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PROCESS FOR ALUMINUM ETCHING

Samuel Spring, Philadelphia County, and Robert Houston Elliott, Jr., Oreland, Pa., assignors to Pennsalt Chemicals Corporation, a corporation of Pennsylvania

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This invention relates to anti-scaling compositions for use in alkaline etching baths and to the utilization of such anti-scaling compositions in the etching of aluminum and aluminum base alloys.

The conventional industrial practice in etching aluminum and aluminum base alloys is to treat the surface of the article to be etched with a hot aqueous solution containing an etching alkali such as sodium hydroxide, potassium hydroxide, sodium carbonate, trisodium phosphate, and the like, or with mixtures of these materials. The aluminum reacts with the alkaline etching materials, and where sodium hydroxide is used as the etchant, a solution of sodium aluminate is formed. However, when the concentration of alkali in the etching bath is reduced below a certain value, the sodium aluminate in the solution reacts with water and the end result of this reaction is the formation of a hard scale which is deposited on the sides and bottom of the tank containing the etchant and on heating coils or other equipment which may be submerged within the tank. This scale is primarily alumina, having the formula

$$Al_2O_3.3H_2O$$

It has heretofore been proposed to add various materials to alkaline etching baths to prevent or decrease the formation of scale during the etching process. Among the materials heretofore tried and found to be unsuitable for this purpose was the tetrasodium salt of ethylene diamine-tetraacetic acid. It has now been discovered that, even though the tetrasodium salt of diamine-tetraacetic acid is ineffective when used alone for this purpose, if this salt or othere alkali metal salt of ethylene diamine-tetraacetic acid is used in combination with tartaric acid, or alkali metal salt thereof, in certain relative proportions, the presence of these materials in a caustic etching solution for the etching or cleaning of aluminum will prevent the formation of the hard aluminum oxide scale heretofore referred to. The presence of the diamine-tetraacetic acid and tartaric acid will also prevent the formation of any appreciable aluminum containing sludge. The prevention of sludge formation is as important as at prevention of initial scale formation for practical purposes since it has been noted that the sludge after a period of time is converted into the same hard objectionable scale.

This scale and sludge prevention by the presence of tartaric acid together with the ethylene diamine-tetraacetic acid is indeed surprising when it is considered that not only is ethylene diamine-tetraacetic acid or alkali metal salt of the same ineffective when used alone but it also slightly increases the scale formation. Furthermore, tartaric acid or its alkali metal salts when used alone in the proportions used in the present application are ineffective for preventing this scale formation. This is well illustrated by the following table. In this table, Additive A is the tetrasodium salt of ethylene diamine-tetraacetic acid and Additive B is sodium tartrate.

TABLE 1

Caustic (NaOH, 97%) (grams)	Aluminum (2S) (grams dissolved)	Additive (grams)	Scale Formation
30.0	10		no scale.
30.0	12		scale.
30.0	14		Do.
30.0	18		Do.
30.0	18.0	A—1.0	Do.
30.0	18.0	A—5.0	Do.
30.0	18.0	A—0.03, B—1.5	Do.
30.0	18.0	A—0.06, B—1.5	no scale.
30.0	18.0	A—0.14, B—1.5	Do.
30.0	18.0	A—.1, B—2.0	Do.
30.0	18.0	A—.2, B—2.0	Do.
30.0	18.0	A—.5, B—2.0	scale.
30.0	18.0	B—1.5	Do.
30.0	18.0	B—2.0	Do.

It will be observed from the foregoing data that each of the Additives A and B is ineffective alone at the concentrations employed. Additive B, sodium tartrate, does have some anti-scaling properties at higher concentrations, i.e., concentrations of 10% and higher, but is not effective at the low concentrations employed in the compositions of the invention. It will also be observed that the concentrations of the Additive A must be within narrow limits or else the formation of scale is not prevented. However, within the limits disclosed, the compositions of the invention completely prevent the formation of the undesirable alumina scale.

Of course, if the ethylene diamine-tetraacetic acid and the tartaric acid are used, when these materials are added to alkaline etching baths, for example, sodium hydroxide solutions, the ethylene diamine-tetraacetic acid and the tartaric acid are converted to their respective sodium salts. Therefore, in the present specification and claims when the acids of these materials are referred to it will be understood that their alkali metal salts are also included.

In practicing the present invention the ethylene diamine-tetraacetic acid, and the tartaric acid may be mixed together and sold and handled as a separate composition which may be added to the alkaline etching solution when preparing the same or the ethylene diamine-tetraacetic acid, tartaric acid and solid caustic may be blended together and the resulting composition stored and sold for later addition to water when preparing aluminum etching solutions.

In preparing compositions of this type the ethylene diamine-tetraacetic acid and tartaric acid may be mixed in proportions of about 4 to 10% by weight of ethylene diamine-tetraacetic acid and 96 to 90% by weight tartaric acid. These materials should preferably be present in the ratio of at least about 10 parts tartaric acid for each part of ethylene diamine-tetraacetic acid used. If these additives are blended directly with the etching alkali the resulting dry composition would have 95.8 to 89% by weight etching alkali, such as sodium hydroxide, 4 to 10% by weight tartaric acid or a molar equivalent quantity of one of the alkali metal salts thereof, and 0.2 to 1.0% by weight of ethylene diamine-tetraacetic acid or a molar equivalent quantity of one of the alkali metal salts thereof.

Since the amount of the ethylene diamine-tetraacetic acid is somewhat critical, care must be taken not to have in the composition amounts in excess of those described unless other materials are added to the composition

which enable a wider range of the ethylene diamine-tetraacetic acid to be used as hereinafter described.

In the preferred operation of the present invention where the ethylene diamine-tetraacetic acid and tartaric acid are used without the addition of the other materials referred to 5 to 7% by weight of ethylene diamine-tetra-acetic acid are used together with 93 to 95% by weight tartaric acid, and if used in conjunction with the caustic in a dry formulation, the preferred ratios are about 95.0 to 93.0% by weight etching alkali, .3 to .5% ethylene diamine-tetraacetic acid and 4.5 to 6.5% tartaric acid.

In etching aluminum and aluminum base alloys it is generally desirable that the aqueous etching bath have an etching alkali content of 1 to 15% by weight etching alkali and 99.0 to 85% by weight water. In practicing the present invention, if the ethylene diamine-tetraacetic acid and tartaric acid are formulated together as above described without the presence of caustic, the resulting composition when used is added to the caustic alkaline bath in such proportions as to give an etching bath containing 1 to 15% by weight caustic and .042 to 1.65% by weight of the composition of ethylene diamine-tetra-acetic acid and tartaric acid. The resulting bath on a proportionate basis would then have 1 to 15% by weight alkali, and 0.2 to 1.0% ethylene diamine-tetraacetic acid, and 4.0 to 10.0% tartaric acid, the percent ethylene diamine-tetraacetic acid and tartaric acid being based on the weight of alkali present, the remainder being water.

As previously stated, though the ethylene diamine-tetraacetic acid and tartaric acid when used together in the proportions described give excellent results insofar as preventing scale formation is concerned, the amount of ethylene diamine-tetraacetic acid present is quite critical. If too much or too little of this material is employed, scaling will result. This is apparent from the preceding table. As a result the formulation of aluminum etching compositions is somewhat critical since care must be taken to add the correct amount of the ethylene diamine-tetraacetic acid.

It was further discovered that the amount of ethylene diamine-tetraacetic acid present could be substantially increased without scale formation and the beneficial non-scaling results obtained, if a reducing sugar together with a small amount of any of the metal ions of the group calcium, barium, zinc and cadmium were also present with the ethylene diamine-tetraacetic acid and tartaric acid.

Various reducing sugars may be employed in the formulations of the invention, the preferred sugars being the pentose and hexose sugars, such as xylose, fructose, dextrose, arabinose, mannose and galactose. Of these sugars, dextrose is preferred, due to its low cost and availability. Also the metal ion may be added in the form of any of the soluble salts of the metal used, the chloride generally being preferred because of its low cost and availability.

Not only does the addition of these materials enable a wider range of the ethylene diamine-tetraacetic acid to be used but a substantially smaller amount of tartaric acid is necessary. This has definite economic advantages due to the relatively high price of tartaric acid as compared to some of the reducing sugars, such as glucose, fructose, mannose and arabinose.

When the reducing sugar is used with the ethylene diamine-tetraacetic acid and tartaric acid without the presence of any of the ions calcium, barium, zinc and cadmium, the scale preventative properties of the composition are not quite as good as when calcium, barium, zinc or cadmium is present. Thus, an alkali etching bath prepared from distilled water using a composition containing ethylene diamine-tetraacetic acid, tartaric acid and glucose is not as effective in scale prevention as an etching solution made of water having some hardness. If hard water is used that has a calcium ion content in excess of .003%, the scale inhibiting properties of the composition are substantially improved.

In preparing compositions of this type, the ingredients are generally present in the range of 0.1 to 1.0 part ethylene diamine-tetraacetic acid, 1 to 3 parts tartaric acid, and 1 to 5 parts reducing sugar. Where the composition also contains calcium or other ion of the group mentioned in the form of some soluble salt of these ions, the dry anti-scaling compositions of the invention may contain, for example, 1 to 3 parts of tartaric acid or a molar equivalent quantity of the alkali metal salts thereof, 0.1 to 1.2 parts of ethylene diamine-tetraacetic acid or a molar equivalent quantity of the alkali metal salts thereof, 1 to 5 parts of reducing sugar, such as dextrose, and 0.2 to 2 parts of calcium chloride dihydrate or a molar equivalent quantity of a soluble barium, zinc, cadmium or other soluble calcium salt. When using the ethylene diamine-tetraacetic acid or the metal salts in their maximum amounts as expressed by the broad range of limits, it is generally desirable that the minimum amounts of other ingredients not be used.

In the preferred practice of the invention, however, where a reducing sugar is used, the dry composition, without the alkali, generally contains 1 to 2 parts tartaric acid, 0.2 to 0.8 part ethylene diamine-tetraacetic acid, 2 to 4 parts of the reducing sugar, dextrose being preferred, and 0.5 to 1.5 parts of calcium chloride dihydrate or a molar equivalent quantity of a soluble barium, zinc, cadmium or other soluble calcium salt. Percent or parts, both here and throughout the specification and claims, unless specifically indicated as otherwise, means percent or parts by weight. Also, it is clear that where the amount of acid is given, tartaric acid or ethylene diamine-tetraacetic acid, the molar equivalent quantity of the corresponding alkali metal salt thereof is also included.

Dry compositions containing an etching alkali may also be prepared containing, for example, 97.7 to 89% by weight of an etching alkali such as sodium hydroxide, 1 to 3% by weight of tartaric acid, or a molar equivalent quantity of the alkali metal salts thereof, such as sodium tartrate, 0.1 to 1.2% by weight of ethylene diamine-tetraacetic acid, or a molar equivalent quantity of the alkali metal salts thereof, such as the tetrasodium salt, 1 to 5% by weight of a sugar such as dextrose, and 0.2 to 2.0% calcium chloride dihydrate or a molar equivalent quantity of a soluble barium, zinc, cadmium or other soluble calcium salt.

Though good baths can be obtained by operating in these ranges the best results and the preferred operation employes composition containing 96.3 to 91.7% etching alkali, .2 to .8% ethylene diamine-tetraacetic acid, 1 to 2% tartaric acid, 2 to 4% reducing sugar and .5 to 1.5% of calcium chloride dihydrate or its disclosed equivalent. A preferred composition of this type may contain 94% by weight of sodium hydroxide (97% purity), 1.5% by weight of sodium tartrate, 0.5% by weight of the tetrasodium salt of ethylene diamine-tetraacetic acid, 3% by weight of dextrose, and 1% by weight of calcium chloride dihydrate.

Though the presence of the metal ion in compositions of this type where the reducing sugar is employed gives a better bath with respect to scale inhibiting properties, the bath has a somewhat slower etching rate, where calcium or barium are employed the ions of these metals apparently having the effect of slowing down the etching rate as described in copending application Ser. No. 492,769, filed March 7, 1955, of Robert Elliott, Jr. In many cases this slower rate is desirable. However, where a somewhat faster etching rate is required, the etching rate can be increased by the addition of small amounts of trisodium phosphate or other alkali metal salt of orthophosphoric acid, as also described in the heretofore mentioned application. The trisodium or equivalent alkali metal phosphate, such for example as tripotassium phosphate, should, however, not be present in amounts in ex-

ess of the molar equivalent amounts of the calcium, barium, zinc or cadmium present.

It will be noted that alkali metal carbonates and the alkali metal phosphates of orthophosphoric acid have been included among the etching alkalis. The formulations containing the calcium or other metals of the group calcium, barium, zinc and cadmium should not be used where the etching alkali contains a substantial amount of carbonate or alkali metal salt of orthophosphoric acid since these alkalis react with the calcium, barium, zinc or cadmium precipitating them from the etching solution, thus removing their effectiveness.

The invention will be further illustrated by reference to the following specific examples:

Example 1

A series of tests was performed in which a series of sodium hydroxide aluminum etching baths was prepared from distilled water, each having a volume of 600 ml. of water and containing 30 grams of sodium hydroxide (97% purity), 0.5 gram of sodium tartrate, 0.2 gram of the tetrasodium salt of ethylene diamine-tetraacetic acid, 1 gram of dextrose, and severally containing the indicated quantity of the compounds shown in the table below. The baths were then heated to a temperature of 150° to 170° F. and 18 grams of aluminum were dissolved in each bath.

After the desired amount of aluminum was dissolved, the etching solutions were allowed to cool, and observations of scale formation were made during the succeeding 18 hours. In those cases where scale formation was pronounced, scale was formed even before the solutions cooled, while in other cases a substantial period of time, i.e., several hours, was required. The criterion for an efficacious product in this case is the complete absence of scale, as any anti-scaling additive which permitted even a slight formation of scale would be undesirable in commercial practice, due to the fact that etching baths are operated continuously and the scale would be continuously deposited, thereby necessitating equipment shutdowns for the removal thereof.

The cation forming compounds added and the results of the tests are as follows:

TABLE 2

Compound	Grams	Scale Formation
Sodium chloride	0.2	scale.
Do	0.5	Do.
Do	1.0	Do.
Do	0.19	Do.
Magnesium chloride	0.32	Do.
Strontium chloride	0.42	no scale.
Barium chloride	0.1	Do.
Calcium chloride	0.22	Do.
Do	0.3	Do.
Do	0.5	Do.
Do	0.7	Do.
Do	1.0	scale.
Do	0.3	no scale.
Calcium hydroxide	0.3	Do.
Calcium nitrate	0.4	Do.
Barium nitrate	0.3	Do.
Zinc chloride	0.4	Do.
Cadmium chloride		

Example 2

A sodium hydroxide aluminum etching bath having a volume of 600 ml. was prepared from 8 grain hard water (approximately .004% calcium ions) and contained 30 grams of sodium hydroxide (97% purity), 17 grams of dissolved aluminum, 0.5 gram of sodium tartrate, 0.2 gram of the tetrasodium salt of ethylene diamine-tetraacetic acid, and 1 gram of dextrose. This solution was prepared in accordance with the procedure of Example 1 above, and no scale was observed during the 18 hour observation period.

Example 3

A series of tests was performed following the procedure of Example 1 above, using baths having a volume of 600 ml. of water and containing 30 grams of sodium hydroxide (97% purity), 0.5 gram of sodium tartrate, 1 gram of dextrose, 0.3 gram of calcium chloride dihydrate, and the quantities indicated in the table below of the tetrasodium salt of ethylene diamine-tetraacetic acid.

TABLE 3

Quantity (grams)	Scale Formation
0.01	scale.
0.1	no scale.
0.3	Do.
0.5	scale.

Example 4

A series of tests was performed in which a series of sodium hydroxide aluminum etching baths was prepared, each having a volume of 600 ml. of water and containing 30 grams of sodium hydroxide (97% purity), 0.5 gram of sodium tartrate, 0.2 gram of the tetrasodium salt of ethylene diamine-tetraacetic acid, 0.22 gram of calcium chloride dihydrate, and severally containing the indicated quantity of the sugar shown in the table below. The baths were then heated to a temperature of 150 to 170° F. and the indicated quantity of aluminum was dissolved in each bath.

The aluminum was added according to the procedure of Example 1 above, and observations of scale formation were made in accordance with the procedure therein described.

The results of the tests are as follows:

TABLE 4

Compound	Grams	Grams Aluminum Dissolved	Scale Formation
Xylose	1	18.0	no scale.
Fructose	1	18.0	Do.
Dextrose	1	18.0	Do.
Arabinose	1	18.0	Do.

A further modification of the ethylene diamine-tetraacetic acid and tartaric acid composition, which enables a substantial reduction in the tartaric acid used may be made by adding a small amount of materials of the general class consisting of ascorbic acid, tannin, saponin, hydroquinone, polyhydric alcohols having the formula

$$CH_2OH(CHOH)_nCH_2OH$$

in which n is at least 3, polyhydric monobasic acids having the formula

$$COOH(CHOH)_nCH_2OH$$

in which n is at least 3, and polyhydric dibasic acids having the formula

$$COOH(CHOH)_nCOOH$$

in which n is at least 3. Instead of the above-identified acids, molar equivalent quantities of alkali metal salts thereof may also be employed. Among the preferred compounds within the above general formulas are mannitol and sorbitol as the polyhydric alcohols, gluconic and arabinic acids as the monobasic acids, and mucic and saccharic acids as the dibasic acid.

Many of these materials have heretofore been used or suggested for use in aluminum etchant compositions for

preventing scale formation. However, in the present application of these materials, they are used in amounts substantially less than would be required to be effective if used alone. Thus for example, if the material to be added to the ethylene diamine-tetraacetic acid composition is gluconic acid, a composition containing .2% ethylene diamine-tetraacetic acid, as little as 1.5% tartaric acid and not more than 0.4% gluconic acid all based on the sodium hydroxide when added to a 5% NaOH etching bath gives excellent scale inhibition. This would be equivalent to a caustic etching solution containing 30 grams NaOH, 0.06 gram ethylene diamine-tetraacetic acid, 0.45 gram tartaric acid and 0.12 gram gluconic acid. However, if the gluconic acid is used alone, at least 0.6% gluconic acid based on the sodium hydroxide must be added to prevent the formation of substantial amounts of sludge or scale.

With respect to these particular compositions, it is found that the addition of calcium or other metal of the group calcium, barium, zinc and cadmium has apparently no beneficial effect insofar as assisting in scale inhibition. In fact when soluble salts of these metals are in the alkali etching bath together with the monobasic acids, such as gluconic acid, in amounts greater than the stoichiometric ratio, they may even cause scale formation to occur. Thus, for example, if 0.2% by weight of calcium chloride based on the sodium hydroxide is added to the above-mentioned ethylene diamine-tetraacetic acid, tartaric acid, gluconic acid formulation, and this is used in an alkali etching bath for aluminum, some scale formation will occur, particularly if the bath is given extensive use.

In practicing the invention, when using a polyhydric alcohol, or polyhydric mono or dibasic acid as above described in combination with the ethylene diamine-tetraacetic acid and tartaric acid, the composition generally contains 0.1 to 1.2 parts ethylene diamine-tetraacetic acid, 1 to 3 parts tartaric acid and 0.2 to 0.8 part of the hydroxy acid or hydroxy alcohol.

When any of the materials ascorbic acid, tannin, saponin and hydroquinone are employed with the ethylene diamine-tetraacetic acid and the tartaric acid, it is generally preferred to use them in somewhat larger amounts, the compositions generally containing 0.1 to 1.2 parts ethylene diamine-tetraacetic acid, 1 to 3 parts tartaric acid, and 0.6 to 3.0 parts of the ascorbic acid, tannin, saponin or hydroquinone or mixtures thereof.

If a dry blend with the alkali is to be prepared, the blend would generally contain from 98.7 to 95.0% alkali, 0.1 to 1.2% ethylene diamine-tetraacetic acid, 1 to 3% tartaric acid and 0.2 to 0.8% of the hydroxy alcohols or acids and 0.6 to 3.0% of the tannin, ascorbic, hydroquinone, or saponin. Though these are the general ranges in which the invention may be practiced, in the preferred practice of the invention, the composition without the caustic would contain ethylene diamine-tetraacetic acid about 0.3 to 0.5 part, tartaric acid about 1 to 2 parts, and the hydroxy alcohol or hydroxy mono or dibasic acids about 0.4 to 0.6 part or tanning, ascorbin acid, hydroquinone or saponin in amounts of about 1.5 to 3.0 parts. For a dry blend with the alkali the composition would then contain approximately 98.3 to 96.9% alkali, 0.3 to 0.5% ethylene diamine-tetraacetic acid, 1 to 2% tartaric acid and 0.4 to 0.6% of the hydroxy alcohol or hydroxy acid or 1.5 to 3.0% of tannin, ascorbic acid, hydroquinone or saponin. Of these additives the preferred materials are gluconic acid, arabonic acid, sorbitol and tannin.

The effectiveness of compositions containing these particular additives is best illustrated by the following table, which also illustrates the scaling produced under the same conditions when operating outside of the given limits. The solutions were prepared using 600 ml. of water and the aluminum was etched at a temperature of 150 to 180° F. until the indicated amount of aluminum had been dissolved. The solutions were then observed for scale after standing 18 hours.

Table 5

Caustic (grams)	Aluminum (grams)	Scale preventative (grams)	Scale Formation
30	18	A {Tartaric acid, 0.6 / Ethylene diamine tetra-acetic acid, 0.12}	scale.
30	18	Gluconic acid, 0.12	scale.
30	18	Gluconic acid, 0.12	No scale.
		A	
30	18	Sorbitol, 0.12	scale.
30	18	Sorbitol, 0.12	No scale.
		A	
30	18	Tannin, 0.6	scale.
30	18	Tannin, 0.6	No scale.
		A	
30	18	Ascorbic acid, 0.3	scale.
30	18	Ascorbic acid, 0.3	No scale.
		A	
30	18	Hydroquinone, 0.3	scale.
30	18	Hydroquinone, 0.3	No scale.
		A	

(In the above table A indicates 0.6 gram tartaric acid and 0.12 gram ethylene diamine-tetraacetic acid.)

In using the etching bath of the present invention, the component parts thereof are mixed together in the proper proportions as above described, and the bath is heated to a temperature between about 120° and 180° F. The etching rate is somewhat slower at the lower temperatures. The aluminum or aluminum base alloy material to be etched is then immersed in the etching bath until the desired degree of etch is obtained. No hard rock-like precipitate is formed from the baths of the present invention, and there is no aluminum sludge formation. The only precipitate observed is a smut-like material formed during the etching process, this smut being made up of iron, silicon, copper or other materials which were present in the aluminum and remained on the surface of the etched article as the aluminum was removed by the etching baths. This smut readily settles to the bottom of the etching tank and can easily be removed at any time.

It is apparent that where an acid additive is mentioned its alkali metal salt in equivalent molar amounts may be used. It is also clear that the acid in the alkaline medium would be converted to the corresponding alkali metal salt. Thus in a sodium hydroxide etching bath the acids would be converted to their sodium salts.

It will be apparent to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof and that the invention includes all such modifications.

Having thus described our invention, we claim:

1. A method of etching aluminum which comprises subjecting the aluminum to the action of an etching solution having a temperature of 120 to 180° F. said etching solution containing a concentration of about 1 to about 15% of an etching alkali selected from the class consisting of sodium and potassium alkalies, about 4% to about 10% by weight, based upon the etching alkali content of the solution, of tartaric acid, and about 0.2 to about 1.0% by weight, based upon the etching alkali content of the solution, of an alkali metal salt of ethylene diamine-tetraacetic acid.

2. A method of etching aluminum which comprises subjecting the aluminum to the action of a hot aqueous etching solution containing from 1 to 15% by weight of an etching alkali selected from the class consisting of sodium and potassium alkalies, said etching solution containing, based upon the etching alkali content of the solution, 1.0% to 3.0% of tartaric acid, 0.1% to 1.2% of ethylene diamine-tetraacetic acid, 1.0% to 5.0% of a reducing sugar and a soluble salt of a metal of the group consisting of calcium, barium, zinc and cadmium in amounts equal to the molar equivalent of 0.2% to 2.0% of calcium chloride dihydrate.

3. A method of etching aluminum which comprises subjecting the aluminum to the action of a hot aqueous etching solution containing from 1 to 15% of an etch-

ing alkali selected from the class consisting of the hydroxides, carbonates and triphosphates of an alkali metal from the group consisting of potassium and sodium, said solution containing, based on the etching alkali content of the solution, 1.0 to 3.0% of tartaric acid, 0.1 to 1.2% of ethylene diamine-tetraacetic acid, and further containing small amounts of a modifying agent of the group consisting of reducing sugars, ascorbic acid, tannin, saponin, hydro-quinone, polyhydric alcohols having the formula $CH_2OH(CHOH)_nCH_2OH$ in which n is at least 3, polyhydric monobasic acids having the formula $COOH(CH_2OH)_nCH_2OH$ in which n is at least 3 and polyhydric dibasic acid having the formula

$$COOH(CH_2OH)_nCOOH$$

in which n is at least 3.

4. A method of etching aluminum which comprises subjecting the aluminum to the action of a hot aqueous etching solution containing from 1 to 15% of an etching alkali selected from the class consisting of the hydroxides, carbonates and triphosphates of an alkali metal from the group consisting of potassium and sodium, said solution containing, based on the etching alkali content of the solution, 1.0% to 3.0% of tartaric acid, 0.1 to 1.2% of ethylene diamine-tetraacetic acid, and 0.2% to 0.8% of a material of the group consisting of polyhydric alcohols having the general formula

$$CH_2OH(CHOH)_nCH_2OH$$

wherein n is at least 3, polyhydric monobasic acids having the general formula $COOH(CHOH)_nCH_2OH$ wherein n is at least 3, and polyhydric dibasic acids having the general formula $COH(CH_2OH)_nCOOH$ wherein n is at least 3.

5. A method of etching aluminum which comprises subjecting the aluminum to the action of a hot aqueous

etching solution containing from 1 to 15% of an etching alkali selected from the class consisting of the hydroxides, carbonates and triphosphates of an alkali metal from the group consisting of potassium and sodium, said solution containing, based on the etching alkali content of the solution, 1.0 to 3.0% of tartaric acid, 0.1 to 1.2% of ethylene diamine-tetraacetic acid, and 0.6% to 3.0% of a material of the group consisting of ascorbic acid, tannin, saponin and hydroquinone.

6. A method of etching aluminum which comprises subjecting the aluminum to the action of a hot aqueous etching solution containing from 1 to 15% of an etching alkali selected from the class consisting of sodium and potassium alkalies, and also containing, based on the etching alkali content of the solution, 1.0 to 3.0% by weight of tartaric acid, 0.1 to 1.0% by weight of ethylene diamine-tetraacetic acid, and 1.0 to 5.0% by weight of a reducing sugar.

7. A method of etching aluminum which comprises subjecting the aluminum to the action of a hot aqueous etching solution containing from 1 to 15% by weight of an etching alkali selected from the class consisting of sodium and potassium alkalies and also containing, based upon the etching alkali content of the solution, 1 to 3% of tartaric acid, .1 to 1.0% of ethylene diamine-tetraacetic acid, 1 to 5% of dextrose, and .13 to 4.1% of calcium ions.

References Cited in the file of this patent

UNITED STATES PATENTS

2,584,017	Dvorkovitz et al.	Jan. 29, 1952
2,650,875	Dvorkovitz et al.	Sept. 1, 1953

OTHER REFERENCES

Versenes Tech. Bulletin No. 2, Bersworth Chemical Co., Framington, Mass., February 1952, Sec. 2, p. 35.