

1

2,942,955

ALUMINUM ETCHING COMPOSITION AND METHOD

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No Drawing. Filed May 20, 1957, Ser. No. 660,094

9 Claims. (Cl. 41—42)

This invention relates to compositions for etching aluminum and aluminum base alloys and more particularly to a scale inhibited aluminum etching composition containing an etching rate accelerator.

The term "aluminum" as used herein and in the claims embraces aluminum and aluminum base alloys including the usual impurities found in aluminum ingot of commercial grade or such impurities as are picked up in the course of the usual handling operations incident to ordinary melting practice. The alloys are well known and include, for example, the wrought, sand casting, permanent mold casting, and die casting aluminum alloys. Extruded aluminum also falls within the scope of the definition of aluminum. The various alloying elements employed in such alloys include copper, magnesium, silicon, manganese and zinc. In some special purpose alloys nickel, tin, lead and bismuth are added as alloying elements.

It is well known in the art that aluminum and aluminum base alloys can be readily etched by either strong acids or strong alkaline solutions. The acid or the alkali reacts with the aluminum and removes a fraction of its surface, generating hydrogen and forming an aluminum salt. An alkaline etch solution, being more convenient and easier to control, is usually preferred to an acid type etching bath. My invention is concerned with the alkaline-type etching baths.

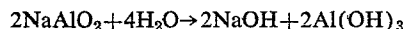
The usual industrial practice in etching an aluminum article is to subject the article to a hot aqueous solution containing an etching alkali such as sodium hydroxide, potassium hydroxide, trisodium phosphate, sodium carbonate, or similar materials or mixtures of these materials in varying proportions. Sodium hydroxide in aqueous solution is the most commonly employed agent, and it reacts with the aluminum as it dissolves or etches the same to yield sodium aluminate and hydrogen, according to the equation:



Although caustic etching of aluminum has generally been employed, it is found that it is not entirely satisfactory because of certain inherent disadvantages. One of the more important of these disadvantages is the formation of a precipitate which deposits as a hard, adherent, rock-like scale on the walls and bottom of the etching tank, on any heating units disposed within the etching tank and in varying degrees on the aluminum articles themselves. Removal of this scale from the reaction vessel is found to be extremely difficult. Chemical removal, as by means of acid, subjects the reaction vessel to corrosive conditions which tend to shorten the life of the etching tank. Generally this scale is removed by mechanical means such as chipping it off with hammers or other tools. Mechanical techniques for removing the scale not only involve expensive labor costs but also can often result in damage to the equipment. This scale is formed when the concentration of the alkali is reduced by

2

the reaction of the alkali with the aluminum article. As the concentration of the alkali decreases the concentration of the sodium aluminate increases. When the molar ratio concentration of aluminum oxide to sodium oxide approaches a ratio of 1:1, a hydrolysis reaction occurs that is a reversion of the original process and the sodium hydroxide consumed is again recovered or regenerated and aluminum hydroxide is precipitated according to the equation:



The aluminum hydroxide is in the form of a gelatinous precipitate which upon standing changes in form to precipitate various hydrated forms of alumina. It is this alumina which forms the hard rock-like scale. Workers in the art have been successful in finding compositions of matter which when added to a caustic aluminum etching bath suppress and delay scale formation in varying degrees and when present in sufficient quantities prevent hard scale altogether. These scale depressing additives are referred to as chelating agents, complexing agents, inhibitors, sequestering agents or stabilizing agents. Lindsay et al. U.S. 2,345,134 (1944) in disclosing a process for preparing a stabilized form of sodium aluminate sets forth that organic polyhydroxy compounds such as Rochelle salts, tartaric acid and its salts, saccharates, gluconic acid and its salts, gallic acid and its salts, pyrogalllic acid and its salts, sugar, invert sugar, dextrin, starch, glycerols, glycols, phenols or phenolates and gelatin can be used to stabilize sodium aluminate so that the aluminate will not react with water to precipitate aluminum hydroxide even upon long standing. Dvorkovitz et al. U.S. 2,650,875 (1953) discloses that water-soluble, saturated, aliphatic polyhydroxy compounds such as sorbitol, corn starch, lactose, glycose, gluconic acid, mucic acid and gum arabic, can be used in a caustic aluminum etching bath to prevent the reversion of sodium aluminate to sodium hydroxide and alumina. Other well known scale inhibitors include monosaccharides, polysaccharides, starches, and naturally occurring gums.

Although the problem of scale formation in the alkaline etching of aluminum has been mitigated by the addition of certain organic polyhydroxy scale inhibitors, this has resulted in a problem not encountered heretofore. It has been found that when certain organic polyhydroxy inhibitors are used in the alkaline etching bath a considerable retardation of the etching rate occurs. In the presence of calcium ions, as would be the case where hard water is used, this retardation of the etching rate is even more pronounced. This is highly undesirable for commercial etching because this impedance of the etching rate increases the cost and time of the etching operation.

It is, therefore, an object of my invention to etch aluminum or aluminum base alloys at an accelerated rate which was not possible heretofore with alkaline solutions containing certain organic polyhydroxy scale inhibitors.

I have found that I can avoid the deleterious effect which certain organic polyhydroxy scale inhibitors have on the rate at which alkaline solutions etch aluminum or aluminum base alloys by adding to the scale inhibited alkaline etching bath an etching rate accelerator.

I have now discovered that an alkali metal chromate selected from the group consisting of sodium chromate, potassium chromate and mixtures thereof has the property of increasing the rate at which certain scale inhibited alkaline solutions etch aluminum or aluminum base alloys.

In accordance with one aspect of this invention, the metal surfaces containing aluminum or aluminum base alloys may be treated with aqueous solutions of alkaline etching agents containing a scale inhibiting agent and an etching rate accelerator. Typical alkaline etching agents

are those which may be selected from the group consisting of sodium hydroxide, potassium hydroxide, trisodium phosphate, and mixtures thereof. In general, the preferred scale inhibiting agents are saturated aliphatic, polyhydroxy, organic compounds such as monosaccharides, polysaccharides, polyhydric alcohols, monobasic and dibasic polyhydric alcohols and naturally occurring gums.

I have also found that a product, which may be prepared according to the process set forth in U.S. Patent 2,563,014 and which is marketed by the Corn Products Refining Company under the trade name of "Polyose," is also useful as a scale inhibitor. This product, a synthetic polysaccharide, is prepared by (1) dehydrating a starch conversion syrup to isolate the solid material and (2) heating the isolated solid under conditions conducive to polymerization. The aluminum etching rate accelerator is an alkali metal chromate selected from the group of sodium chromate and potassium chromate and mixtures thereof. A preferred form of the alkali metal chromate is sodium chromate.

In accordance with certain of its other aspects, this invention comprises new compositions of matter which may be employed in aqueous etching baths to treat aluminum or aluminum-containing surfaces. These compositions contain from 75 to 97.5 weight percent of an alkaline etching agent typical of which is one selected from the group consisting of sodium hydroxide, potassium hydroxide, trisodium phosphate, and mixtures thereof, a scale inhibiting agent in the amount of 1 to 20%, an etching rate accelerator in the amount of .25 to 5 weight percent and a dust inhibiting agent in the amount of approximately 1 weight percent which may take the form of a hydrocarbon solvent suitable of which is kerosene. The scale inhibiting agents useful in the compositions of this invention include, in general, saturated, aliphatic, polyhydroxy, organic compounds. The etching rate accelerator is an alkali metal chromate, selected from the group consisting of sodium chromate, potassium chromate and mixtures thereof. The preferred form of the alkali metal chromate is sodium chromate.

The compositions of this invention may be formed by mixing the scale inhibiting agent, etching rate accelerator and dust inhibitor with an alkaline etching agent and then dissolving the composition so formed in water so as to make up an aqueous etching bath. However, each of the components of the composition may be added separately to water and in this manner form an aqueous etching solution.

The alkaline materials which are applicable in the compositions and processes of my invention include sodium hydroxide, potassium hydroxide, trisodium phosphate, borax, tripotassium phosphate, and potassium borate. Mixtures of two or more of the alkaline reagents can be used, or other alkaline substances equivalent to these materials can be employed.

The scale inhibitors which are applicable in the compositions and processes of my invention include, generally, saturated organic polyhydroxy compounds. Examples of these scale inhibitors include, but are not limited to, the following: Rochelle salts, tartaric acid and its salts, saccharates, gluconic acid and its salts, gallic acid and its salts, pyrogalllic acid and its salts, sugar, lactose, invert sugar, dextrin, starch, glycerols, glycols, phenols and phenolates, gelatin, monosaccharides, polysaccharides, synthetic polysaccharide and the like. Mixtures of two or more of these scale inhibitors can be used, or other substances equivalent to these materials can be employed.

The etching rate accelerators which are applicable in the compositions and processes of my invention include alkali metal chromates selected from the group consisting of sodium chromate and potassium chromate. Mixtures of sodium chromate and potassium chromate can also be used. I have found that trivalent chromium salts, when

used initially in the compositions and methods of my invention, do not provide the same advantageous features as the hexavalent chromium salts. However, when the hexavalent chromium salts are employed in alkaline etching solutions containing certain scale inhibiting, reducing sugars, the chromium is reduced from the hexavalent state to the trivalent state. I have noted that this transition of the chromium, from the hexavalent to the trivalent state, does not adversely affect the property possessed by the chromium of increasing the rate at which certain scale inhibited alkaline solutions etch aluminum or aluminum base alloys. It has also been found that the rate of etch can be accelerated by the use of orthophosphate type compounds. However, the addition of the orthophosphate type compound has an adverse effect on the anti-scaling additive so that hard scale again tends to form when the tank becomes concentrated with dissolved aluminum.

In general, the compositions of my invention are useful over a wide temperature range. Alkaline etching solutions containing a scale inhibiting agent and an etching rate accelerator of my invention are preferably employed at elevated temperatures in order to etch the aluminum, and good results are obtained at temperatures varying from 70 to 210° F. Preferred temperatures, however, are in the range of 140 to 180° F. The aluminum article to be etched is subjected to the etching solution for a time period which is dependent upon the degree of etch desired and the temperature of the etching solution.

Aqueous etching solutions are prepared by adding the compositions of my invention to water. The composition of the present invention is a mixture of solids and consists generally of from 75 to 97.5 weight percent of an alkaline material, from 1 to 20 weight percent of an organic polyhydroxy scale inhibitor, and from .25 to 5.0 weight percent of an alkali metal chromate selected from the group consisting of sodium chromate, potassium chromate and mixtures thereof. A dust inhibitor such as kerosene is usually added to the extent of about 1%. An alkaline etching product having the proportions indicated is added to water to form an etching solution containing from about 2 to about 8 ounces of said product per gallon of water. Preferred concentrations, however, are in the range of 4 to 6 ounces of said product per gallon of water. When it is desired to carry out an etching process known commercially as chemical milling, then the compositions of my invention are employed in the range of 8-16 ounces of product per gallon of water and the temperature is in the range of 180-210° F. The alkaline material should be present in a concentration to provide a pH greater than 10.

In carrying out the process of the present invention the aluminum article to be etched is first subjected to a cleaning operation in order to remove any organic material or foreign matter on the surface of the aluminum. This step is preferably carried out by subjecting the aluminum article to either a dilute acid or dilute alkaline solution. Chlorinated hydrocarbons are also suitable cleaning agents.

The etching solution is prepared in accordance with the requirements previously outlined, and is then heated to the desired temperature which is generally in the range of 70 to 190° F. By the use of higher temperatures the time of etching is reduced. The most desirable temperature for optimum industrial efficiency falls within the range of 140 to 160° F.

The aluminum article to be etched is subject to the etching solution for a period of from 5 seconds to 30 minutes, depending upon the temperature, the concentration of the solute, the degree of etching desired, the type of aluminum alloy being treated, the type of alkaline substance employed and related factors. For ordinary

Industrial etching of aluminum a period of from about 30 seconds to 15 minutes is usually sufficient. Although it is ordinarily desirable to immerse the aluminum article in the etching solution, the etching operation can be carried out by spraying the solution on the article or by other techniques. During the etching of the aluminum article by a solution of caustic soda, for example, the aluminum is dissolved but certain alloying elements in the aluminum are insoluble in the caustic soda and remain on the surface of the aluminum. The insoluble alloying elements form dark oxide films on the surface and these oxide films are known in the trade as smut.

After the aluminum article has been subjected to the etching solution for the required period of time, the aluminum article is thoroughly rinsed in order to remove any residual alkali. This rinsing operation is usually carried out with ordinary rinse water. Subsequent to the rinsing operation, the aluminum article is subjected to a desmutting operation which ordinarily consists in dipping the aluminum article in an acid bath to remove the insoluble oxide film. The aluminum article is thus prepared for final treatment which can consist of putting a protective adherent oxide coating on the aluminum article by well known anodizing techniques.

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

EXAMPLE I

Two scale inhibited alkaline etching compositions were prepared, one with sodium chromate and the other without sodium chromate, in order to compare the rates at which aqueous solutions of these alkaline compositions would etch aluminum. The composition containing sodium chromate, composition A of Table I, consisted of 95.5 parts by weight of sodium hydroxide, 1 part by weight of tartaric acid, 2 parts by weight of lactose, 1 part by weight of kerosene and 0.5 part by weight of sodium chromate. The composition without sodium chromate, composition B of Table I, consisted of 96 parts by weight of sodium hydroxide, 1 part by weight of tartaric acid, 2 parts by weight of lactose and 1 part by weight of kerosene. These compositions were added to water in varying amounts at a temperature of 160° F. so as to prepare aqueous etching solutions having solute concentrations of 4 ounces per gallon, 8 ounces per gallon, 12 ounces per gallon and 16 ounces per gallon. A sufficient quantity of aluminum was added to the 8, 12 and 16 ounces per gallon solutions so as to produce etching solutions in which there were 4 ounces per gallon free sodium hydroxide. The rates at which each of these compositions etched the aluminum samples are set forth in Table I.

Several aluminum samples which were to be used in determining the rate at which the alkaline solution would etch aluminum were made up as follows: 3" x 5/8" strips of aluminum foil were cut from commercially pure aluminum foil which is sold by the Reynolds Aluminum Company for the retail market and which is marketed as Reynolds Wrap Pure Aluminum Foil. The aluminum foil strip was attached to an ordinary microscope glass slide by means of a rubber band. These slides were then placed in an etching solution which was to be tested. The time was recorded when the slides were placed in the etching bath and the time was recorded when all the aluminum was dissolved by the etching solution. If the solution was too cloudy to determine at which time all of the aluminum was consumed, then the time was recorded upon the cessation of gas bubbles, this being indicative of the fact that all the aluminum was consumed.

Table I

	A Parts by weight	B Parts by weight
Sodium hydroxide.....	95.5	96.0
Tartaric acid.....	1.0	1.0
Lactose.....	2.0	2.0
Kerosene.....	1.0	1.0
Sodium chromate.....	0.5	-----
	Etching Time in Minutes	
Concentration:		
4 oz./gal.....	2.1	4.5
8 oz./gal. (theoretical aluminum added).....	1.5	3.1
12 oz./gal. (theoretical aluminum added).....	1.7	2.3
16 oz./gal. (theoretical aluminum added).....	2.0	2.7

The etching times set forth in the table for the various concentrations are the average of three runs. It will be noted from the table that the etching rate was considerably increased when sodium chromate was present. The time of etching the aluminum sample was reduced by one-half when the scale inhibited caustic soda etching composition containing sodium chromate was added to water to the extent of 8 ounces per gallon. This was a significant improvement over the etching compositions of the prior art which contained primarily caustic soda and an organic polyhydroxy scale inhibitor.

EXAMPLE II

Aluminum samples prepared in accordance with the procedure set forth in Example I were used to determine the rate at which alkaline scale inhibited compositions C and D would etch aluminum. Composition C, set forth in Table II, consisted of 93.5 parts by weight of sodium hydroxide, 5.0 parts by weight of lactose, 1.0 part by weight of kerosene and 0.5 parts by weight of sodium chromate. Composition D, set forth in Table II, consisted of 94.0 parts by weight of sodium hydroxide, 5.0 parts by weight of lactose and 1.0 part by weight of kerosene. These compositions were added to water in varying amounts at a temperature of 160° F. so as to prepare aqueous etching solutions having solute concentrations of 4 ounces per gallon, 8 ounces per gallon and 12 ounces per gallon. A sufficient quantity of aluminum was added to the 8 and 12 ounces per gallon solutions so as to produce etching solutions in which there were 4 ounces per gallon free sodium hydroxide. The rates at which each of these aqueous alkaline compositions etched the aluminum samples are set forth in Table II.

Table II

	C Parts by weight	D Parts by weight
Sodium hydroxide.....	93.5	94.0
Lactose.....	5.0	5.0
Kerosene.....	1.0	1.0
Sodium chromate.....	0.5	-----
	Etching Time in Minutes	
Concentration:		
4 oz./gal.....	2.2	4.1
8 oz./gal. (theoretical aluminum added).....	1.5	2.4
12 oz./gal. (theoretical aluminum added).....	1.8	2.0

The etching rate of caustic soda in the presence of lactose as the scale inhibitor is markedly improved by the addition of sodium chromate as will be noted from the etching times set forth in Table II. Although the most significant increase in the rate of etch occurred at a concentration of 8 ounces per gallon, considerable im-

provement in the rate was also obtained at 4 and 12 ounces per gallon. These results represent a marked improvement over etching time of the scale inhibited caustic soda etching compositions of the prior art.

What is claimed is:

1. A composition for etching aluminum and aluminum base alloys which comprises an alkaline etching agent selected from the group consisting of sodium hydroxide, potassium hydroxide and mixtures thereof, an organic polyhydroxy scale inhibitor and an etching rate accelerator selected from the group consisting of sodium chromate, potassium chromate and mixtures thereof, said alkaline etching agent being in the proportion of about 75 to 97.5 weight percent, said organic polyhydroxy scale inhibitor being from about 1 to 20 weight percent, and said etching rate accelerator being from about .25 to 5.0 weight percent.

2. A composition in accordance with claim 1 wherein the alkaline etching agent is in the proportion of about 90 to 98 weight percent, the organic polyhydroxy scale inhibitor being from about 2 to 9.5 weight percent and the etching rate accelerator being from about .5 to 3 weight percent.

3. A composition in accordance with claim 1 wherein the alkaline etching agent is sodium hydroxide.

4. A composition in accordance with claim 1 wherein the organic polyhydroxy scale inhibitor is a member selected from the group consisting of tartaric acid, lactose and mixtures thereof.

5. An alkaline bath for etching aluminum and aluminum base alloys which comprises an aqueous solution of an alkaline etching product, said alkaline etching product consisting essentially of about 75 to 97.5 weight percent of an alkaline etching agent selected from the group consisting of sodium hydroxide, potassium hydroxide and mixtures thereof, about 1 to 20 weight percent of an organic polyhydroxy scale inhibitor and about 0.25 to 5.0 weight percent of an etching rate accelerator selected from the group consisting of sodium chromate, potassium chromate and mixtures thereof and wherein the concentration of the alkaline etching product is in the range of about 2 to 16 ounces per gallon of water.

6. An alkaline bath in accordance with claim 5 wherein the alkaline etching agent is in the proportion of 90 to 97.5 weight percent, the organic polyhydroxy scale inhibitor being from 2 to 9.5 weight percent, the etching rate accelerator being from 0.5 to 3.0 weight percent and wherein the concentration of the alkaline etching

product is in the range of about 2 to about 8 ounces per gallon of water.

7. A process for etching aluminum which comprises contacting an article of aluminum with an aqueous solution of an alkaline etching product, said alkaline etching product comprising about 75 to 97.5 weight percent of an alkaline etching agent selected from the group consisting of sodium hydroxide, potassium hydroxide and mixtures thereof, about 1 to 20 weight percent of an organic polyhydroxy scale inhibitor and about 0.25 to 5.0 weight percent of an etching rate accelerator selected from the group consisting of sodium chromate, potassium chromate and mixtures thereof.

8. A process for etching aluminum which comprises contacting an article of aluminum with an aqueous solution of an alkaline etching product, the concentration of said etching product being in the range of about 2 to about 16 ounces per gallon of water, said etching product consisting essentially of (1) an alkaline etching agent selected from the group consisting of sodium hydroxide, potassium hydroxide, and mixtures thereof and being in the proportion of about 75 to 97.5 weight percent, (2) an organic polyhydroxy scale inhibitor selected from the group consisting of monosaccharides, polysaccharides, gum arabic, gum karaya, starches, synthetic polysaccharides, polyhydroxymonobasic acids, polyhydroxy dibasic acid and mixtures thereof and being in the proportion of about 1 to 20 weight percent and (3) an etching rate accelerator selected from the group consisting of sodium chromate, potassium chromate and mixtures thereof and being in the proportion of about 0.25 to 5 weight percent.

9. A process in accordance with claim 8 wherein the alkaline etching agent is sodium hydroxide, the organic polyhydroxy scale inhibitor is a mixture of tartaric acid and lactose and the etching rate accelerator is sodium chromate, the alkaline etching agent being in the proportion of about 90 to 97.5 weight percent, the scale inhibitor being from about 2 to 9.5 weight percent and the etching rate accelerator being from about 5 to 3 weight percent.

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