ALKALI ETCHING SOLUTION FOR ALUMINUM
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8 Claims. (Cl. 252—79.3)

This invention is directed to aqueous alkali etching solutions for aluminum and aluminum alloys which produce a novel architectural finish on the aluminum. This invention is also directed to solid metallic compositions which are added to water to form the aqueous solutions for producing the novel architectural finish on aluminum and aluminum alloys. This invention is also directed to conventional compositions which are used to etch the aluminum so that they will produce the novel architectural finish on aluminum and aluminum alloys. The invention is also directed to methods of producing the new architectural finish on aluminum and aluminum alloys.

In another aspect of the present invention I have discovered that my new etching solutions are capable of preventing galvanizing of alkali etching solutions for aluminum and aluminum alloys.

Industrial aluminum finishers usually process their product in an alkaline etching system to remove surface imperfections and generally to enhance the appearance of the aluminum or aluminum alloy product. The finishes so obtained are subject to a continuing demand by the processor for improved quality and increased esthetic appeal. I have discovered novel etching solutions which produce an architectural finish on aluminum and aluminum alloys which has never been heretofore obtained.

This architectural finish may be described as an etched finish, gray white to white in color, having a non-metallic appearance, having a low or matte reflectance, having a uniform fine-grained appearance independent of any underlying aluminum grain boundaries and having what is known in the trade as an excellent hide, that is, all extrusion, die marks and scratches are completely hidden.

In addition to the new architectural finish which my solutions and compositions impart to aluminum and aluminum alloys, my compositions have the added advantage in that no sludge or scale is formed in their use and that they are of low cost. I have also discovered that my compositions eliminate the galvanizing effect which so often causes loss or reprocessing of aluminum metal parts in finishing operations.

The novel solutions used in obtaining the new architectural finish comprise caustic alkali in aqueous solution which also contains hexavalent chromium ion, fluoride ion and a special surface modifying agent. The combination of hexavalent chromium, fluoride ion and special surface modifying agent acts as an etch modifier upon the attack of the caustic alkali on aluminum surfaces. The novel combination modifies both the mode of attack of the caustic alkali on the aluminum surface and also changes the rate of this attack.

The new etchant solutions contain one or more alkali metal hydroxides at a concentration of 13 to 90 grams per liter. Sodium hydroxide is the principal source of the alkali metal hydroxide because it is inexpensive as compared to potassium or lithium hydroxide. However, potassium hydroxide is equally efficient in these compositions. In addition to the alkali metal hydroxide my etching solutions must contain hexavalent chromium and fluoride ion and at least one specific chelating agent as more fully described below. All three of these ingredients must be present in addition to the alkali metal hydroxide. Moreover, they must be present at certain particular weight relationships in order to produce the new architectural finish on aluminum and aluminum alloys.

The standard etching solution usually comprises a strong sodium hydroxide solution of about 25 to 30 grams per liter and a chelating agent to keep the dissolved aluminum from redepositing sodium aluminate on the metal surface. These etching solutions normally produce a silver to silver gray metallic appearance. In addition to the silver color such surfaces will have a high reflectivity and will be shiny. In addition the etched surface will be non-uniform in character and there will be no uniform grained appearance. The resulting overall surface will not hide the die or extrusion marks and scratches are often visible.

In contrast to the normal alkaline etching with sodium hydroxide solutions my new solutions will produce an etched surface which is gray white to white in color with a non-metallic appearance. The surface will not reflect and will have what is known as a matte finish. The surface will have a uniform fine grain and all underlying surface die marks and scratches will be concealed.

The hexavalent chromium ion concentration in my etching solutions must lie within the range of 0.02% to 4.5% of the alkali metal hydroxide concentration. The presence of the hexavalent chromium ion solution importantly modifies the attack of the alkali metal hydroxide on the aluminum surface. Consequently, the hexavalent chromium ion concentration is directly related to the alkali metal hydroxide concentration. This modifying attack of the alkali metal hydroxide on the aluminum is accomplished in conjunction with the simultaneous effect of the fluoride ion and the special chelating agents which I have found useful for this purpose.

The source materials for the hexavalent chromium ion are one or more of the water soluble ionizable chromium containing compounds. They may be selected from the group which includes sodium dichromate, potassium dichromate, ammonium dichromate, sodium chromate, potassium chromate, chromic anhydride, sodium chrom glucoate, potassium chrom glucoate, sodium chromate, potassium chromate, ferric chromate, chromium oxalate, chromium acetate, chromium sulfate, chromium nitrate and chromium phosphate. The above sources of hexavalent chromium ion are all normally solid materials and of course are useful in preparing the solid granular concentrates which are used in making my etching solutions. Generally the hexavalent chromium ion concentration will vary from 0.15 to 0.7 gram per liter. The preferred range of hexavalent chromium ion concentration is between 0.2 and 0.32 gram per liter.

The second etchant modifier which is necessary in my compositions is fluoride ion. This ion contributes its own special characteristic to the non-metallic, non-reflecting surface obtained by my compositions. Since the fluoride ion is modifying the surface attack, its concentra-
ion will also be related to the alkali metal hydroxide concentration. I have found that the fluoride ion concentration must be within the range of 0.04% to 2% of the alkali metal hydroxide concentration. Generally the fluoride concentration will vary from 0.1 to 0.6 gram per liter. Preferably the concentration of fluoride is between 0.2 and 0.3 gram per liter. Conveniently the fluoride ion obtained from sodium fluoride because of its low cost and good water solubility.

The source materials for the fluoride ion are one or more of the water soluble ionizable fluorides which can be selected from the group which includes sodium fluoride, potassium fluoride, sodium acid fluoride, potassium acid fluoride, sodium aluminum fluoride, sodium floroborate, sodium florosilicate, sodium phosphorous fluoride, ammonium fluoride, ammonium acid fluoride, chronic fluoride and magnesium fluoride.

The third component which acts as a surface modifier with respect to the action of the alkali metal hydroxide techant on aluminum and aluminum alloys is a special group of surface modifying agents of the chelating type which combine with the hexavalent chromium and fluoride to modify the action of the caustic soda. As was the case with the hexavalent chromium and the fluoride on the amount of surface modifying agent of the chelating type which will be present in my solution, the fluoride ion will depend on the alkali metal hydroxide concentration and in addition will vary with the amount of hexavalent chromium present.

I have found that the chelating agent concentration must be at least one hundred percent of the chromium ion concentration and 2.0% of the alkali metal hydroxide concentration. Generally the concentration of the surface modifying agent of the chelating type will be between 0.4 and 2 gram per liter and preferably will be between 0.6 and 0.9 gram per liter.

The upper concentration limit of the surface modification agent of the chelating type is an economic limit and is not a limit imposed by chemical considerations. Amounts greater than two grams per liter appear to be unnecessary and to be without effect on the type of surface obtained. The surface modification agents of the chelating type which are useful in my compositions for modifying the surface finish on the aluminum produced by the alkali metal hydroxide along with the hexavalent chromium ion and fluoride ion include sorbitol, mannitol, ascorbic acid, sorbose, tannic acid, ethylenediamine, saccharic acid, sodium chromate, diglycemic acid, nicotinic acid, aspartic acid, dihydroxamic acid, and gluconic acid. For control in this specification and in the claims, I will hereafter refer to this group as Group A surface modifying agents.

It is not every chelating agent which can be used in my etching solutions to modify the type of etch obtained on aluminum and aluminum alloys. For example, recognized and well established chelating agents such as gluconic acid and sodium gluconate do not produce the non-reflecting matte etched finish which I desire. Similarly, fructose, manose, and citric acid and oxalic acid are unsuitable in my compositions.

In using my etching solutions the aluminum or aluminum alloy is first cleaned with a conventional aluminum cleaner which may be of the alkaline or acid type, since it is necessary to remove oxides and soil which obstruct the etching action. After cleaning, the aluminum is rinsed with water, preferably warm, and is then immersed in or sprayed with my etching solutions. The etching solution must be held at a temperature within the range of 100° to 200° F. The desired finish is not obtained. However, at temperatures less than 140° F, my solutions are effective in preventing the unwanted effect known in the industry as galvanizing which is described more fully below. The preferred temperature range for securing the preferred architectural finish brought about by my etching solutions is within the range of 160 to 180° F. Following cleaning the metal work piece is allowed to remain in solution until the desired etch is obtained. Generally this will vary from one to 15 minutes depending on the concentration of the ingredients and the temperatures used. Suitable etching is often obtained in about 3 to 7 minutes.

Following etching the work piece is then rinsed at least once with water, preferably warm, and then the work piece is desmutted to remove the metal particles which are insoluble in the etching solution. Since my etching solutions have a considerable concentration of chromium contained therein it is unnecessary to use a phosphated desmuter, and, in fact, a non-chromated desmuter is preferred.

A preferred solution for producing the new architectural finish on aluminum of the non-reflecting, matte-etched type would have an alkali metal hydroxide concentration of 20.7 grams per liter and a hexavalent chromium ion concentration of 0.24 gram per liter, a fluoride ion concentration of 0.2 gram per liter and a Group A surface modification agent at a concentration of 0.7 gram per liter. Conveniently the alkali metal hydroxide is supplied by sodium hydroxide, the hexavalent chromium ion by sodium or potassium dichromate, the fluoride ion by sodium fluoride and the Group A surface modification agent by sorbitol.

Since it is uneconomical to ship aqueous solutions for very long distances, one aspect of my invention comprises the solid granular compositions which are capable of forming the aqueous solutions described above. The principal etching ingredients of the solid compositions are the alkali metal hydroxides such as sodium hydroxide, potassium hydroxide or mixtures thereof. The sources of the hexavalent chromium ion, the fluoride ion and of the Group A surface modifying agent of the chelating type described above for the aqueous solutions are the same sources for supplying these components in my solid granular compositions.

In the solid granular compositions the alkali metal hydroxide concentration will lie within the range of 80 to 97.5% by weight. The water soluble ionizable hexavalent chromium content of these compositions will lie within the range of 0.002 to 3.81% by weight. The water soluble ionizable fluoride concentration will lie within the range of 0.4 to 1.7% by weight. The special surface modification agent of the chelating type will have a concentration in my solid granular compositions within the range of 2 to 10% by weight.

In a preferred use of solid granular compositions the alkali metal hydroxide concentration will be within the range of 80 to 97.5% by weight, the water soluble ionizable hexavalent chromium content of the solid compositions will be within the range of 0.002 to 4% by weight, the water soluble ionizable fluoride concentration will be within the range of 0.004 to 2.0% by weight and the Group A surface modification agent will be within the range of 2 to 10% by weight.

A preferred solid composition for producing the aqueous etching solutions of my invention comprises caustic soda—91.7% by weight, potassium dichromate—3.0% by weight, sorbitol—3.3% by weight and sodium fluoride—2.0% by weight. This solid granular concentrate is used in aqueous solution at a concentration of 2 to 12 ounces per gallon, preferably at a concentration of 3 to 4 ounces per gallon.

In many instances the aluminum metal processor or finisher may desire a highly reflective etch instead of a non-reflective finish produced by the inventions described above. In order to meet the needs of this processor and in order to give the processor the greatest amount of flexibility, it is possible to supply him with a conventional etching solution which would contain alkali metal hydroxide and a chelating agent and to supply separately
A solid granular concentrate comprising water soluble ionizable hexavalent chromium, water soluble ionizable fluoride and a Group A surface modification agent described above. By adding a certain proportion of this concentrate of hexavalent chromium, water soluble fluoride and surface modification agent to caustic alkali solutions, it is possible to convert them into an etching solution which will produce the unusual architectural finish of my invention.

The special granular concentrate for adding to conventional etching solutions comprises water soluble ionizable hexavalent chromium at a concentration within the range of 6 to 12% by weight, water soluble ionizable fluoride in the range of 12% to 20% by weight and a Group A surface modification agent of the etching type as described above at a concentration of at least 6% by weight. Conveniently, the Group A surface modification agent is present at a concentration of 6 to 16% by weight.

A preferred solid granular composition contains water soluble ionizable hexavalent chromium at concentration of 8.9% by weight, water soluble ionizable fluoride at a concentration of 7.6% by weight and a Group A surface modification agent at a concentration of 8.3% by weight. In many instances these constituents are combined with inert material such as sodium sulfate or potassium sulfate which is uniformly in the nature of a filler. The filler may be present within the range of 40 to 60% by weight. Non-causing agents and/or conventional detergents may be incorporated as may be desired.

A solid composition which will give the required weight ratios of the ingredients specified above comprises sodium dichromate—50% by weight, sodium fluoride—33% by weight, and sorbitol—17% by weight. Another solid composition which would give the necessary ratio of components comprises potassium dichromate—25% by weight, ammonium fluoride—16.7%, mannitol—8.3% and sodium sulfate—30.0%. As discussed in connection with the etchant solutions, the amount of Group A surface modification agent is not limited with respect to the maximum present and the maximum amount will be at the discretion of the user since the upper limit is dictated only by economic considerations and not by the type of finish which is obtained.

As mentioned earlier in this application, in the etching of aluminum extrusions and sheets, industrial metal finishers are periodically troubled by the occurrence of an undesirable etch finish known as galvanizing or galvanized etched finish. This undesirable and unpredictable etched finish may be described as displaying a highly reflective, grossly crystalline appearance. Often the galvanizing is so severe that all usable part must be scrapped. In less severe cases the aluminum must be mechanically polished before it can be reprocessed. Such losses and/or multiple processing contribute greatly to the cost of aluminum etching.

I have discovered that the addition of a small amount of the special granular concentrate of chromium, fluoride and Group A surface modifying agent described above to a normal alkaline etching bath will prevent the occurrence of this galvanizing effect. As little as 0.1 ounce per gallon of the concentrate may be added to conventional alkali etching baths and as long as this concentration is maintained galvanizing will not occur. Since the amount of solid granular concentrate added to a normal etching bath to prevent galvanizing will also produce the new architectural etched finish described earlier in this application, special precautions with respect to temperature must be observed. If it is desired to merely prevent galvanizing without obtaining the new architectural etched finish, it is merely necessary that the temperature of the etching bath be maintained below 150°. Below this temperature the new matte-etched finish is not produced. Amounts of the solid granular concentrates higher than 0.1 ounce per gallon may be added to the conventional etching baths but greater amounts are unnecessary to prevent galvanizing. In order to prevent galvanizing, the etching solution must have an alkali metal hydroxide concentration of 15 to 90 grms per liter, a minimum concentration of hexavalent chromium ion of 0.06 gram per liter, a minimum concentration of fluoride ion of 0.06 gram per liter and concentration of a Group A surface modifying agent of 0.36 gram per liter. While as little as one-tenth of an ounce per gallon of solid granular concentrate will prevent galvanizing in a normal aluminum etching bath of the alkali metal hydroxide type, generally the solid granular concentrate is added at a concentration of about 0.2 to 0.5 ounce per gallon.

The alkaline etching solutions of my invention which are used to prevent galvanizing will contain alkali metal hydroxide at a concentration of 15 to 90 grms per liter, hexavalent chromium ion within the range of 0.06 to 0.9 gram per liter, fluoride ion at a concentration within the range of 0.06 to 0.4 gram per liter and a minimum concentration of at least one surface modifying agent of the etching type from Group A of at least 0.36 gram per liter. It will be apparent that the solid granular concentrates described above for adding the alkali metal hydroxide solutions to produce the new architectural finish on aluminum are the same solid concentrates which are used to prevent galvanizing.

The best mode of practicing my invention will be apparent from a consideration of the following examples:

**Example I**

An etching solution containing 20.7 grams per liter of sodium hydroxide, 0.675 gram per liter of sorbitol and 0.45 gram per liter of sodium fluoride was maintained at a temperature of 165° F. Varying amounts of potassium dichromate were dissolved in the solution to observe the effect of the hexavalent chromium ion concentration on the etch finish produced by the solution.

Sections of 6063 aluminum alloy were cleaned, rinsed and then immersed in the etchant solution for a given minute period. After etching the sections were rinsed with water, were desmutted in an acid solution, rinsed with water and dried. The results are presented in Table I.

<table>
<thead>
<tr>
<th>Concentration of</th>
<th>0</th>
<th>0.001</th>
<th>0.003</th>
<th>0.005</th>
<th>0.006</th>
<th>0.007</th>
<th>0.008</th>
<th>0.009</th>
<th>0.010</th>
<th>0.011</th>
<th>0.012</th>
<th>0.013</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(IV)</td>
<td>1.0</td>
<td>0.001</td>
<td>0.003</td>
<td>0.005</td>
<td>0.006</td>
<td>0.007</td>
<td>0.008</td>
<td>0.009</td>
<td>0.010</td>
<td>0.011</td>
<td>0.012</td>
<td>0.013</td>
</tr>
<tr>
<td>NaOH</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Example II**

Etching solutions containing 20 grams per liter of sodium hydroxide, 0.675 gram per liter of sorbitol and 0.675 gram per liter of potassium dichromate were maintained at a temperature of 165° F. Varying amounts of sodium fluoride were added to separate portions of these solutions and the etching effect observed on aluminum sheets. Prior to etching the sections of aluminum metal...
were cleaned, rinsed and then etched in the solutions for seven minute period. After etching the aluminum sheets were rinsed, desmutted in an acid desmutting solution, rinsed again in water and dried. The results of the comparisons are described in Table II below.

### Table II: Effect of Fluoride Concentration

<table>
<thead>
<tr>
<th>Gram/liter</th>
<th>NaF</th>
<th>F⁻</th>
<th>Etched Finish</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.0</td>
<td>0</td>
<td>White, frosty matte finish with no imposed grain—surface marks are visible.</td>
</tr>
<tr>
<td>0.02</td>
<td>0.009</td>
<td>0.000387</td>
<td>Frosty white matte finish with uniform fine imposed grain.</td>
</tr>
<tr>
<td>0.45</td>
<td>0.098</td>
<td>0.008</td>
<td>White matte finish with uniform fine imposed grain.</td>
</tr>
<tr>
<td>9.00</td>
<td>0.407</td>
<td>0.02</td>
<td>White matte finish with uniform fine imposed grain but with notable decrease in frostiness. (Some increase in reflectivity.)</td>
</tr>
</tbody>
</table>

1. Control.

The above experiments demonstrate that the fluoride to sodium hydroxide ratio within the range of 0.04% to 1.0% will provide the imposed type of grain finish which produces the frosty white matte etched non-reflecting surface with good hide characteristics.

### Example III

The range of chelating agent concentrations which are useful in my etching solutions was determined by approaching the problem from the aspect of that amount of sorbitol which would act together with the hexavalent chromium ion and fluoride ion to produce the desired finish on the aluminum surface and in addition would provide enough chelating agent to prevent the redeposition of the aluminum on the etched work pieces in the form of a hard aluminate while avoiding a large excess of the agent.

Sections of aluminum alloy extrusions were cleaned, rinsed and etched in solutions containing 20.6 grams per liter of sodium hydroxide, 0.6 gram per liter of potassium dichromate and 0.45 gram per liter of sodium fluoride. After immersion of an aluminum panel in this solution for several minutes at 165° F., the panels were desmutted, rinsed and dried and then examined for the nature of the etched finish produced. The panels immersed in the etchant solution without any chelating agent produced a frosty white fine grained etched surface having considerable reflectance. In the next run 0.675 gram of sorbitol per liter were added to a separate portion of the solution described above and the process repeated at the same temperature. In this solution the ratio of sorbitol to sodium hydroxide was 0.326 and the sorbitol to chromium ion ratio was 2.82. The surface produced by this solution was the desired silver gray non-metallic matte-etched finish with excellent hide.

To another portion of the first solution 0.34 gram per liter of sorbitol were added and a new aluminum panel was immersed in the solution for seven minutes at a temperature of 155° F. The etchant finish obtained in this solution was unsatisfactory since the panel showed considerable less frostiness and therefore increased reflectance. In this solution the ratio of sorbitol to alkali metal hydroxide was 0.0165 while the sorbitol to chromium ion ratio was 1.42.

In another series of runs designed to measure the effectiveness of the special group of chelating agents in preventing the redeposition of solids on the metal surface, test solutions containing 18.0 grams of aluminum alloy powder dissolved in 600 mls. of water with 30.1 grams of sodium hydroxide and 0.656 gram NaF were prepared and maintained at a temperature of about 150° F. Varying amounts of chelating agents and potassium dichromate were added to separate portions of this solution and the amount of precipitate which was produced after 18 hours was measured. Any considerable amount of precipitate would indicate that the chelating agent was ineffective.

In the first run, 0.984 gram of sorbitol and 0.984 gram of K₂CrO₇ (0.348 gram Cr⁴⁺) were added to a 600 ml. portion of the test solution. There was no noticeable precipitate after 18 hours. The ratio of sorbitol to NaOH was 0.0326 (2.36%) while the ratio of sorbitol to Cr⁴⁺ was 2.83 (283%). When only 0.328 gram of sorbitol and 0.984 gram of K₂CrO₇ were used per 600 mls. of test solution, there was considerable precipitation with a one-eighth inch layer of dense floe and a three-quarters inch layer of hard crystalline deposits. Here, the ratio of sorbitol to NaOH ratio of 0.011 (1.1%) and sorbitol to Cr⁴⁺ of 0.945 (94.5%) were too low.

In the next run the sorbitol was increased and 0.656 gram with 0.984 gram of K₂CrO₇ was used. A test run of 18 hour observation very little floe and no hard deposits were noticeable, indicating satisfactory chelating. The sorbitol to NaOH ratio was 0.0218 (2.18%) while the sorbitol to Cr⁴⁺ ratio was 1.88.

The runs described above and others demonstrated that the minimum amount of surface modifying chelant required was 0.02 or 0.2% of the alkali metal hydroxide concentration plus an amount equivalent to 100% by weight of the hexavalent chromium present. Varying the fluoride ion concentration at this level of chelate concentration did not affect the chelating or surface modifying effects.

In another run a one liter solution containing 20.7 grams of potassium hydroxide, 4.6 grams of chromium trioxide (equivalent to 0.24 gram of hexavalent chromium), and 0.298 gram of aluminum fluoride (equivalent to 0.2 gram of fluoride ion) was prepared. Sorbitol was then added to the solution in the amount of 2.93 grams giving a sorbitol to NaOH ratio of 14%. Sections of aluminum alloy were cleaned, rinsed and etched in this solution for approximately 6 minutes. After desmutting, rinsing and drying the finish was examined. The desired architectural finish was obtained and as the metal had a silver gray matte non-reflecting etched finish of uniformly fine imposed grain, no disadvantage nor advantage could be ascertained by the large amount of sorbitol present in the solution.

### Example IV

In order to determine what agents were effective in combination with the hexavalent chromium ion and fluoride ion in producing my new architectural finish in alkaline etching solutions, the following runs were made:

An etching solution containing 20.7 grams of sodium hydroxide per liter, 0.24 gram of hexavalent chromium per liter, and 0.2 gram of fluoride ion per liter was used as the base for separate additions of various chelating agents, a separate solution being used for each chelating agent. The sections of aluminum selected from alloys 11100, 1052 and 3003 and 6053 were prepared by first cleaning them in an alkaline solution containing 6 ounces per gallon of a granular concentrate containing 70% borax, 17G tetroxysodium pyrophosphate, 5% sodium dichromate, and 8% organic detergents for 6 minutes at 165° F. The etchant finish obtained in this solution was unsatisfactory since the panel showed considerable less frostiness and therefore increased reflectance. In this solution the ratio of sorbitol to alkali metal hydroxide was 0.0165 while the sorbitol to chromium ion ratio was 1.42.

In another series of runs designed to measure the effectiveness of the special group of chelating agents in preventing the redeposition of solids on the metal surface, test solutions containing 18.0 grams of aluminum alloy powder dissolved in 600 mls. of water with 30.1 grams of sodium hydroxide and 0.656 gram NaF were prepared and maintained at a temperature of about 150° F. Varying amounts of chelating agents and potassium dichromate were added to separate portions of this solution and the amount of precipitate which was produced after 18 hours was measured. Any considerable amount of precipitate would indicate that the chelating agent was ineffective.

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then rinsed with cold water and dried. The following table sets forth the concentration of the chelant and the etchant effect obtained on the aluminum alloys.

### TABLE III

<table>
<thead>
<tr>
<th>Surface Modifier Agent</th>
<th>Concentration</th>
<th>Etched Finish</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grams/liter</td>
<td>Percent of NaOH</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>0.67</td>
<td>3.25</td>
</tr>
<tr>
<td>Diethylene Glycol</td>
<td>0.67</td>
<td>3.25</td>
</tr>
<tr>
<td>Ethylene-diamine tetra-acetic acid</td>
<td>0.67</td>
<td>3.25</td>
</tr>
<tr>
<td>Pianacetic Acid</td>
<td>0.67</td>
<td>3.25</td>
</tr>
<tr>
<td>Tannic Acid</td>
<td>0.45</td>
<td>2.2</td>
</tr>
<tr>
<td>Sodium Chromate Gluconate</td>
<td>0.45</td>
<td>2.2</td>
</tr>
<tr>
<td>Dithiooxamidone</td>
<td>0.67</td>
<td>2.2</td>
</tr>
<tr>
<td>Sorbose</td>
<td>0.45</td>
<td>2.2</td>
</tr>
<tr>
<td>Do</td>
<td>1.125</td>
<td>3.5</td>
</tr>
<tr>
<td>Sorbic Acid</td>
<td>0.45</td>
<td>2.2</td>
</tr>
<tr>
<td>Do</td>
<td>1.125</td>
<td>5.5</td>
</tr>
<tr>
<td>Maltitol</td>
<td>0.45</td>
<td>2.2</td>
</tr>
<tr>
<td>Do</td>
<td>1.125</td>
<td>5.5</td>
</tr>
<tr>
<td>d-Glucoronoacetone</td>
<td>0.45</td>
<td>2.2</td>
</tr>
<tr>
<td>Do</td>
<td>1.125</td>
<td>5.5</td>
</tr>
<tr>
<td>L-ascorbic acid</td>
<td>0.45</td>
<td>2.2</td>
</tr>
<tr>
<td>Do</td>
<td>1.125</td>
<td>5.5</td>
</tr>
<tr>
<td>Do</td>
<td>1.125</td>
<td>5.5</td>
</tr>
</tbody>
</table>

While the above chelating agents were effective in producing the desired silver matte-etched, non-reflecting finish on aluminum and aluminum alloys in combination with fluorides and hexavalent chromium ion, other chelating agents such as tartaric acid, citric acid, sodium gluconate, gluconic acid, sodium a-heptoglucconate, and sodium b-heptoglucconate were ineffective in producing the desired etched finish. Organic detergents were generally ineffective in producing the desired finish although a 1% solution of sodium tetrabromophenathrele sulfonate gave a somewhat improved architectural finish whereas a 5% solution of the same material was ineffective. A 2% by weight solution of sodium oxalate gave borderline results whereas a sodium oxalate solution at a concentration of 5% by weight of the caustic soda gave a total elimination of the desired architectural finish. A 1% solution of Sorbitol P, a 65% alkyl naphthalene sulfonate material gave a somewhat desired architectural finish but not of the degree of modification that was desired. Organic phosphate esters at a concentration of 1% sold under the trademarks GAFAC-RM 710 and Vicita Wet 12 gave a modified finish which was somewhat improved but was not of the acceptable non-reflecting, matte-etch finish. Naxonate G (a sodium xylenesulfonate detergent) at a concentration of 1% of the alkali metal hydroxide concentration gave a somewhat improved finish but not of the desired level.

### Example V

High purity aluminum sheets were cleaned in an alkaline cleaner, rinsed with cold water, deoxidized, rinsed again in cold water and then placed in an etching solution prepared from three ounces per gallon of a solid concentrate containing 91.7% potassium hydroxide, 3.0% potassium dichromate, 2.3% sorbitol, 2.0% sodium fluoride and 1.0% sorbose. The aluminum panels were placed in this etching solution at 165° F. for above seven minutes. After removal they were rinsed in cold water, desmutted in a 50% by volume nitric acid solution, rinsed again with cold water, dried and the etch finish was observed. The surface was of a frosty white matte-etched finish with a fine imposed square grain. There were excellent hide characteristics.

### Example VI

The above run was repeated except that the etching solution was made from a granular concentrate containing 46.7 grams of potassium hydroxide, 45.0 grams of sodium hydroxide, 2.0 grams of potassium dichromate, 2.3 grams of sorbitol, 2.0 grams of sodium fluoride and 1.0 gram of sorbose. The etched finish produced by this solution prepared in the manner described in the preceding run was quite satisfactory.

### Example VII

Aluminum sheets of the same type as described in Example V were immersed in an etching solution prepared by dissolving three ounces per gallon of a solid granular concentrate containing 29.0 grams per liter of potassium hydroxide, 0.675 gram per liter of potassium dichromate, 0.52 gram per liter of sorbitol, 0.45 gram per liter of sodium fluoride and 0.23 gram per liter of sorbose. After etching in this solution for seven minutes at about 170° F., a good architectural finish of the matte-etched type was obtained.

### Example VIII

Sheets of aluminum alloy 6063 and 3003 were prepared for etching by cleaning them in a 6 ounce per gal-
Ion aqueous solution of a concentrate containing 70% borax, 25% tetrasodium pyrophosphate and 10% inorganic detergent at 165° F. for six minutes. After cleaning, rinsing and drying the aluminum sheets were then placed in etchant solutions prepared from various sources of fluoride ion. The etchant solution comprised 20.7 grams per liter of sodium hydroxide, 0.24 gram per liter of chromium ion, 0.7 gram per liter of sorbitol and fluoride compounds as given to approximately 0.2 gram fluoride per liter:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Etched Finish</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium dichromate, 55%; Sodium fluoride, 33%; Sorbitol, 12%</td>
<td>Frosty, white, matte-etched finish with very fine grain and good hide.</td>
</tr>
<tr>
<td>Potassium dichromate, 26.8%; Sodium fluoride, 13.2%; Sorbitol, 5.9%; Sodium sulfate, 39.5%</td>
<td>Frosty, white, matte-etched finish with fine grain and good hide.</td>
</tr>
<tr>
<td>Potassium dichromate, 60.6%; Sodium fluoride, 38.4%; Sorbitol, 1%</td>
<td>Frosty, white, matte-etched finish with faint grain and very good hide.</td>
</tr>
<tr>
<td>Potassium dichromate, 25.6%; Sodium fluoride, 16.7%; Sorbitol, 8.9%; Sodium sulfate, 36.8%</td>
<td>Frosty, white, matte-etched finish with very fine grain and good hide.</td>
</tr>
</tbody>
</table>

I claim:
1. The aqueous solution consisting essentially of alkaline metal hydroxide, water soluble hexavalent chromium ion, water soluble fluoride ion, and at least one surface modifying agent selected from the group consisting of mannnitol, ascorbic acid, sorbose, sorbitol, tannic acid, ethylenediaminetetraacetic acid, sodium chrom glucosate, d-glycolic acid, picolinic acid, aspartic acid, dithiooxamide, d-glyconolactone, and L-rhamnose in which the alkaline metal hydroxide concentration is within the range of 20% to 45% of the alkaline metal hydroxide concentration, in which the water soluble fluoride ion concentration is within the range of 13 to 60 grams per liter in which the water soluble hexavalent chromium ion concentration is within the range of 0.2 to 4.5% of the alkaline metal fluoride concentration, in which the water soluble chromium ion concentration is within the range of 0.04% to 2% of the alkaline metal hydroxide concentration, and in which the concentration of the said surface modifying agent is at least the sum of 100% of the water soluble chromium ion concentration to 2% of the alkaline metal hydroxide concentration.
2. The aqueous solution for etching aluminum and aluminum alloys consisting essentially of alkaline metal hydroxide, water soluble hexavalent chromium ion, water soluble fluoride ion, and at least one surface modifying agent selected from the group consisting of mannnitol, ascorbic acid, sorbose, sorbitol, tannic acid, ethylenediaminetetraacetic acid, sodium chrom glucosate, d-glycolic acid, picolinic acid, aspartic acid, dithiooxamide, d-glyconolactone, and L-rhamnose in which the alkaline metal hydroxide concentration is within the range of 20 to 28 grams per liter in which the water soluble hexavalent chromium ion concentration is within the range of 0.2 to 0.32 gram per liter in which the water soluble fluoride ion concentration is within the range of 0.2 to 0.5 gram per liter, in which the concentration of the said surface modifying agent is at least within the range of 0.6 to 0.9 gram per liter.
3. The aqueous solution for etching aluminum and aluminum alloys consisting essentially of alkaline metal hydroxide, water soluble hexavalent chromium ion, water soluble fluoride ion, and at least one surface modifying agent selected from the group consisting of mannnitol, ascorbic acid, sorbose, sorbitol, tannic acid, ethylenediaminetetraacetic acid, sodium chrom glucosate, d-glycolic acid, picolinic acid, aspartic acid, dithiooxamide, d-glyconolactone, and L-rhamnose in which the alkaline metal hydroxide concentration is 20.7 grams per liter, the water soluble hexavalent chromium ion concentration is 0.24 gram per liter, in which the water soluble fluoride ion concentration is 0.2 gram per liter, and in which the concentration of the said surface modifying agent is at least within the range of 0.6 to 0.9 gram per liter.
4. The solid granular composition capable of forming the aqueous etching solution of claim 1 consisting essentially of alkaline metal hydroxide, water soluble fluoride, water soluble hexavalent chromium, and at least one water soluble surface modifying agent selected from the group consisting of mannnitol, ascorbic acid, sorbose, sorbitol, tannic acid, ethylenediaminetetraacetic acid, sodium chrom glucosate, d-glycolic acid, picolinic acid, aspartic acid, and d-glyconolactone.

Example IX
Aluminum alloy panels of the 6063 type were prepared for etching in the manner described in Example VIII. Separate panels were then placed in solution prepared by dissolving 20.7 grams per liter of sodium hydroxide, 0.7 gram per liter of sorbitol and 0.45 gram per liter of sodium fluoride. To this solution separate portions of various chromium compounds from the following group were added individually to the solutions to provide chromium ion having a content of 0.24 gram per liter. After etching for seven minutes at 155° F. the aluminum panels were removed from the etching solution, rinsed in water, desmutted in a conventional desmutting solution, rinsed with water and dried. The chromium compounds used individually in the etching solutions were chromium acetate, chromium bromide, chromium nitrate, chromium oxalate, and chromium sulfate. The aluminum panels from each etchant solution were of a frosty, white, matte-etched finish having excellent hide characteristics.

Example X
Four ounces per gallon of water of each of the following solid granular compositions were tested for their ability to produce the new architectural etched finish:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Etched Finish</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium hydroxide 97.1%; potassium dichromate 0.006%; sodium fluoride 0.009% and sorbitol 2.675%</td>
<td>Frosty, white, matte-etched finish with very fine grain and good hide.</td>
</tr>
<tr>
<td>Sodium hydroxide 7.786%; potassium dichromate 9.800%; sodium fluoride 3.474% and sorbitol 8.933%</td>
<td>Frosty, white, matte-etched finish with fine grain and good hide.</td>
</tr>
</tbody>
</table>

Panels of aluminum alloy 6063 which had been cleaned in alkaline solution, de-oxygenized, rinsed and dried were immersed in the etchant solutions at 165° F. for eight minutes. The first solution produced panels with a moderately frosty, white-etched finish with uniformly imposed fine grain. The finish had good hide characteristics. The second composition also produced a fine architectural etched finish.

Example XI
Three ounces of each of the following solid granular concentrates were added to different one gallon portions of water to form four different etching solutions. In each solution the sodium hydroxide concentration was 20.7 grams per liter and the sorbitol concentration was 0.24 gram per liter. Cleared sections of 6063 aluminum extrusions were etched in these solutions at 195° F. during a seven minute etching period. The results appear in Table IV.
I-rhamnose, in which composition the alkali metal hydroxide concentration is within the range of 80 to 97.5%, in which the water soluble hexavalent chromium concentration is within the range of 0.002 to 4.0%, in which the water soluble fluoride concentration is within the range of 0.004 to 2.0%, and in which composition the concentration of the said water soluble surface modifying agent is within the range of 2 to 10%.

5. The solid granular composition capable of forming an aqueous etching solution as described in claim 1, consisting essentially of sodium hydroxide 91.7%, potassium dichromate 3.0%, sorbitol 2.3%, aqueous sorbitol (70%) 1.0%, and sodium fluoride 2%.

6. The solid granular concentrate for adding to aqueous alkali metal hydroxide solutions to form the etching solution of claim 1, consisting essentially of water soluble hexavalent chromium containing salts—6 to 12%, water soluble fluorides—6 to 12%, at least one surface modifying agent selected from the group consisting of mannanol, ascorbic acid, sorbose, sorbitol, tannic acid, ethylenediaminetetraacetic acid, sodium chromogluco side, diglyceroic acid, picolinic acid, aspartic acid, dithiooxamide, d-glucosylfuctose, and l-rhamnose—6 to 16%, and an inert filler—40-60%.

7. Solid granular concentrate for adding to aqueous alkali metal hydroxide solutions to form the etching solution of claim 1, consisting essentially of potassium dichromate—25%, sodium fluoride—16.7%, sorbitol—8.3%, and an inert filler—50% by weight.

8. Solid granular concentrate for adding to aqueous alkali metal hydroxide solutions to form the etching solutions of claim 1, consisting essentially of potassium dichromate—60%, sodium fluoride—33%, and sorbitol—17%.

References Cited by the Examiner

UNITED STATES PATENTS
2,687,346 8/1954 McDonald 252—142 X
2,817,612 12/1957 Brennan 252—156 X
2,882,134 4/1959 Spring et al. 156—22 X
2,931,778 4/1960 Ikeda et al. 252—156
2,939,772 6/1960 Newman et al. 156—21

OTHER REFERENCES

LEON D. ROSDOL, Primary Examiner.
ALBERT T. MEYERS, SAMUEL H. BLECH, Examiners.
S. E. DARDEN, Assistant Examiner.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,314,890

Harold Vernon Smith

April 18, 1967

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 40, after "than" insert -- about --; column 6, line 25, for "the" read -- to --; column 7, TABLE II, first column, line 4 thereof, for "9.90" read -- 0.90 --; second column, line 4 thereof, for "9.407" read -- 0.407 --; fourth column, line 4 thereof, for "Fosty" read -- Frosty --; same TABLE II, fourth column, line 5 thereof, for "gralning" read -- graining --; same column 7, line 54, for "0.326" read -- 0.0326 --; column 8, line 38, for "aluminum" read -- aluminum --; line 61, for "17G" read -- 17% --; column 13, line 26, for "hydroxide" read -- hydroxide --.

Signed and sealed this 7th day of November 1967.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents