0.009, 0.014, 0.017, 0.026, 0.035, 0.044, 0.049, 0.054, 0.058, 0.061, 0.065, or 0.068 g/l and independently preferably is not more than, with increasing preference in the order given, 0.70, 0.52, 0.044, 0.35, 0.26, 0.17, 0.16, 0.14, 0.13, 0.12, 0.11, 0.10, 0.087, 0.079, or 0.072 g/l. When boric acid is included as a buffering agent, its concentration preferably is at least, with increasing preference in the order given, 0.05, 0.08, 0.10, 0.15, 0.20, 0.25, 0.28, 0.31, 0.33, 0.35, 0.37, or 0.39 g/l and independently preferably is not more than, with increasing preference in the order given, 4.0, 3.0, 2.5, 2.0, 1.5, 1.0, 0.90, 0.80, 0.75, 0.70, 0.65, 0.60, 0.55, 0.50, 0.45, or 0.41 g/l.

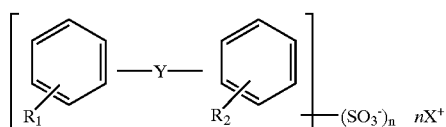
[0031] Furthermore, independently of the actual concentrations, when boric acid is included, the ratio by mass of the concentrations of boric acid and fluoride in a first sealing composition according to the invention preferably is at least, with increasing preference in the order given, 0.10:1.00, 0.20:1.00, 0.30:1.00, 0.35:1.00, 0.40:1.00, 0.45:1.00, 0.50:1.00, 0.55:1.00, 0.60:1.00, 0.65:1.00, 0.70:1.00, 0.72:1.00, 0.74:1.00, or 0.76:1.00 and independently preferably is not more than, with increasing preference in the order given, 5:1.00, 3:1.00, 2.5:1.00, 2.0:1.00, 1.7:1.00, 1.4:1.00, 1.10:1.00, 1.00:1.00, 0.95:1.00, 0.90:1.00, 0.85:1.00, 0.82:1.00, 0.80:1.00, or 0.78:1.00. Also and independently, in a first sealing composition according to the invention in which boric acid is included, the mass ratio of the boric acid to the lithium cations preferably is at least with increasing preference in the order given, 0.10:1.00, 0.20:1.00, 0.30:1.00, 0.35:1.00, 0.40:1.00, 0.45:1.00, 0.49:1.00, 0.51:1.00, 0.53:1.00, 0.55:1.00, 0.57:1.00, 0.59:1.00, or 0.60:1.00 and independently preferably is not

more than, with increasing preference in the order given, 5:1.0, 3:1.0, 2.5:1.00, 2.0:1.00, 1.7:1.00, 1.4:1.00, 1.10:1.00, 1.00:1.00, 0.95:1.00, 0.90:1.00, 0.85:1.00, 0.80:1.00, 0.75:1.00, 0.70:1.00, 0.65:1.00, or 0.62:1.00.

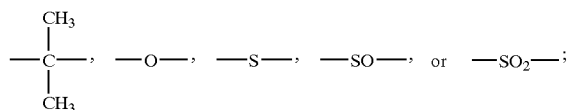
[0032] When boric acid, a boric acid salt and/or other boron-containing species is included, the ratio by mass of boron and fluoride in a first sealing composition according to the invention preferably is at least, with increasing preference in the order given, 0.017:1.0, 0.035:1.0, 0.052:1.0, 0.061:1.0, 0.070:1.0, 0.79:1.0, 0.087:1.0, 0.096:1.0 or 0.10:1.0 and independently preferably is not more than, with increasing preference in the order given, 0.87:1.0, 0.52:1.0, 0.44:1.0, 0.35:1.0, 0.30:1.0, 0.24:1.0, 0.19:1.0 or 0.17:1.0. Also and independently, in a first sealing composition according to the invention in which boric acid, a boric acid salt and/or other boron-containing species is included, the mass ratio of boron to lithium cations preferably is at least, with increasing preference in the order given, 0.017:1.0, 0.035:1.0, 0.052:1.0, 0.061:1.0, 0.070:1.0, 0.079:1.0, 0.086:1.0, or 0.089:1.0 and independently preferably is not more than, with increasing preference in the order given, 0.87:1.0, 0.52:1.0, 0.44:1.0, 0.35:1.0, 0.30:1.0, 0.24:1.0, 0.19:1.0 or 0.17:1.0 or 0.15:1.0

[0033] The presence of at least one surfactant in a composition to be used in a first sealing step in a process according to this invention is ordinarily preferred. Surprisingly, the most preferred type of surfactant is one selected from the group recognized as "smut reducers" or "smut inhibitors" in traditional hot sealing processes for anodized aluminum. Although smut is not formed even in the absence of any such surfactant in a first sealing process according to this invention, presumably because of the low temperature used, it has been found that the presence of one of these materials in a first sealing composition used in a first sealing process operation according to this invention is advantageous in improving general seal quality. The most preferred surfactants for this purpose are those conforming to the general formula and explanation thereof taught in column 2 lines 36 through 58 of U.S. Pat. No. 5,362,317 of Nov. 8, 1994 to Patel et al., which is hereby incorporated herein by reference, as are column 4 lines 15 through 35 of the same U.S. patent, except that for the purposes of this invention, in the moieties designated as "R₁" and "R₂" in the general formula incorporated by reference, the preference is for a number of carbon atoms from 12 through 16, rather than from 12 through 20, and there is no greater preference for a number of carbon atoms between 14 and 16 or for the specific number of 16 than for a number of 12 or 13.

[0034] The preferred surfactants thus correspond to compounds having the following general structure



[0035] wherein Y is a direct bond or a group of formula



[0036] R₁ and R₂ are each individually selected from H or C₅-C₂₅ alkyl, subject to the proviso that R₁ and R₂ are not both H, n is 1-4, and X is an H or an alkali metal. Preferred compounds of this type include those where Y=O, n is 1 or 2, and R₁ and R₂ are each para to the Y group. It is also preferred that at least one of R₁ and R₂ is C₁₂-C₁₆ alkyl and the sulfonate group or groups is or are ortho to the Y group. Suitable preferred surfactants are available commercially from Dow Chemical under the tradenames DOWFAX 8390 and DOWFAX 2A1.

[0037] Other suitable surfactants of the class known for smut reduction in hot sealing processes include cyclic polycarboxylic acids having 4 to 6 carboxyl groups per molecule, more preferably trimesic acid, trimellitic acid, pyromellitic acid, mellitic acid, cyclohexane pentacarboxylic acid, and cyclohexane-hexacarboxylic acid; and phosphonic acids, more preferably those selected from the group consisting of 1-phosphono-propane-1,2,3-tricarboxylic acid, 1,1-diphosphono-propane-2,3-dicarboxylic acid, 1-hydroxy-propane-1,1-diphosphonic acid, 1-hydroxy-butane-1,1-diphosphonic acid, 1-hydroxy-1-phenyl-methane-1,1-diphosphonic acid, 1-hydroxy-ethane-1,1-diphosphonic acid, 1-amino-ethane-1,1-diphosphonic acid, 1-amino-1-phenyl-methane-1,1-diphosphonic acid, dimethylamino-ethane-1,1-diphosphonic acid, propylamino-ethane-1,1-diphosphonic acid, butylamino-ethane-1,1-diphosphonic acid, aminotri-(methylene-phosphonic acid), ethylene-diaminotetra(methylene-phosphonic acid), di-ethylenetriaminopenta(methylene-phosphonic acid), hexamethylene-diaminotetra-(methylene-phosphonic acid), n-propyliminobis(methylene-phosphonic acid), amino-tri-(2-propylene-2-phosphonic acid), phosphonosuccinic acid, 1-phosphono-1-methyl-succinic acid and 1-phosphonobutane-1,2,4-tricarboxylic acid, most preferably from the group consisting of, 1-phosphonopropane-1,2,3-tricarboxylic acid, 1,1-diphosphonopropane-2,3-dicarboxylic acid and aminotri-(methylene-phosphonic acid). However, none of these materials are as preferred as those conforming to the general formula incorporated by reference above.

[0038] In a first sealing composition used in a first sealing operation of a process according to this invention, there is preferably a concentration of the type of surfactants described in the two immediately preceding paragraphs that is at least, with increasing preference in the order given, 0.050, 0.090, 0.11, 0.13, 0.15, 0.17, 0.19, 0.21, or 0.23 g/l and independently preferably is not more than, with increasing preference in the order given, 2.5, 2.0, 1.5, 1.2, 0.90, 0.70, 0.60, 0.55, 0.50, or 0.45 g/l. If the concentration of this material is either too high or too low, its beneficial effects in promoting a seal with a low acid dissolution test (hereinafter usually abbreviated as "ADT") value and increasing the

tolerance of the bath for certain contaminants such as silicon, will be too small to be significant. In addition, if this concentration is higher than necessary to achieve the maximum benefit, there will be economic waste. Accordingly, for economy, the concentration of this material still more preferably is not more than, with increasing preference in the order given, 0.40, 0.35, 0.30, or 0.25 g/l.

[0039] In addition to the surfactants known as smut reducers in hot sealing, it has been found normally advantageous to include at least one other surfactant in any composition to be used as the sealing composition in a first sealing operation according to this invention. Without limiting the invention by any theory, it is hypothesized that this second surfactant is useful in aiding the penetration of the liquid composition into very small pores in the anodized coating. For this second surfactant, any surfactant may be used (and none is required), nonionic surfactants are preferred. Ethoxylates of fatty amines are suitable for use, for example. The concentration of this second type of surfactant in a composition to be used in a first sealing step in a process according to this invention preferably is at least, with increasing preference in the order given, 0.02, 0.05, 0.10, 0.15, 0.20, 0.23, 0.25, or 0.27 milligrams of surfactant per liter of total composition, a unit of concentration that may be used for other constituents as well as for surfactant and is hereinafter usually abbreviated as "mg/l", and independently, primarily for economy, preferably is not more than, with increasing preference in the order given, 20, 10, 6, 4, 2.0, 1.5, 1.0, 0.80, 0.60, 0.50, 0.45, 0.42, 0.38, 0.35, 0.33, 0.31, or 0.29 mg/l.

[0040] The value of pH in a composition to be used in a first sealing step in a process according to this invention has been found to have a significant effect on the degree of corrosion protection achieved by the sealing treatment. This pH value preferably is at least, with increasing preference in the order given, 7.0, 7.5, 7.8, 8.0, 8.2, 8.4, or 8.6 and independently preferably is not more than, with increasing preference in the order given, 10, 9.8, 9.6, 9.4, 9.2, 9.0, or 8.8. If acidification is required to bring the pH within a preferred range, acetic acid is preferred for this purpose, particularly if a substantial fraction of the lithium cation content has been supplied by lithium acetate (either directly or by mixing lithium hydroxide and acetic acid in solution), so that the acetate and acetic acid contents can act as a buffer to retard pH changes. If alkalization is needed, sodium hydroxide is the preferred alkalizing agent, primarily because it is available at relatively low cost in a sufficiently pure form to avoid contaminating the sealing liquid with silicon or other common chemical species such as phosphate that are capable of harming the sealing process. Any other strong base available in the needed purity could alternatively be used.

[0041] As already briefly noted, silicon in some undetermined chemical form that occurs in many sources of fluoride ions can be highly detrimental to the quality of corrosion resistance achieved by a sealing process according to this invention. Accordingly, a liquid composition to be used in a first sealing step in a process according to this invention, if it does not contain at least 0.5 g/l of total surfactant molecules conforming to the general formula incorporated by reference above, preferably contains not more than, with increasing preference in the order given, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.80, 0.70, 0.65, or 0.60 ppm of silicon, measured as its stoichiometric equivalent as silica. On the

other hand, if the same liquid composition contains at least 0.5 g/l of total surfactant molecules conforming to the general formula incorporated by reference above, this composition may contain at least up to 50, or preferably up to 40 ppm, of silicon measured as its stoichiometric equivalent as silica without harm to the ADT values achieved in the sealing process according to the invention. Inasmuch as silicon contamination is often difficult to avoid, this increase of silicon tolerance is a valuable practical benefit of the inclusion of surfactant molecules conforming to the general formula incorporated by reference above.

[0042] A liquid used as a first sealing composition in a first sealing operation of a process according to this invention preferably does not contain more than, with increasing preference in the order given, 6.5, 6.0, 5.5, or 5.0 ppm of phosphate anions, measured as their stoichiometric equivalent, with the stoichiometry being based on equal numbers of phosphorus atoms, as PO_4^{-3} anions. A phosphate concentration of 7.0 ppm or more in a first sealing composition to be used in a first sealing operation according to this invention normally greatly reduces the corrosion protective value of the seal eventually obtained. On the other hand, a first sealing composition to be used in a first sealing operation according to this invention may contain at least as much as 1900 ppm of sodium cations, at least as much as 2000 ppm of sulfate anions, and/or at least as much as 30 ppm of dissolved aluminum without making it impossible for substrates sealed with such a first sealing composition to pass an ADT test, although lesser amounts of all of these materials are preferred.

[0043] During use of a sealing composition in a first sealing step process according to this invention, the temperature of the sealing composition preferably is at least, with increasing preference in the order given, 30, 31.0, or 32.0° C., and, unless the second sealing composition to be used in a second sealing operation according to this invention:

[0044] contains at least 0.3 g/l of smut inhibitor molecules as described above; and/or

[0045] is used at a temperature of at least 87° C. for a time of at least 5.0 min,

[0046] the temperature of the first sealing composition used in a first sealing operation according to this invention still more preferably is at least, with increasing preference in the order given, 33.0, 34.0, 35.0, 35.5, 36.0, 36.5, 37.0, or 37.5° C. Even if one of the conditions that would allow a lower temperature is satisfied, one of these higher temperatures is often preferred as a safety factor. However, in order to avoid inordinate waste of energy, the temperature during contact between the substrate being sealed and the first sealing composition used in a first sealing operation according to this invention preferably is not more than, with increasing preference in the order given, 43.0, 42.5, 42.0, 41.5, 41.0, 40.5, 40.0, 39.5, 39.0, 38.5, or 38.0° C. If the temperature is below 30° C., a satisfactory seal quality as measured by an ADT will not usually be obtained, while if the temperature is above 43° C., there is considerable danger of developing a bluish discoloration of the surface being sealed, particularly if this surface has been electrocolored.

[0047] The time of contact between an anodized substrate being treated and a liquid composition being used in a first

sealing operation in a process according to this invention preferably is at least, with increasing preference in the order given, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, or 9.7 minute(s), hereinafter usually abbreviated as "min", and independently, primarily for reasons of economy, preferably is not more than, with increasing preference in the order given, 30, 25, 20, 18, 16, 14, 12, or 10.5 min. If this time is too short, adequate corrosion resistance of the seal formed will only rarely be achieved, while if this time is longer than necessary, there will be economic waste.

[0048] After treatment in a first sealing step according to this invention, the surface of an anodized substrate preferably is rinsed with water, more preferably deionized or other equally well-purified water, for a time of at least, with increasing preference in the order given, 0.1, 0.3, 0.5, 0.7, 0.90, or 0.98 min and preferably is then transferred, preferably without being allowed to dry, to contact with the second necessary sealing composition in a process according to this invention. The second liquid sealing composition to be used in this second sealing step in a process may consist of pure water only, and may contain any other constituents known in the art to be useful in hot sealing compositions for anodized aluminum. Preferably, a liquid composition to be used in a second sealing step in a process according to this invention contains, in addition to water, at least one, or more preferably both, of:

[0049] a neutral buffer, such as ammonium acetate; and

[0050] a smut inhibiting component selected from the group consisting of:

[0051] diphosphonic acids, cyclic polycarboxylic acids, and their salts; and

[0052] molecules conforming to the general formula already incorporated herein by reference to U.S. Pat. No. 5,362,317.

[0053] The latter of these smut inhibitors is preferred, and narrower preferences as already specified above for the molecules of this general formula to be used in the first sealing liquid composition in a first sealing operation according to the invention also apply to the molecules for use in the second sealing liquid of the second sealing operation of a process according to the invention. Among smut inhibitors not conforming to the general formula incorporated herein by reference above, the pentasodium salt of cyclohexanhexacarboxylic acid is most preferred but is still less preferable than the molecules conforming to the general formula incorporated herein by reference.

[0054] A liquid used as the sealing composition in a second sealing operation according to the invention preferably contains a concentration of neutral buffer that is at least, with increasing preference in the order given, 0.10, 0.20, 0.30, 0.35, 0.40, 0.45, 0.50, or 0.55 g/l and independently preferably, at least for economy, is not more than, with increasing preference in the order given, 10, 8, 6, 4, 3.0, 2.5, 2.0, 1.8, 1.6, 1.4, or 1.2 g/l. Independently, a liquid used as the sealing composition in a second sealing operation

according to the invention preferably contains a concentration of smut inhibitor that is at least, with increasing preference in the order given, 0.020, 0.040, 0.050, 0.060, 0.070, 0.080, 0.090, 0.095, or 0.100 g/l and independently preferably is not more than, with increasing preference in the order given, 1.0, 0.80, 0.70, 0.60, 0.50, 0.45, or 0.40 g/l and for greater economy still more preferably is not more than, with increasing preference in the order given, 0.35, 0.30, 0.25, 0.18, 0.15, or 0.12 g/l. If the concentration of smut inhibitor is too low, there will be little or no increase in silicon tolerance and/or decrease in the necessary temperature for effective second sealing, while if this concentration is too high, the sealing quality may be reduced and there will be economic waste.

[0055] Independently of other preferences, a second sealing composition used in a second sealing operation according to this invention preferably has a pH value that is at least, with increasing preference in the order given, 3.0, 4.0, 4.5, 5.0, 5.5, or 5.9 and independently preferably is not more than, with increasing preference in the order given, 10.0, 9.0, 8.0, 7.5, 7.0, 6.5, or 6.1.

[0056] Independently of other preferences, a second sealing composition used in a second sealing operation according to the invention preferably does not contain, independently for each preferably minimized component stated below:

[0057] more than, with increasing preference in the order given, 0.100, 0.085, 0.070, 0.010, or 0.0070 part of fluoride ions per thousand parts of total composition (this unit of concentration being hereinafter usually abbreviated as "ppt"); and

[0058] more than, with increasing preference in the order given, 1.0, 0.8, 0.6, 0.4, 0.2, 0.15, or 0.11 ppt of lithium cations.

[0059] Independently of other preferences, in a second sealing operation according to this invention, the second sealing composition preferably has a temperature that is at least 84° C. and, unless the second sealing composition has a concentration of at least 0.060 g/l of smut inhibitor as described above, the second sealing composition more preferably has a temperature that is at least, with increasing preference in the order given, 87, 89, 91, or 93° C. To avoid economic waste, this temperature preferably is not more than, with increasing preference in the order given, 99, 97, or 95° C., and if the second sealing composition has a concentration of at least 0.060 g/l of smut inhibitor as described above, this temperature still more preferably is not more than, with increasing preference in the order given, 91, 89, 87, or 85° C.

[0060] The time of contact between the substrate surface being sealed and the second sealing composition in the second sealing operation of a process according to the invention preferably is at least, with increasing preference in the order given, 2.0, 3.0, 4.0, 4.5, or 4.9 min (this unit being hereinafter usually abbreviated as "min") and, unless the second sealing composition has a concentration of at least

0.060 g/l of smut inhibitor as described above, still more preferably is at least, with increasing preference in the order given, 6.0, 7.0, 8.0, 9.0, or 9.9 min. If these minimum times are not used, the corrosion protective quality of the seal obtained will often be inadequate. To avoid economic waste, the time consumed in the second sealing operation of a process according to the invention preferably is not more than, with increasing preference in the order given, 20, 15, 13, or 11 min and, if the second sealing composition has a concentration of at least 0.060 g/l of smut inhibitor as described above, the time consumed in the second sealing operation of a process according to the invention still more preferably is not more than, with increasing preference in the order given, 10, 9.0, 8.0, 7.0, 6.0, or 5.5 min.

[0061] At least where non-pollution requirements are stringent, any composition used in a process according to this invention preferably contains not more than, with increasing preference in the order given, 1000, 750, 500, 300, 200, 150, 110, 100, 90, 80, 70, 50, 30, or 10 ppm of a total of cobalt, nickel, or other heavy metals.

[0062] Practice of and benefits of this invention may be further appreciated from consideration of the working and comparison examples described below.

[0063] General Processing Procedure

[0064] The following process steps were performed in the order shown on all substrates before any sealing treatment, unless specifically indicated to the contrary below:

[0065] 1. Clean by immersion for 5 min in a solution in water of 22-30 g/l of RIDO-LINE® 18 or 15 g/l of NOVACLEAN® 120 LF cleaner concentrate at 60° C.

[0066] 2. Rinse for 1 min with tap water.

[0067] 3. Etch by exposure: (i) for 10 min to a solution in water of 6.5-7.5% of free NaOH, 25-45 g/l of dissolved aluminum, and 1.2 milliliters of P3® ALMECO 46 concentrate per liter of solution, the solution being maintained at 57° C.; or (ii) for 7.0 min to a solution in water of 85 g/l of free NaOH and 20 milliliters of EA-1010 concentrate per liter of solution, the solution being maintained at 57

[0068] 4. Rinse once or twice, for 1 min each time, with tap water.

[0069] 5. Desmut by exposure at normal ambient human comfort temperature (20-27° C.): (i) for 2 min to a solution in water of about 7% by volume of DEOXALUME® D90 concentrate, to provide 6 to 8 titration points, and of sulfuric acid, to provide 20-25 titration points; or (ii) for 1 min to NOVOX® 320 desmutting liquid.

[0070] 6. Rinse once or twice, for 1 min each time, with tap water.

[0071] 7. Anodize at a current density of 1.9 amperes per square decimeter in a solution in water of 165 to 185 g/l of sulfuric acid, 4 to 9.5 g/l of dissolved

aluminum, and, optionally but preferably, 2.3 percent by volume of ANOMAX® 9000 organic anodizing additive, the solution being maintained within a temperature range from 20 to 22° C., for about 35 min to produce an anodized layer with a thickness of 18 to 20 micrometers, these anodization conditions being preferred for preceding a process of sealing according to this invention.

[0072] 8. Rinse for 1 min with tap water at ambient normal human comfort temperature.

[0073] 9. Electrocolor by electrolyzing for 3 min at 15 volts AC in a solution of 9.4 percent by volume of COLORMAX® 9000 concentrate and 20 g/l of H₂SO₄ in water, the solution being maintained at 19.4° C. during the electrolysis.

[0074] 10. Rinse for 1 min with tap water at ambient normal human comfort temperature. RIDOLINE® 18 cleaner concentrate, NOVACLEAN® 120 LF cleaner concentrate, P3®almeco 46 concentrate, EA-1010 concentrate, DEOXALUME® D90 concentrate, NOVOX® 320 desmutting liquid, ANOMAX® 9000 organic anodizing additive, and COLORMAX® 9000 concentrate are all commercially available from the Henkel Surface Technologies Div. of Henkel Corp. (hereinafter usually abbreviated as "HST"), Madison Heights, MI, and directions for determining the titration points noted in step 5 above are available from the same source in connection with the purchase of DEOXALUME® D90 concentrate.

[0075] After step 10, substrates were subjected to the various sealing conditions noted below, without being allowed to dry. In addition to the first and second sealing operations shown below, there was a rinse for 1 min with tap water at ambient normal human comfort temperature between the first and second sealing operations.

[0076] After sealing and drying, the corrosion protective value of the seal coat formed was usually evaluated by an Acid Dissolution Test according to American Society for Testing and Materials Procedure 680, which is the same as International Standards Organization Procedure 3210. If the loss is no more than 0.040 grams per square decimeter of surface (this unit being hereinafter usually abbreviated as "g/dm²"), the test is passed. Lower values are more preferable. Substrates were tested immediately after completion of sealing, unless otherwise noted.

EXAMPLE AND COMPARISON EXAMPLE GROUP 1

[0077] The following sealing compositions were used for this group:

[0078] The low temperature sealing composition for the comparison examples (when used) contained the following ingredients:

[0079] 0.34 g/l of a 45% solution of H_2ZrF_6 in water;

[0080] 2.64 g/l of lithium acetate;

[0081] 0.35 g/l of a 70% solution of sorbitol in water.

[0082] Water constituted the balance of this composition, which had a pH of 6.0.

[0083] The low temperature sealing composition for the examples according to the invention was prepared from two concentrates and boric acid. The lithium containing concentrate had the following ingredients, the balance not shown being water:

[0084] 3.8% of lithium hydroxide monohydrate;

[0085] 5.6% of glacial acetic acid;

[0086] 0.010% of CHEMEEN™ C-12G surfactant (a product of Chemax, Inc.)

[0087] The fluoride containing concentrate had the following ingredients, the balance not shown being water:

[0088] 4.0% of potassium fluoride dihydrate;

[0089] 0.01% of CHEMEEN™ C12G surfactant.

[0090] The working low temperature sealing composition had the following ingredients, the balance not shown being water:

[0091] 4% by volume of the lithium containing concentrate noted next above;

[0092] 4% by volume of the fluoride containing concentrate noted next above; and

[0093] 0.40 g/l of boric acid.

[0094] This working composition had a pH value of 8.7.

[0095] The high temperature sealing composition used was made from a concentrate that contained the following ingredients in addition to water, which constituted the balance of the concentrate:

[0096] 35% of a 65% solution in water of ammonium acetate;

[0097] 5.0% of DOWFAX™ 2A1 surfactant (commercially supplied and reported by its supplier, Dow Chemical, to be a 45% solution in water of a mixture of sodium dodecyl and di-dodecyl diphenyl oxide disulfonates);

[0098] 0.25% of CHEMEEN™ C-12G surfactant (commercially supplied and reported by its supplier Chemax, Inc. to be 100% active ethoxylated cocoamine, with an average of about 12 ethoxyethylene units per molecule); and

[0099] 0.15% of FOAMBAN™ MS-575 antifoam agent (commercially supplied and reported by its supplier Ultra Additives to be a proprietary emulsion in water of a blend of glycols). The working second sealing composition contained 0.5% by volume of this concentrate and was used for both examples and comparison examples.

[0100] Sealing conditions and ADT results for this Group are shown in Table 1 below. If the entry under the heading "Colored?" in Table 1 is "No", process steps 9 and 10 as described above were not used; instead the sealing process was begun without allowing the substrates to dry after step 8.

TABLE 1

Identifier	Low Temperature Sealing Process Conditions		High Temperature Sealing Process Conditions		Colored?	Smut	ADT Results(s), g/dm ²
	Time, Min	Temp., ° C.	Time, Min	Temp., ° C.			
CE 1.1	10	29	20	85	No	None	0.28, 0.18
CE 1.2	10	29	20	85	Yes	Heavy	0.23, 0.21
CE 1.3	10	29	20	96	No	None	0.0045
CE 1.4	10	29	20	96	Yes	Heavy	0.016, 0.013
CE 1.5	10	29	5	96	No	None	0.15, 0.077
CE 1.6	10	29	5	96	Yes	Heavy	0.012, 0.021
CE 1.7	5	29	20	96	Yes	Medium	0.016
CE 1.8	5	29	20	96	No	None	0.019
CE 1.9	3	29	20	96	Yes	Medium	0.10
CE 1.10	3	29	20	96	No	None	0.073
Ex 1.1	10	38	5	85	No	None	0.011, 0.016
Ex 1.2	10	38	5	85	Yes	None	0.021, 0.017
Ex 1.3	10	38	10	85	Yes	None	0.010, 0.008
Ex 1.4	10	38	5	96	No	None	0.013, 0.013
Ex 1.5	10	38	5	96	Yes	None	0.015
Ex 1.6	10	38	3	96	Yes	None	0.012, 0.012
Ex 1.7	10	38	3	96	No	None	0.023

NEW ABBREVIATIONS AND OTHER NOTES FOR TABLE 1

"CE" = "Comparison Example";

"Ex" = "Example According to the Invention";

"Temp." = "Temperature".

If there is more than one value in the rightmost column, the values are individual readings of replicates.

[0101] The results in Table 1 indicate that passing ADT results cannot be obtained in the Comparison Examples unless the hot sealing part of the process is performed at a temperature above 85° C. for at least 5 min, with no actual specific satisfactory results obtained with less than 20 min of hot sealing. In contrast to this, with the Examples according to the invention, fully satisfactory ADT results could be obtained with the same hot sealing composition at only 85° C. for 5 min or in 3 min if the temperature of the hot sealing composition is raised to 96° C.

EXAMPLE AND COMPARISON EXAMPLE
GROUP 2

[0102] In this group, the sensitivity of the anodized coatings to mechanical disturbance was tested. The same preparatory processes before sealing and the same low temperature and high temperature sealing compositions as for Group 1 above were used. The first sealing process was for 10 min for both comparison examples and examples according to the invention, with the temperature being 29° C. for comparison examples and 38° C. for examples according to the invention. The second, high temperature sealing process was always at 96° C. but varied in time. Two substrates were used under each set of sealing conditions. Comparison examples that were colored always developed smut under these sealing conditions. One sample from each set of conditions that developed smut was rubbed gently with pumice over its smutted surface until the smut was removed. One sample from each set of conditions that did not develop smut was similarly rubbed with pumice for about the same time as was necessary to remove smut from the most heavily smutted sample in the group. The variable factors in sealing and the ADT results for samples with and without this abrasive treatment with pumice are shown in Table 2. The results in Table 2 show that the corrosion resistance conferred by sealed anodized coatings produced by a process according to the invention is far more resistant to mechanical damage of the sealed anodized coating than the corrosion resistance of identical anodized coatings sealed according to the teachings of WO 99/10567.

TABLE 2

Identifier	Colored?	Hot Sealing Time, Minutes	ADT Values, g/dm ²	
			Before Wiping	After Wiping
CE 2.1	No	No hot sealing	0.031	0.27
CE 2.2	Yes	5	0.021	0.22
CE 2.3	No	5	0.078	0.23
CE 2.4	No	20	0.012	0.16
Ex 2.1	No	3	0.020	0.025
Ex 2.2	Yes	3	0.013	0.014

EXAMPLE AND COMPARISON EXAMPLE
GROUP 3

[0103] In this group, no actual sealing was performed. Instead, the resistance of first sealing compositions according to the invention to pH changes was compared with that of first sealing compositions according to the teachings of WO 99/10567. Comparison Composition Example 3.1 was prepared by using the lithium containing and fluoride containing concentrates described in detail in Group 1 to prepare a solution of both concentrates in water that contained 0.56 ppt of lithium cations and 0.53 ppt of fluoride anions (and no boric acid). Example Composition 3.1 was prepared by using the same concentrates and boric acid to prepare a solution containing 0.52 ppt of lithium cations, 0.53 ppt of fluoride anions, and 0.40 g/l of boric acid, and Example Composition 3.2 was prepared from the same materials as 3.1 but contained 0.51 ppt of lithium cations, 0.53 ppt of fluoride anions, and 0.80 g/l of boric acid. Sulfuric acid was then added to each composition to reduce its pH value to 5.5.

[0104] Each composition was then titrated with 1.0 N sodium hydroxide solution to a succession of pH values increasing by 0.5 pH unit intervals, with the amount of sodium hydroxide required to reach each pH value recorded. These results are shown in Table 3.1 below.

TABLE 3.1

Identifier	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5
Milliliters of 1.0 N NaOH to Raise 1.0 Liter of Composition from pH 5.5 to pH:										
CE 3.1	8.1	10.6	11.5	11.7	11.8	11.9	12.0	12.0	12.2	12.3
Ex 3.1	9.4	12.2	13.0	13.4	13.8	15.0	16.4	18.5	20.0	21.0
Ex 3.2	9.4	12.0	13.0	13.8	14.5	16.3	19.6	23.7	26.7	28.5
Incremental Milliliters from Previous Value										
CE 3.1	8.1	2.5	0.9	0.2	0.1	0.1	0.1	<0.1	0.2	0.1
Ex 3.1	9.4	2.8	0.8	0.4	0.4	1.2	1.4	2.1	1.5	1.0
Ex 3.2	9.4	2.6	1.0	0.8	0.7	1.8	3.3	4.1	3.0	1.8

[0105] In a second part of the comparison, sodium hydroxide was added to the initial compositions to raise their pH to 10.5 instead of adding sulfuric acid, and the resulting mixtures were titrated with 1.0 N sulfuric acid instead of sodium hydroxide. The results are shown in Table 3.2 below.

silicate were also added to all four of these solutions. The second sealing composition used with all of these first sealing compositions contained 1.14 g/l of ammonium acetate and 0.60 g/l of DOWFAX™ 8390 surfactant and had a pH value of 6.0.

TABLE 3.2

Identifier	10.0	9.5	9.0	8.5	8.0	7.5	7.0	6.5	6.0	5.5
Milliliters of 1.0 N H ₂ SO ₄ to Lower 1.0 Liter of Composition from pH 10.5 to pH:										
CE 3.1	0.1	0.2	0.25	0.4	0.5	0.6	0.8	1.7	4.2	6.8
Ex 3.1	1.0	2.5	4.6	6.0	7.2	7.6	8.0	8.8	11.6	21.0
Ex 3.2	1.8	4.8	8.9	12.2	14.0	14.7	15.5	16.5	19.1	28.5
Incremental Milliliters from Previous Value										
CE 3.1	0.1	0.1	0.05	0.15	0.1	0.1	0.2	0.9	2.5	0.1
Ex 3.1	1.0	1.5	2.1	1.4	1.2	0.4	0.4	0.8	3.2	2.4
Ex 3.2	1.8	3.0	4.1	3.3	1.8	0.7	0.8	1.0	2.6	9.4

[0106] The data in Tables 3.1 and 3.2 show that, within the preferred pH range of 7.5 to 9.5, a composition according to the invention is far more effective at resisting large changes of pH caused by addition of non-optimal amounts of acid or alkali than is a first sealing composition as taught by WO 99/10567.

EXAMPLE AND COMPARISON EXAMPLE GROUP 4

[0107] This group illustrates the greater silicon tolerance of a first sealing composition to be used in a first sealing operation according to this invention when it contains a sufficient amount of surfactant molecules that conform to the general formula incorporated herein by reference.

[0108] A lithium concentrate and a fluoride concentrate according to the invention were first prepared by mixing materials as follows: for the Lithium Concentrate, 74 parts of deionized water, 10.0 parts of lithium hydroxide monohydrate, 15.0 parts of glacial acetic acid (98% pure), 1.00 part of boric acid, and 0.001 part of CHEMEEN™ C-12 G surfactant; for the Fluoride Concentrate, 97 parts of DI water, 2.9 parts of sodium fluoride, and 0.001 part of CHEMEEN™ C-12 G surfactant.

[0109] These concentrates were then used to make three example first sealing compositions to be used in a first sealing operation according to this invention and one comparison Example. All of these compositions contained 4% by volume of each of the Lithium and Fluoride Concentrates as described above and had a pH value of 8.8. Example first sealant 4.1 also contained 0.50 g/l of DOWFAX™ 8390 surfactant, Example 4.2 contained 1.00 g/l of the same surfactant, Example 4.3 contained 0.50 g/l of DOWFAX™ 2A1 surfactant, and Comparison Example 4 contained no surfactant other than that already contained in the Lithium and Fluoride Concentrates. (DOWFAX™ 8390 surfactant has the same characteristics as DOWFAX™ 2A1 surfactant, except that its active ingredient concentration is only 36% instead of 45% and its alkyl groups are hexadecyl instead of dodecyl.) As indicated in Table 4 below, varying amounts of

[0110] Test substrates of conventional anodizing grade aluminum alloy were subjected to the full processing sequence as described above, with the specific conditions for the first and second sealing operations being shown in Table 4 along with the resulting ADT values. In all instances shown in Table 4, the first sealing operation was conducted at 38° C. for 10 min and the second sealing operation was conducted at 84° C. for 5 min. None of the substrates first sealed with an example first sealant according to the invention formed any visible smut, but all of the substrates sealed instead with the comparison example had heavy smut. Although all of the ADT values were satisfactory for silicon concentrations of 50 ppm and below, the smutting exhibited when Comparison First Sealant 4 was used made it unsatisfactory at any silicon concentration. With a silicon concentration of 60 ppm, all results were unsatisfactory because of high ADT values, and those using the Comparison First Sealant also continued to be unsatisfactory because of smut formation.

EXAMPLE GROUP 5

[0111] This group illustrates a variety of satisfactory conditions for first and second sealant compositions and for operation of a process according to the invention. In this group, the same lithium concentrates and fluoride concentrates as for Group 4

TABLE 4

Concentration of Silicon in ppm	ADT Value in Milligrams per Square Inch for Substrates Treated with First Sealant:			
	Example 4.1	Example 4.2	Example 4.3	Comparison Example 4
0.0	1.04	0.89	0.30	0.44
5.0	0.53	1.03	0.76	0.60
10.0	0.58	0.52	0.75	0.98
15.0	0.50	1.03	0.76	0.60
20	0.49	0.51	0.75	0.64
25	1.12	0.80	0.82	1.17
30	0.62	0.58	0.83	0.55
35	1.47	0.91	0.89	0.63
40	0.77	0.64	0.70	0.79

TABLE 4-continued

Concentration of Silicon in ppm	ADT Value in Milligrams per Square Inch for Substrates Treated with First Sealant:			
	Example 4.1	Example 4.2	Example 4.3	Comparison Example 4
50	1.78	2.28	2.6	1.8
60	3.44	6.75	4.3	3.3

[0112] were used. All of the first sealing compositions contained 4% by volume of each of the Lithium and Fluoride Concentrates as described above, had a pH value of 8.8, and contained an amount of DOWFAX™ 8390 surfactant as shown in Table 5 below. Each second sealing composition contained 1.14 g/l of ammonium acetate, had a pH value of 6.0, contained an amount of DOWFAX™ 8390 surfactant as shown in Table 5 below, and was maintained at a temperature of 84° C. during its contact with the first sealed substrate. Deionized water constituted any part of both sealants not specified above.

[0113] Test substrates of conventional anodizing grade aluminum alloy were subjected to the full processing sequence as described above, with the specific conditions for the first and second sealing operations being shown in Table 5 along with the resulting ADT values. All of the sealed samples made as indicated in Table 5 also passed a standard Modified Dye Stain test, and none of them had any visible smutting. Some replicate values are shown in Table 5 as an indication of the reproducibility of the ADT results under the conditions shown.

EXAMPLE GROUP 6

[0114] In this group the consumption of some of the active ingredients was measured.

[0115] A lithium concentrate and a fluoride concentrate according to the invention were first prepared by mixing materials as follows: for the Lithium Concentrate, 72.2 parts of deionized water, 10.0 parts of lithium hydroxide monohydrate, 15.0 parts of glacial acetic acid (98% pure), 1.00 part of boric acid, 0.50 part of DOWFAX™ 2A1, 1.2 parts of a 50% solution of sodium hydroxide (rayon grade), and 0.004 part of

TABLE 5-continued

First Sealing Conditions			Second Sealing Conditions		Resulting ADT
Concentration of 8390 Sur- factant, g/l	Temperature ° C. (° F.)	Time, Min- utes	Concentration of 8390 Sur- factant, g/l	Time, Min- utes	Values, mg/Square Inch
2.0	42.2 (108)	5	1.0	5	2.38
0.4	42.2 (108)	5	0.6	5	0.69
0.4	42.2 (108)	5	0.6	5	0.78
1.0	43.3 (110)	10	0.3	5	0.82
2.0	43.3 (110)	10	1.0	5	1.60
0.4	43.3 (110)	10	0.6	5	0.62
1.0	42.2 (108)	7	0.3	5	1.35
2.0	42.2 (108)	7	1.0	5	1.73
0.4	42.2 (108)	7	0.6	5	0.91

[0116] CHEMEEN™ C-12 G surfactant; for the Fluoride Concentrate, 96 parts of DI water, 2.9 parts of sodium fluoride, 1.00 part of DOWFAX™ 2A1, 0.010 part of FOAMBAN™ MS-575 antifoam agent, and 0.005 part of CHEMEEN™ C-12 G surfactant. Also, a second sealing concentrate was prepared to contain 59.6 parts of DI water, 35 parts of a solution of 65% ammonium acetate in water; 5.0 parts of DOWFAX™ 2A1, 0.15 part of FOAMBAN™ MS-575 antifoam agent, and 0.25 part of CHEMEEN™ C-12 G surfactant.

[0117] An initial first sealant composition was made by mixing 4.0% by volume of each of the Lithium and Fluoride Concentrates and adjusting the pH (if needed) to 8.5. The initial second sealant composition was a 0.5% by volume solution in water of the second sealing concentrate last noted above and had a pH value of 5.9. The volume of the first sealant composition was 4.5 liters. A total of 21 square meters of anodized aluminum was sealed in a process according to this invention, with analysis of the first sealant composition after about each 3 to 4 square meter and addition of sufficient amounts of the Lithium and/or the Fluoride concentrate after each analysis to restore the concentration of lithium and/or fluoride to approximately its original level. The replenishment thus required corresponded to about 1.3 grams of lithium acetate and about 0.7 grams of fluoride per square meter of anodized aluminum processed.

What is claimed is:

1. A process for sealing an anodized aluminum surface, said process comprising:

- (I) bringing the anodized aluminum surface into contact for not more than 30 min at a temperature not greater than 75° C. with a liquid first sealing composition that has a pH value from 7.0 to 10.0, this pH value being sufficiently well buffered that at least 0.15 milliequivalent of strong alkali per liter of sealing composition is required to raise the pH of the sealing composition by 0.50 pH unit and at least 0.15 milliequivalent of strong acid per liter of sealing composition is required to lower the pH of the sealing composition by 0.50 pH unit, said liquid first sealing composition comprising water and:

- (A) lithium cations; and
- (B) fluoride anions.

TABLE 5

First Sealing Conditions			Second Sealing Conditions		Resulting ADT
Concentration of 8390 Sur- factant, g/l	Temperature ° C. (° F.)	Time, Min- utes	Concentration of 8390 Sur- factant, g/l	Time, Min- utes	Values, mg/Square Inch
1.0	37.8 (100)	10	0.3	5	0.73
2.0	37.8 (100)	10	1.0	5	0.84
0.4	37.8 (100)	10	0.6	5	0.64
1.0	37.8 (100)	10	0.6	5	0.75
2.0	37.8 (100)	10	0.3	5	0.67
0.4	37.8 (100)	10	0.6	5	1.71
1.0	37.8 (100)	7	1.0	5	1.72
2.0	37.8 (100)	7	1.0	5	1.71
0.4	37.8 (100)	7	1.0	5	0.73
1.0	40.6 (105)	7	0.6	5	1.42
2.0	40.6 (105)	7	0.6	5	1.08
0.4	40.6 (105)	7	0.6	5	1.48
1.0	42.2 (108)	5	0.3	5	2.32

2. The process of claim 1 wherein the first sealing composition is comprised of less than about 50 ppm of dispersed or dissolved silicon atoms.

3. The process of claim 1 comprising an additional step after completion of step (I) of bringing the anodized aluminum surface into contact at a temperature of at least 82° C. with a second sealing composition comprising steam or liquid water.

4. The process of claim 1 wherein said liquid first sealing composition is comprised of one or more boron-containing species selected from the group consisting of boric acid, boric acid salts, and mixtures thereof.

5. The process of claim 1 wherein the pH value of the liquid first sealing composition is sufficiently well buffered that at least 0.45 milliequivalent of strong alkali per liter of the liquid first sealing composition is required to raise the pH of the liquid first sealing composition by 0.50 pH unit.

6. The process of claim 1 wherein the pH value of the liquid first sealing composition is sufficiently well buffered that at least 0.45 milliequivalents of strong acid per liter of liquid first sealing composition is required to lower the pH of the liquid first sealing composition by 0.50 pH unit.

7. The process of claim 1 wherein said liquid first sealing composition has a ratio by mass of boron and fluoride that is at least 0.017:1.00.

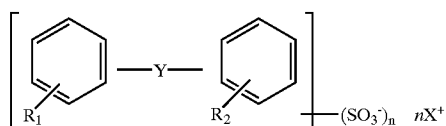
8. The process of claim 1 wherein said liquid first sealing composition has a ratio by mass of boron and fluoride anions that is not more than 0.87:1.00.

9. The process of claim 1 wherein said liquid first sealing composition has a ratio by mass of boron to lithium cations that is at least 0.017:1.00.

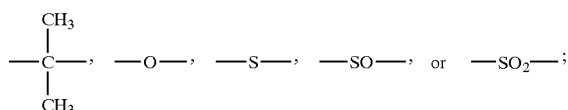
10. The process of claim 1 wherein said liquid first sealing composition has a ratio by mass of boron to lithium cations that is not more than 0.87:1.0.

11. The process of claim 1 wherein said liquid first sealing composition is additionally comprised of at least one surfactant.

12. The process of claim 1 wherein said liquid first sealing composition is additionally comprised of at least one surfactant having the general structure



wherein Y is a direct bond or a group of formula:



R₁ and R₂ are each individually selected from H or C₅-C₂₅ alkyl, provided that R₁ and R₂ are not both H; n has a value of from 1 to 4; and X is H or alkali metal.

13. The process of claim 12 wherein said liquid first sealing composition is additionally comprised of at least one nonionic surfactant which is an ethoxylate of a fatty amine.

14. The process of claim 1 wherein the liquid first sealing composition is maintained at a temperature of at least 30° C. during step (I).

15. A liquid sealing composition useful for sealing an anodized aluminum surface, said liquid sealing composition having a pH value of from 7.0 to 10.0 and comprising water and:

(A) lithium cations;

(B) fluoride anions; and

(C) an amount of one or more buffering agents, which in total is effective to buffer the pH value such that at least 0.15 milliequivalent of strong alkali per liter of liquid sealing composition is required to raise said pH value by 0.50 pH unit and at least 0.15 milliequivalent of strong acid per liter of liquid sealing composition is required to lower said pH value by 0.50 pH unit, wherein at least one of said buffering agents is a material other than an acetate or acetic acid.

16. The liquid sealing composition of claim 15 wherein said liquid sealing composition is comprised of less than 50 ppm of dispersed or dissolved silicon atoms.

17. The liquid sealing composition of claim 15 wherein at least one buffering agent is selected from the group consisting of boric acid, boric acid salts and mixtures thereof.

18. The liquid sealing composition of claim 17 additionally comprising acetate, acetic acid or both acetate and acetic acid.

19. The liquid sealing composition of claim 15 comprising at least 0.05 g/L boric acid.

20. The liquid sealing composition of claim 17 wherein the ratio by mass of boron and fluoride anions is at least 0.017:1.00.

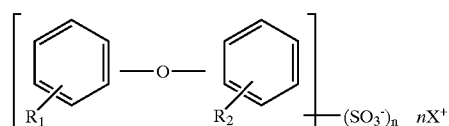
21. The liquid sealing composition of claim 17 wherein the ratio by mass of boron and fluoride anions is not more than 0.87:1.00.

22. The liquid sealing composition of claim 17 wherein the ratio by mass of boron and lithium cations is at least 0.017:1.00.

23. The liquid sealing composition of claim 17 wherein the ratio by mass of boron and lithium cations is not more than 0.87:1.0.

24. The liquid sealing composition of claim 15 additionally comprising at least one surfactant.

25. The liquid sealing composition of claim 15 additionally comprising at least one surfactant having the general structure



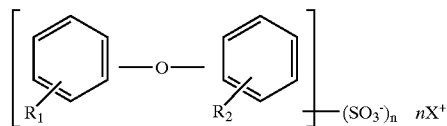
wherein R₁ and R₂ are each individually selected from H or C₁₂-C₁₆ alkyl, subject to the proviso that R₁ and R₂ are not both H, n is 1 or 2, and X is Na.

26. The liquid sealing composition of claim 25 additionally comprising at least one nonionic surfactant which is an ethoxylate of a fatty amine.

27. A liquid sealing composition useful for sealing an anodized aluminum surface, said liquid sealing composition having a pH value of from 7.0 to 10.0 and comprising water and:

- (A) 0.07 to 5.0 g/l lithium cations;
- (B) 0.08 to 6.0 g/l fluoride anions;
- (C) 0.05 to 9.0 g/l boric acid; and
- (D) at least one surfactant.

28. The liquid sealing composition of claim 27 wherein at least one surfactant has the general structure



wherein R_1 and R_2 are each individually selected from H or $\text{C}_{12}\text{-C}_{16}$ alkyl, subject to the proviso that R_1 and R_2 are not both H, n is 1 or 2, and X is Na.

29. The liquid sealing composition of claim 27 wherein at least one surfactant is an ethoxylate of a fatty amine.

30. The liquid sealing composition of claim 27 wherein the ratio by mass of boric acid and fluoride anions is from 0.10:1.00 to 5:1.00.

31. The liquid sealing composition of claim 27 wherein the ratio by mass of boric acid and lithium cations is from 0.10:1.00 to 5:1.0

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