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ETCHING ALUMINUM USING HEXAHYDROXYHEPTANOIC ACID AS A MODIFIER

Walter R. Meyer, Hamden, Conn., assignor to
Enthone, Incorporated, New Haven, Conn., a
corporation of Connecticut

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This invention relates to a process of etching of aluminum, to solutions useful in the process, and to compositions adapted for the preparation of the aluminum-etching solutions.

Aluminum has been etched industrially by strongly alkaline solutions. Although a solution of sodium hydroxide initially has etched aluminum at a rapid rate and in a generally satisfactory manner, such good performance has not been prolonged. Such a solution has developed a murkiness attributable to the gelatinous aluminum hydroxide, and the reaction rate has gradually diminished until the solution has been unsatisfactory for etching aluminum. Hence, it has been necessary heretofore to discard sodium hydroxide solutions after use as aluminum etching baths for a relatively short time. It has been possible to calculate the amount of aluminum which should have been dissolved on the basis of the quantity of sodium hydroxide or other alkaline material employed in preparing the etching bath. The efficiency of a solution has been determined by comparing the amount of aluminum in fact dissolved with the amount theoretically dissolved. Concentrated alkaline solutions have heretofore been very inefficient for dissolving aluminum. It has been necessary heretofore to discard aluminum etching solutions containing significant amounts of residual alkali. Analysis of a discarded solution for residual alkali has provided a convenient means of evaluating its efficiency. One of the several disadvantages of using sodium hydroxide solutions for industrially etching aluminum has been the extreme wastefulness of alkali, together with the labor and other expenses related to frequent replacement of the etching bath.

The murky etching baths have also been troublesome because of their tendency to deposit aluminum hydroxide in an adherent form onto the heating coils, drainage pipes, etching vats, and other surfaces contacting the solution. It has been necessary to chip off such deposits periodically, thus increasing the expense of the industrial etching of aluminum. Sludges of aluminum hydroxide have sometimes formed in the etching vats, thus increasing the labor and expense of disposing of the bath.

Difficulty has also arisen because under some conditions the action of an alkaline solution upon an aluminum article has been uneven and irregular. In using murky alkaline baths the aluminum hydroxide has tended to deposit as a partially protective film upon the aluminum article. Sometimes the effectiveness of the aluminum hydroxide thus deposited upon certain

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spots on the aluminum article has been sufficient to completely inhibit etching action at such spots, and partial inhibition at some spots has occurred even more frequently. In order to obtain an adequate etching of the entire article, it has been necessary to conduct the etching operation for a prolonged period of time, controlled by the zone most completely inhibited by the aluminum hydroxide adhering to the article. The slime adhering to the etched aluminum has been troublesome. Rinse water alkaline enough to dissolve the slime has merely prolonged the etching. Rinse water of a lower pH has precipitated the slime in a more adherent state. Sprays providing powerful jets of water were sometimes employed to rinse etched aluminum articles.

An important object of the present invention is to provide an aluminum etching bath useful for dissolving more nearly the theoretical amount of aluminum indicated by its alkaline content. It is also an object to provide a process of etching aluminum whereby all portions of the surface of aluminum articles are etched evenly and uniformly. Further objects of the present invention are to provide a process for etching aluminum more rapidly than has heretofore been attainable, and particularly for providing an etching bath adapted to etch at a nearly uniform rate from its initial use until its alkaline reserve is nearly exhausted. The elimination of most problems related to the deposition of residual sludges, slimes and/or solids upon the apparatus employed in etching aluminum constitute a further object of the invention. The provision of a process whereby the waste liquors are readily disposed of is also an object and feature of the present invention. A process requiring a simplified rinsing procedure is also an object of the invention.

These and other objects are achieved by the use of an aluminum-etching process employing an alkaline solution containing a salt of hexahydroxyheptanoic acid. Such a solution is prepared by adding a composition to water. The composition of the present invention is a mixture of solids and consists generally of from 75% to 99% of an alkaline material, from 0.05% to 15% of soluble salt of hexahydroxyheptanoic acid, and, if desired, from 0.1% to 5% of a wetting agent such as sodium 2-ethylhexyl sulfate and, optionally, from 0.1% to 20% of sodium fluoride or other soluble fluoride salt. A composition having the proportions indicated is added to water to form a solution containing from 0.5% to 35% of said concentrate. Thus the concentration of alkaline substance in the aluminum-etching so-

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lution is within the range of from approximately 0.1 to 9 normal, which corresponds to approximately from $\frac{1}{2}$ to 48 ounces per gallon. The alkaline material should be present in a concentration to provide a pH greater than 10.

The alkaline material should desirably be chosen from the group consisting of sodium hydroxide, trisodium phosphate, sodium carbonate, borax, potassium hydroxide, tripotassium phosphate, potassium carbonate, and potassium bo-

rate. Mixtures of two or more of the alkaline reagents can be used, or other alkaline substances equivalent to these materials can be employed.

It is believed that the action of the soluble fluoride salt is that of aiding in the prevention of the formation of an inhibiting film upon the aluminum article. The fluoride ion accelerates the etching rate, possibly by speeding the rate at which the dissolved aluminum leaves the zone of the metallic surface. The solubility of fluoride ion in alkaline solutions is very limited, but is somewhat greater in alkaline solutions containing certain anions such as the phosphate ion than in the absence of such cooperating anions. The amount of fluoride salt employed is limited by the solubility limit of the fluoride in the maximum concentration intended for the composition, or inversely, no composition is ordinarily employed at a concentration high enough to precipitate any of its components. In order to obtain the fastest etching, the concentration of fluoride should desirably but not necessarily be high enough to be close to the room temperature solubility limit thereof in relatively concentrated solutions of the composition.

Hexahydroxyheptanoic acid can be prepared by the hydrolysis of glucosecyanohydrin, which is prepared by reacting hydrogen cyanide with glucose.

The action of the salt of hexahydroxyheptanoic acid in the process is believed to be that of maintaining the dissolved aluminum in a relatively non-adherent condition. One of the many benefits is that of minimizing the formation of an inhibiting film of aluminate on the article being etched. The concentration of the hexahydroxyheptanate salt relative to the alkaline material employed must be such as to amount to at least 0.05% of the composition used in making the etching solution. Ordinarily it is desirable to use approximately 1% of the hexahydroxyheptanate salt. It was found that large amounts of the hexahydroxyheptanate salt could be dissolved in the alkaline solutions, but that increasing amounts did not provide increasing benefits for the aluminum-etching process and that excess hexahydroxyheptanate was harmful. The use of quantities greater than 15% of the hexahydroxyheptanate salt adversely affected the viscosity, foaming characteristics, etc. of the solution as to make such concentrates commercially unsatisfactory.

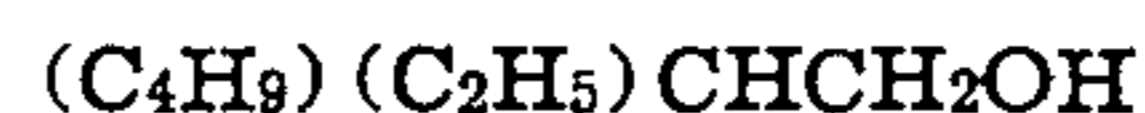
In the development of the present invention numerous substances were tested in an effort to find an equivalent for a salt of hexahydroxyheptanoic acid in the aluminum-etching process. The theory was developed that the modifying agent inhibited the formation of gels or even large colloidal sized particles of dissolved aluminum, and kept the aluminum in solution as anions or as tiny colloidal particles or in some variety of coordination complex. Neither heptanoic acid nor mannitol was operable, so it was concluded that neither the carboxylic acid group

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nor the several hydroxy groups were alone effective in coagulating the aluminum hydroxide in a non-adherent form. Tartaric acid, malic acid, lactic acid, salicylic acid, citric acid, glycolic acid, and other hydroxy carboxylic acids were all found to be inoperative in aluminum etching. Numerous other modifiers deemed likely to solubilize the aluminum hydroxide in a non-adherent form were tested and proven inoperative from a commercial standpoint, although some had detectable effectiveness. In the development of the present invention, it was clearly established that the peculiarities affecting aluminum etching were such that no prediction could be made concerning the action of a class of compounds on the basis of structure, and that only proven experimental results could determine whether or not a specific compound could function in a commercially operable etching solution.

In application Serial No. 341,329 filed simultaneously herewith by the same inventor, it is explained that saccharic acid is commercially effective in coagulating the aluminum hydroxide in a non-adherent state.

Examples of suitable wetting agents include: the sodium salts of 2-ethylhexyl acid sulfate, also designated as $(C_4H_9)(C_2H_5)CHCH_2SO_4Na$, and sold as Tergitol 08; naphthalene sulfonic acid, also designated as $C_{10}H_7SO_3Na$; and tolyl sulfonic acid, also designated as $H_3CC_6H_4SO_3Na$. The wetting agent is desirably stable in hot alkaline solutions. Branched chain alcohols such as 2-ethylhexanol, also designated as



water insoluble alcohols such as decanol, and/or other antifoam agents, are desirably included in the wetting agent formulation.

In carrying out the process of the present invention the aluminum article to be etched is first subjected to a cleaning operation to remove any exceptionally adherent organic material. Organic contaminants such as light lubricating oil are desirably but not necessarily cleaned prior to the etching operation.

The solution is prepared in accordance with the requirements previously outlined, and is then heated to a temperature between 60° and 190° F. By the use of a higher temperature, the time of etching is reduced. The temperature is desirably maintained at approximately 160° F. for optimum industrial efficiency.

The aluminum article to be etched is subjected to the solution for a period of from 5 seconds to one hour, depending upon the temperature, the concentration of fluoride, the concentration of hexahydroxyheptanate, the degree of etching desired, the type of aluminum alloy being treated, the type of alkaline substance employed, the concentration of alkaline substance, and related factors. For ordinary industrial etching of aluminum a period of from about 5 to 60 seconds is usually sufficient. Although it is ordinarily desirable to immerse the aluminum article in the solution, the operation can be conducted by spraying the solution onto the article, or by other techniques.

After the aluminum article has been subjected to the solution for the required period of time, the aluminum article is thoroughly rinsed in order to remove any residue from the article. This rinsing operation may be conducted either with ordinary rinse water or with a solution containing additional surface-treating reagents such as

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phosphoric acid. By reason of the presence of the hexahydroxyheptanate in the etching solution, the etched article does not have an adherent slime, but only a thin layer of clear liquid which is readily removed by the rinse water.

Hydrogen is evolved by the etching action and tends to agitate the etching solution. The escaping hydrogen can create a spray or mist of the solution, and eventually can bring about a loss of some of the solution as spray. Moreover, the escaping hydrogen creates a fire hazard warranting ventilation of the etching tank. One of the purposes of utilizing a wetting agent such as Tergitol 08, either alone or in combination with a branched chain alcohol, is to provide a foam on top of the solution having the stability characteristic which minimize the fire hazard and spray loss problems of the operation.

The specific examples next to be referred to are merely for purposes of illustration of ways in which the invention may be practiced.

Example 1

A concentrate consisting of sodium hydroxide, sodium hexahydroxyheptanate and Tergitol 08, was prepared by mixing:

	Grams
NaOH	97
$\text{HOCH}_2(\text{CHOH})_5\text{CO}_2\text{Na}$	1
$\text{C}_7\text{H}_{15}\text{CH}_2\text{SO}_4\text{Na}$	1

A solution might be prepared consisting of water and 0.5% of said concentrate. This solution might be heated to 190° F. and employed for etching a cleaned aluminum article during a period of 20 seconds. After rinsing, the article would be satisfactorily etched.

A solution was prepared consisting of water and 3% of said concentrate. The solution was heated to 160° F. and aluminum articles were satisfactorily etched by a 5-second treatment.

A solution was prepared consisting of water and 35% of said concentrate. Aluminum articles were satisfactorily etched by said solution at room temperature by a 10-second treatment.

Example 2

A concentrate might be prepared consisting of:

	Grams
NaOH	88
NaF	10
$\text{HOCH}_2(\text{CHOH})_5\text{CO}_2\text{Na}$	1
$\text{C}_7\text{H}_{15}\text{CH}_2\text{SO}_4\text{Na}$	1

A solution could be prepared consisting of water and 3% of said concentrate. A 5-second treatment at 160° F. would provide a deeper etching of aluminum articles than could be obtained with slower solutions containing no sodium fluoride.

Example 3

A concentrate consisting of sodium carbonate, sodium fluoride, sodium hexahydroxyheptanate, and sodium naphthyl sulfonate, could be prepared by mixing:

	Grams
Na_2CO_3	98
NaF	0.1
$\text{HOCH}_2(\text{CHOH})_5\text{CO}_2\text{Na}$	1
$\text{C}_{10}\text{H}_7\text{SO}_3\text{Na}$	0.9

A solution could be prepared consisting of water and 6% of said concentrate. The solution, when heated to 160° F., would be a relatively slow-acting etching solution, requiring approximately one minute for a typical etching operation.

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Example 4

A concentrate consisting of trisodium phosphate, sodium fluoride, sodium hexahydroxyheptanate and sodium tolyl sulfonate could be prepared by mixing:

	Grams
Na_3PO_4	75
NaF	20
$\text{HOCH}_2(\text{CHOH})_5\text{CO}_2\text{Na}$	4
$\text{H}_3\text{CC}_6\text{H}_4\text{SO}_3\text{Na}$	1

An excess of said concentrate could be mixed with water, the portion exceeding the solubility limit of the concentrate remaining as a residue in the bottom of the etching vat. The solution would be an effective etching solution for aluminum at room temperature.

Example 5

A concentrate consisting of potassium hydroxide, potassium carbonate, tripotassium phosphate, borax, potassium fluoride, potassium hexahydroxyheptanate, and sodium benzene sulfonate could be prepared by mixing:

	Grams
KOH	20
K_2CO_3	20
K_3PO_4	20
$\text{Na}_2\text{B}_4\text{O}_7$	20
KF	3
$\text{HOCH}_2(\text{CHOH})_5\text{CO}_2\text{K}$	15
$\text{C}_6\text{H}_5\text{SO}_3\text{Na}$	2

A solution consisting of water and 3% of said concentrate, when heated to 160° F., would be an effective etching solution for aluminum articles.

Example 6

A composition similar to that of Example 5, but containing only 0.1% potassium hexahydroxyheptanate, and 23.5% of each alkaline substance, and 3.4% potassium fluoride would, when used to prepare a 3% solution at 160° F., provide effective etching of aluminum.

Each of the etching solutions described in Examples 1 to 6 has numerous advantages over aluminum etching solutions heretofore employed, such as solutions containing only sodium hydroxide. The aluminum hydroxide and/or sodium aluminate is kept in solution in a non-adherent form, simplifying waste removal, eliminating deposits on heating coils, etc. The solutions of the present invention continue to be effective in etching until considerable depletion of the alkali. Solutions of pH 10 or lower are unsatisfactory for industrial etching of aluminum, and the solutions of the present invention remain effective as this lower limit is approached. Thus the solutions of the present invention do not require the waste of large amounts of alkali, as was necessary in the use of sodium hydroxide etching solutions, which sometimes ceased etching even though the alkali concentration was of the magnitude of 0.5 normal.

The above examples illustrate preferred embodiments of the invention, but are merely illustrative thereof, the invention being defined in the appended claims.

What I claim is:

1. An aluminum-etching composition for making with water an aluminum-etching solution comprising a mixture of 75% to 99% alkaline substance, and 0.05% to 15% soluble salt of hexahydroxyheptanoic acid.

2. An aluminum-etching composition for making with water an aluminum-etching solution

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comprising a mixture of 75% to 99% alkaline substance chosen from the class consisting of the hydroxides, carbonates, phosphates, and borates of potassium and sodium and mixtures thereof, and 0.05% to 15% soluble salt of hexahydroxyheptanoic acid.

3. An aluminum-etching composition for making with water an aluminum-etching solution comprising a mixture of 75% to 99% alkaline substance, 0.1% to 20% soluble fluoride salt, a wetting agent, and 0.05% to 15% soluble salt of hexahydroxyheptanoic acid.

4. An aluminum-etching composition for making with water an aluminum-etching solution comprising a mixture of 75% to 99% alkaline substance, 0.1% to 20% soluble fluoride salt, a salt of 2-ethylhexyl sulfate, and 0.05% to 15% soluble salt of hexahydroxyheptanoic acid.

5. The composition of claim 1 in which the concentration of the salt of hexahydroxyheptanoic acid is approximately 1%.

6. An aluminum-etching solution consisting

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of water and from 0.5% to 35% by weight of the composition of claim 1.

7. An aluminum-etching solution consisting of water and approximately 3% by weight of the composition of claim 1.

8. An aluminum-etching solution consisting of water and approximately 20% by weight of the composition of claim 1.

9. The process of etching a metal article consisting principally of aluminum which includes the steps of cleaning the article, preparing the solution of claim 6, heating said solution to a temperature between 60° and 190° F., subjecting the article to said solution for a period from 5 to 3600 seconds, and rinsing residual solution from the article.

WALTER R. MEYER.

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