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METHOD OF ETCHING OF ALUMINUM AND ITS ALLOYS

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This invention relates to a method of etching of aluminum and its alloys used in decorative arts or in structures or machine arts, hereinafter collectively referred to as aluminum, by means of alkaline etching agents.

In such methods, it is at times desirable to coat selected portions of the aluminum surface with a protective masking coating to inhibit or prevent attack by such etching agents while adjacent portions are available for such attack. The edge of the mask thus is along a line of separation between the masked and unmasked portion.

In such procedures it is of importance to assure a sufficient bond between the metal at its surface with masking material since as the etchant corrodes the unmasked metallic surface it also corrodes laterally underneath the masking coating adjacent the unmasked portion. Thus in some operations the surface will be etched underneath the edge of the mask for a lateral distance substantially equal to the depth of the etch.

If the bond is uniform then the etching rate laterally is controlled so that it undercuts the mask at a uniform rate underneath the entire line of separation of the masked portion and the adjacent unmasked portion undergoing the attack by the etching solution. However, if the bond be not uniform then the etching solution will creep by capillary action between the mask and the base metal at the portions where the bond is insufficient.

In order to avoid this difficulty it is possible to improve the bond by first coating the aluminum or aluminum alloy with a primer undercoat which will improve the adhesion of the superimposed overcoat of the surface coating composition used. This procedure is similar to that generally employed in the paint and lacquer industry.

Thus, if the surface coating composition is an alkali resistant surface coating compositions in which the film former is a resin of the following types which are alkali resistant, i. e., acrylate, phenol-formaldehyde, polyvinyl chloride, polyvinyl chloride-polyvinyl acetate copolymer, or alkyd or modified alkyd epoxy resin, silicone resin, melamine resin base, one may first coat the clean aluminum surface with a conventional acid wash primer usually used as undercoats for such paints in the paint industry where aluminum is to be painted. A suitable example for this purpose, as is well known in such arts, are the zinc chromate acid wash primers.

The grave difficulty presented by the use of such acid wash primers is that while they give an excellent bond between the mask and the aluminum, they are extremely difficult to remove. Since such removal of the mask is in most cases important, a serious dilemma is presented.

Therefore, where I wish to employ the mask for the purposes of modifying a portion of the surface by removing a superficial layer of aluminum for purposes of changing the appearance of the surface, or etch deeply so as to modify the aluminum article in its structural characteristic or to change its mechanical utility as a machine part or a structural part, I must use a highly adherent

mask to avoid uncontrolled undercutting and am then faced with the extreme difficulty of removing the mask completely—a procedure which becomes of extreme importance where the etched part must be worked on or must receive a spot weld or similar operation. Or, if I use a more easily removable mask which is not so adherent, I am faced with the difficulty of accidental and uncontrolled undercutting.

I have solved this dilemma by discovery that I can so condition the surface of an aluminum part so that surface coating compositions, which otherwise require the presence of an acid wash primer in order to bond sufficiently to prevent deleterious and uncontrolled undercutting may be bonded to the base metal so that such uncontrolled undercutting is avoided and limit the undercut to be at a uniform rate along the entire line of juncture of the masked and unmasked portion. The masking coat in my process has, however, an inferior adhesion to the metal than where the undercoat is used so that it is relatively easy to remove to give a clear base metallic surface. The process thus permits of the etching in a sharp edged predetermined pattern to a desired depth, and results in a clean and bare metallic part on the subsequent removal of the mask.

I have discovered that an aluminum part which normally requires an undercoat of the acid wash type to bond surface coatings of the type described can be treated to avoid the necessity of the undercoat by contacting the surface with a solution which has a suitable acid pH. The acid modified surface is then receptive to coating with the paint or lacquer to form the desired pattern of masked and unmasked portions of the surface. I may then expose the masked and unmasked portions to attack by the etching solution to etch the unmasked portion to any desired depth, etching also under the masked portion, uniformly along the line of juncture between the masked and unmasked portion and laterally underneath the masked portion for a distance substantially equal to the depth of etch from the adjacent surface and then after interrupting the etch and washing the part, I may readily remove the masked portion by any conventional paint remover solvent used to remove such paints or lacquers.

In carrying out my process, I prefer to treat the aluminum part, after it is cleaned to remove superficial dirt and oils, by reacting the surface with an acid solution. I prefer to employ acidic water solutions which will not markedly attack the aluminum metal, since my purpose is not to dissolve the base aluminum metal but rather to condition the surface.

Thus, I may use water solutions of HNO_3, water solutions of H_2SO_4, water solutions of acid salts, such as sodium acid sulphate, sodium dihydrogen phosphate, sodium dichromate or sodium nitrate acidified with sulphuric acid, all such solutions having a pH value of about 4 or less. All of these will condition the surface without substantially corroding, i. e., dissolving the base aluminum metal. Aqueous solutions of hydrochloric acid, are not included in this class since such acid, along with chlorides generally, are highly corrosive to the base metal and cannot be classed as "safe on aluminum" as the term is employed herein to classify the group of acidic solutions which I find desirable to employ. The distinguishing chemical characteristics of these solutions which are suitable for the purposes of this invention are in that they have a high solvency power for aluminum oxide but have a very low or insubstantial corrosive action on the base aluminum surface especially when this surface is of a massive aluminum, such as cast, rolled, forged or machined sheet or part having extended surfaces as distinguished from aluminum powder or chips.

The acidity of such acidic solutions suitable for the use are such as to give a pH value of less than about 4. The temperature at which the treatment is conducted is suitable for removal of the oxide coat but sufficiently low to aid in the limitation of this corrosive attack on the aluminum.

While I do not wish to be bound by any theory of the chemical and physical mechanism whereby the aluminum surface is conditioned to improve the binding power between the surface and the surface coating composition, I believe a result of such surface treatment is that the acidic solution removes oxide film on the metal and the substantially oxide free metallic surface is thus contacted with the acidic solution. This produces, when the metal is removed, a metal surface substantially free of oxides and having a surface which is acidic in nature. This acidic surface retains its acidic nature even after it is thoroughly washed.

In order to further reduce and make sure the metallic surface of the aluminum is not substantially attacked or corroded by the acidic solutions, while permitting the removal of any aluminum oxide film on the surface of the aluminum, I may employ corrosion inhibitors to protect the aluminum against the corrosive attack of the acidic solution.

Such corrosion inhibitors are nitrate ions, nitrite ions, chromate ions, bichromate ions, mercapto benzothiazole and other mercapto compounds, alkyl sulfides, such as amyl sulfide and anthraquinone.

Such aluminum corrosion inhibitors, to inhibit the corrosive attack of inorganic acid solutions on aluminum in arts other than those to which the present invention is directed are well known as will be understood by those skilled in this art.

These acidic solutions which, either used alone or after addition to the acidic solutions of such inhibitors against acid corrosion of aluminum, will not corrode the aluminum, in the manner discussed at the temperatures at which they are employed, but will dissolve aluminum oxide film on the aluminum and will also condition the surface to improve the bond to the surface of coating compositions as described, may be termed "aluminum non-corrosive acidic solutions" or "acidic solutions safe on aluminum" and will be so termed in this specification and claims.

Examples of such acid solutions which may be used are as follows:

HNO_3 solution in water, preferably not containing more than 25% volume of concentrated HNO_3 in the solution; H_2SO_4 in water 1 to about 25% by weight H_2SO_4.

I may employ $NaHSO_4$ or $KHSO_4$ to which may be added sodium or potassium dichromate in amount of about 25 to 30% by weight of the acid sulfate. I may employ NaH_2PO_4 acidified with a small amount of phosphoric acid for example 2–3% by weight of phosphoric acid.

I have also found that the addition of wetting agents to the acid solution improves the treatment and the conditioning of the surface. I prefer to use the acid stable non-ionic wetting agents. Such wetting agents are well known in the wetting agent art and form a well recognized class of wetting agents. Examples of these are: Alkyl aryl polyether alcohols (Triton X–45 and Triton X–100, sold by Rohm and Haas Co. of Philadelphia), alkyl phenoxy polyoxyethylene ethanols (Igepal CO–630, Igepal CO–730 and Igepal CO–850, sold by Antaro Products Div., General Dyestuffs Corp. of N. Y.), polyoxyethelene thioether (Sterox SK, sold by Monsanto Chemical Co. of St. Louis, Mo.).

They are widely known and commercially produced and need not be further identified since those skilled in this art will recognize them readily.

I prefer to use these non-ionic wetting agents since the cationic wetting agents appear to be less useful. While

I do not desire to be bound by any theory, I believe that they plate out on the aluminum and interfere with the conditioning of the surface in the manner described above.

The metal, when washed clean of dirt and oils, and other superficial coatings removable by ordinary washing solutions, as for example, detergent solutions, and when treated as above with aluminum noncorrosive acidic solutions, as described above, may now be directly masked at the selected parts with the coating composition which may be sprayed on or painted on or applied by dipping to give the desired surface pattern of coated and uncoated aluminum surface or which may produce such selectively coated and uncoated surfaces after photographic development as is conventionally employed in the printing art. No undercoat such as an acid wash primer or other undercoat is employed between the outer layer of the surface coat and the metal surface to bridge the bond between the outer coat and the metallic surface.

I select as a coating material those materials which will make a sufficiently tight bond with the base metal when treated with the acidic solutions described above.

The coating composition should be able to withstand the attack of the alkaline etching agent as should also the bond between the acid washed surface, and the bond should not be so strong as to cause difficulty in removing the masking coat when the etching process is completed. Such coating compositions are those well known alkali resistant coatings of which the film formers are the alkali resistant resins specified above. Such coatings are well known as useful for painting aluminum but require and are generally used together with acid wash primers as described above when they are employed in paints for aluminum. I shall refer to such paints as "resin based coating compositions for aluminum." They are well known and those skilled in the art will be able to identify the commercially available film formers and coating compositions which are useful in my invention.

The above important advantages of my process for conditioning the surface of the aluminum body to be etched is accompanied by another effect which is important in etching aluminum bodies whether or not they be partly masked to expose portions only of the surface of the aluminum body or whether the aluminum body be not partially masked so as to expose all surfaces thereof to corrosive attack.

This invention thus also relates to a method for the controlled etching of aluminum and aluminum alloys. Etching solutions employed are alkaline solutions. Such procedures involve the exposure at suitable temperatures of the aluminum body to corrosive attacks by the etching solutions. The procedure depends on the end to be sought. For example, where the object is an aluminum part whose surface is to be altered in appearance, the part is only superficially etched in order to change the appearance of the surface. When the aluminum body is to be deeply etched in order to modify the mechanical characteristics of the aluminum as a structural part or a machine part, the aluminum body is etched for a degree sufficient to alter the mechanical or structural character of the part.

In such cases the part, in order to control the appearance or mechanical characteristics of the part, may be masked at selected portions with a mask which isolates, i. e., separates from the etching solution the part of the object which it is desired not to react with the etching solution.

Experience with such etching process has shown that where it is used for alteration of surface appearance of the aluminum part that the surface instead of being of a uniform matt finish contains portions of greater light reflectivity than adjacent portions giving a surface with highlights. This I believe is due to the fact that the depth of etch, where it is not uniform across the entire surface, results in high lights but where it is uniform a uniform matt surface is produced. When the proce-

dure is used as a substitute for mechanical forming or machining to give aluminum bodies of altered mechanical and structural characteristics, the process results in a body which is not etched to a uniform depth across the entire exposed surface. This does not give the desired contour to the etched parts to conform with design characteristics.

I have found that the non-uniformity of the depth of etch across the entire exposed surface may be avoided and a uniform depth of etch across such entire surface achieved by a proper conditioning of the surface prior to etching.

I have found that if the surface to be etched is treated with the above aluminum non-corrosive acidic solutions, the surface may thereafter be etched with an alkaline etchant in such manner that the etching rate is uniform across the entire etched surface. In such case the surface is etched to a substantially uniform depth across the entire surface.

While I do not wish to be bound by any theory of why the process of my invention produces uniformly etched surfaces, I believe that the uniformity of etch produced by my process results from the fact that I expose the base elemental metal or alloyed surface to the etching solution.

As is well known, aluminum surfaces are coated with thin films of aluminum oxide produced by atmospheric oxidation of the aluminum. These aluminum oxide surfaces may or may not be uniformly distributed over the surface since the depth and density of the oxide coating depends upon factors. The influence of many of these factors are not known to the knowledge of applicant. However, I have postulated that the depth of etch of the alkaline etchant depends upon the thickness and density of the oxide coat for in order to reach the base metal the alkali etchant must first remove the oxide coat. However, if the coat is not uniform across the entire surface part of the base metal will be exposed to the etching solution before other parts are so exposed. Therefore, even if the etching rate is uniform after the base metal is reacted the etched metallic surface will have a topograph which indicates a variation in depth of etch across its area.

I have found, however, that by removing the oxide film by solution with a deoxidant solution (i. e., one that reacts with the oxide film to remove it), which however, unlike the alkali etching solutions, does not react at a substantial rate with the base metal at the temperature of treatment, I may produce a surface which may then be etched with an alkaline etching agent at a uniform rate across the entire surface of the etched aluminum part.

If such elemental metallic surface as it is produced is immediately etched before any substantial build-up of oxide occurs on the surface of the exposed metal such uniform corrosion is obtainable. I have found that an aluminum or aluminum alloy surface after such treatment may be safely stored for about one-half hour to an hour without any substantial oxidation occurring sufficiently to interfere with the uniform rate of attack described above.

I cannot say with assurance that the metal after such storage does not have an oxide film. It may be that as a result of the exposure of the elemental metallic surface an oxide film of uniform character forms across the surface. If any oxide coating is formed it is a uniform coating throughout the entire surface so that the subsequent corrosion attack by the alkali etching solution results in a uniform rate of solution of the oxide coat followed by a uniform corrosion of the metal across the entire surface of the etched part. This also will give a uniform depth and rate of etch across the entire surface.

The following examples are given for the purpose of illustrating my invention rather than as limitations thereof.

Example 1

The aluminum part to be etched, if it is not clean, as for example, if it is coated with a forming or heat treating oil, is washed thoroughly in an alkaline or other detergent solution. It is then thoroughly rinsed to produce a clean washed aluminum piece.

The washed aluminum part is sprayed with or immersed in a solution made by dissolving from 4 to 30 ounces per gallon of water, of a mixture composed of the following:

77.1% by weight of $NaHSO_4$ (sodium acid sulfate) 1%
by weight of $NH_4F.HF$ (ammonium bifluoride)
21.8% by weight $K_2Cr_2O_7$ (Potassium dichromate)
0.1% by weight Nacconol Z

Nacconol Z (alkyl aryl sodium sulfonate) is sold by National Aniline Div., Allied Chemical & Dye Corp.

I have found that about 16 oz. of the above mixture in a gallon of water will result in a satisfactory surface if the metal is immersed in the solution for about 3 minutes, at atmospheric temperatures for example about 60 to about 100° F. Higher concentration will give these results in a shorter time.

Care must be taken to remove the part when the base metal is exposed, i. e., after solution of the oxide film, since especially in the presence of dissolved oxygen in the solution or if the solution is sprayed on to the metal part, the ambient or dissolved oxygen readily attacks the highly reactive metal surface produced by this conditioning operation, and the rate of oxide formation may exceed the rate of solution so that the resultant part is coated with an oxide film. Experience has shown that with a 3 minute exposure of a solution of the above character, the oxide formation is not a material factor and the surface is successfully conditioned in the manner described above.

The treated surface is then thoroughly washed with plain water and dried and is ready for application of the coating compositions such as described above.

The masking composition is painted directly on the dried surface in the desired pattern, covering the portions which it is not desired to etch. For example, by coating the part of the object to be protected against etching with a coating composition having the following formulation:

88% polyvinyl acetate
4% polyvinyl chloride
6% vinyl alcohol
2% dioctyl phthalate
Dissolved in methyl isobutyl ketone.

The part to be etched is thus outlined by the coating and the coating is cured in the conventional manner. After drying the coated object may be etched. It is etched by contact with an alkali solution of, for example, aqueous caustic soda solution and other alkaline solutions in water, such as solutions of trisodium phosphate, sodium carbonate and the corresponding potassium compounds. I may add to such solutions a small percentage gluconic or saccharic acid in the range of about .1 to 20% of the alkali, preferably about 3–5% and more preferably about 3–5% of citric acid or citrate salts, based on the alkali as disclosed in the copending application, Serial No. 445,197, filed of even date herewith, now Patent No. 2,739,883, granted March 27, 1956.

The masked aluminum part is reacted with the above solutions by immersion or by a spray of such solutions at an elevated temperature of from 140° F. to 210 degrees F. and cause a reaction between the alkali etching solution and the unmasked (exposed) portions of the surface of the aluminum object.

Thus, for example, an aluminum sheet of 0.250 inch thickness is sprayed with such a water solution containing 7 parts by weight of a mixture composed of 96 parts by weight of dry NaOH and 4 parts by weight of dry citric acid crystals for one hour at 180° F. to cause an etch

which is approximately 0.060 inch in depth on each surface exposed to the etching solution and which undercuts the mask on such surface at the line of juncture for a distance of approximately 0.060 inch. The exposure time depends on the depth of etch desired. The etch line, i. e., the edge of the edge pattern of the etch will be sharp and uniform showing that the bond between the mask and aluminum had maintained its integrity along the whole front of alkali attack along the line of juncture and underneath the undercut mask.

After the removal of the part from contact with the solution it is then washed thoroughly with plain water and dried. The mask (i. e. the coating composition which has protected parts of the aluminum surface) is readily stripped, i. e., removed, either mechanically or with the aid of a paint remover such as is used for aluminum paints of the kind described above. It will be much more easily and thoroughly removed than when an acid wash primer coat is employed.

Example 2

The above procedures may be carried out substantially as described with like results employing as the acid conditioning agent which is aluminum noncorrosive, a mixture made up as follows:

84.6% by weight of dihydrogen sodium phosphate (NaH_2PO_4)
2.0% by weight of orthophosphoric acid acid H_3PO_4
5.0% by weight sodium pyrophosphate ($Na_2P_2O_7$)
7.0% by weight nonionic agent Triton X–100
1.4% by weight of isopropyl alcohol

Triton X–100 is alkyl aryl polyether alcohol sold by Rohm & Haas Co.

The above mixture is added to water in the ratio of 2 to 6 oz. per gallon of water and the aluminum is treated and etched by the procedure substantially in the manner of Example 1.

The etch rate across the entire surface in both of the above examples will be uniform without the highlights and that with a perfectly flat plate and uniform distribution of the etching solution or/and uniform movement of the etching solution if etching solution is sprayed on the surface, will be etched to a uniform depth. The rate of attack will be the same across the entire surface similarly exposed to the etching solution.

It will be clear that where I wish to rely on the function of my process to cause uniform etching of the surface of the aluminum object and do not wish to mask portions thereof, my process may be employed for such purpose on a completely unmasked article. Thus, after treating the cleaned surface with the acidic solution safe on aluminum, and rinsing, I may pass the part directly or after storage, to the alkaline etchant.

Example 3

The above procedure described under Example 1 may be employed with the following composition instead of the Example 1:

93.6 parts by weight of sodium acid sulfate ($NaHSO_4$)
6 parts by weight of chromic oxide (Cr_2O_3)
0.4 part by weight of Nacconol Z, identified above

The above mixture may be employed in amounts ranging from 4 to 32 ounces per gallon of water. A preferred concentration is 16 oz. per gallon of water.

Example 4

The procedures of Example 1 may be employed using the composition given below in place of the composition of Example 1.

81 parts by weight of sodium dihydrogen phosphate (NaH_2PO_4)
5 parts by weight of sodium dihydrogen pyrophosphate ($NaH_2P_2O_7$)
2 parts by weight of ortho-phosphoric acid (H_3PO_4)
5 parts by weight of sodium nitrate ($NaNO_3$)
1 part by weight of sodium silico fluoride (Na_2SiF_6)
6 parts by weight of Sterox SK (a polyoxyethylene thioether sold by Monsanto Chemical Co.)

The above mixture may be used in water in concentrations ranging from 2 to 6 oz. per gallon. A preferred concentration is 5 oz. per gallon of water.

Example 5

The following composition which is a liquid may also be employed in the procedure of Example 1:

72.8 parts by weight of water
22.0 parts by weight of concentrated sulfuric acid (H_2SO_4)
3.96 parts by weight of chromic oxide (Cr_2O_3)
1.24 parts by weight of ammonium silico fluoride $(NH_4)_2SiF_6$

The above composition is used diluted in water in amounts ranging from 2 to 20 volumes of water to 1 volume of the above composition. A preferred concentration is 1 part of the above liquid to 10 parts of water.

While I have described a particular embodiment of my invention for the purpose of illustration, it should be understood that various modifications and adaptations thereof may be made within the spirit of the invention as set forth in the appended claims.

I claim:

1. A method of etching an aluminum object which comprises: treating the aluminum with an aluminum noncorrosive acidic solution, the temperature and acid concentration of said treating solution being related to render the solution an active reagent for the removal of aluminum oxide from said object and substantially noncorrosive to aluminum, the duration of said treating being only substantially for the time required to remove an oxide coating from said object; and treating the aluminum object with an alkaline etching solution; thereby etching the surface of said object treated with said etching solution.

2. A method as set forth in claim 1, wherein said acidic solution is chosen from the group consisting of the water solutions of nitric acid, sulfuric acid, sodium acid sulfate, sodium dihydrogen phosphate and the equivalent potassium salts of said acid salts, said solution having a pH value of about 4 or less.

3. A method as set forth in claim 2, wherein the aluminum treated with said acidic solution is washed with water before being treated with said alkaline solution.

4. A method as set forth in claim 2, wherein said acidic solution also contains an aluminum corrosion inhibitor.

5. A method as set forth in claim 4, wherein the aluminum treated with said acidic solution is washed with water before being treated with said alkaline solution.

6. A method of etching an aluminum object which comprises: treating the aluminum with an aluminum noncorrosive acidic solution, the temperature and acid concentration of said treating solution being related to render the solution an active reagent for the removal of aluminum oxide from said object and substantially non-corrosive to aluminum, the duration of said treating being only substantially for the time required to remove an oxide coating from said object; coating a portion only of the treated surface of the object with an alkali resistant resin based coating composition for aluminum; and treating the aluminum object with an alkaline etching solution; thereby etching said surface treated with said etching solution.

7. A method as set forth in claim 6, wherein the aluminum treated with said acidic solution is washed with water and dried prior to said treating with said alkaline solution.

8. A method as set forth in claim 6, wherein said acidic solution contains a non-ionic wetting agent.

9. A method as set forth in claim 8, wherein the aluminum treated with said acidic solution is washed with water and dried prior to said treating with said alkaline solution.

10. A method as set forth in claim 6, wherein said acidic solution is chosen from the group consisting of the water solutions of nitric acid, sulfuric acid, sodium acid sulfate, sodium dihydrogen phosphate, and the equivalent potassium salts of said acid salts, and said acidic solution has a pH value of about 4 or less.

11. A method as set forth in claim 10, wherein the aluminum treated with said acidic solution is washed with water and dried prior to said treating with said alkaline solution.

12. A method as set forth in claim 10, wherein said acidic solution contains an aluminum corrosion inhibitor.

13. A method as set forth in claim 12, wherein the aluminum treated with said acidic solution is washed with water and dried prior to said treating with said alkaline solution.

14. A method as set forth in claim 10, wherein said acidic solution contains a non-ionic wetting agent.

15. A method as set forth in claim 14, wherein the aluminum treated with said acidic solution is washed with water and dried prior to said treating with said alkaline solution.

16. A method as set forth in claim 10, wherein said acidic solution contains an aluminum corrosion inhibitor and a non-ionic wetting agent.

17. A method as set forth in claim 16, wherein the aluminum treated with said acidic solution is washed with water and dried prior to said treating with said alkaline solution.

18. A method as set forth in claim 1, wherein said acidic solution contains sodium acid sulfate, potassium dichromate, and ammonium bifluoride, said sodium acid sulfate being present in a major proportion, said acidic solution having a pH value of about 4 or less, and wherein the aluminum treated with said acidic solution is washed with water prior to said treating with said alkaline solution.

19. A method as set forth in claim 1, wherein said acidic solution contains sodium dihydrogen phosphate, orthophorphoric acid, sodium pyrophosphate, and a non-ionic wetting agent, said sodium dihydrogen phosphate being present in a major proportion, said acidic solution having a pH value of about 4 or less, and wherein the aluminum treated with said acidic solution is washed with water prior to said treating with said alkaline solution.

20. A method as set forth in claim 1, wherein said acidic solution contains sodium acid sulfate, chromic oxide, and a non-ionic wetting agent, said sodium acid sulfate being present in a major proportion, said acidic solution having a pH value of about 4 or less, and wherein the aluminum treated with said acidic solution is washed with water prior to said treating with said alkaline solution.

21. A method as set forth in claim 1, wherein said acidic solution contains sodium dihydrogen phosphate, sodium dihydrogen pyrophosphate, orthophosphoric acid, and sodium nitrate, said sodium dihydrogen phosphate being present in a major proportion, said acidic solution having a pH value of about 4 or less, and wherein the aluminum treated with said acidic solution is washed with water prior to said treating with said alkaline solution.

22. A method as set forth in claim 1, wherein said acidic solution contains sulfuric acid, chromic oxide, and ammonium silico fluoride, said sulfuric acid being present in a major proportion, said acidic solution having a pH value of about 4 or less, and wherein the aluminum treated with said acidic solution is washed with water prior to said treating with said alkaline solution.

23. A method as set forth in claim 6, wherein the aluminum treating temperature of said acidic solution is from about 60° to about 100° F., and wherein the aluminum surface is washed with water and dried after said treating with said acidic solution.

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