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CHEMICAL COMPOSITION AND PROCESS FOR ALUMINUM ETCHING

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This invention relates to the etching of aluminum and aluminum base alloys and more particularly to slow etching compositions and aluminum etching processes employing the same.

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 or potassium hydroxide. The aluminum reacts with the alkaline etching materials and where sodium hydroxide is used as the etchant, a solution of sodium aluminate is formed.

It has heretofore been the practice in the etching of aluminum with caustic baths to add to the caustic etching solution small amounts of certain materials to prevent the formation of hard scale occurring. Unless such materials are added to the alkaline etching solution, the formation of a hard aluminum oxide scale necessitates the periodic shutdown of equipment while this scale is chipped from the inside of the etching tank and from the surface of heating coils and other equipment that may be located therein. In the preferred operation for etching aluminum, it is therefore desirable that some such scale preventative be present in the alkaline etching solution.

In processing aluminum or aluminum base alloys to obtain a cleaned and etched surface, the aluminum is first treated with a caustic etching solution at a temperature of about 110° F. to 200° F. then rinsed in a water bath, and finally desmutted by treating with a solution of nitric acid or immersed in an anodizing bath, such as an aqueous solution of sulfuric acid. Care must be taken not to let the aluminum pieces dry between the caustic etching bath and the rinse in order to avoid staining of the surface. The aluminum pieces which may be in the form of rods, bars, sheets, etc. are frequently 20 or more feet long. These are held in racks and a lift moves the rack successively from the one solution to the next. In conventional practice a single lift is employed to move the racks of aluminum through the successive baths.

If the etching process is too fast the etching is completed before the rinsing and smut removal or anodizing with the result that the aluminum is either over-etched or piles up prior to the rinse or finishing treatment. This results in staining due to the etching solution drying on the aluminum surface.

The reaction between the caustic alkali and the aluminum in the etching bath is exothermic. Also, a rise in the temperature of the etching bath substantially increases the etching rate. Thus a rise from 150° F. to 170° F. will double the etching rate. Because of this, particularly where the etching tanks are relatively small so that there is not a sufficiently large body of etching solution to absorb the heat, difficulty is encountered with the etching rate becoming too rapid and the processing cycle being interfered with as described. Higher temperatures naturally cause more rapid drying of the work between the etch and rinse tanks.

It has now been discovered that the addition, in small amounts, of any of the metal ions of the group consisting of calcium, strontium and barium have a substantial effect on the rate of etching, the presence of any of these ions slowing down the etching rate of the etching solution. Of these strontium is the most effective. Calcium, particularly with solutions of caustic alone, or with caustic etching solutions containing sodium gluconate as a scale inhibitor, will tend to cause scaling to occur before amounts sufficient to have any appreciable effect on the etching rate can be used. However, the calcium can be used satisfactorily with alkali etching solutions containing as a scale inhibitor any of the materials of the group consisting of hydroxy alcohols of the formula $CH_2OH(CHOH)_nCH_2OH$ and dibasic acids of the general formula $COOH(CHOH)_nCOOH$ where n, in each instance, is an integer of 3 to 6. Of these scale inhibitors sorbitol and mannitol are preferred among the hydroxy alcohols and saccharic and mucic acid are preferred among the dibasic hydroxy acids.

As previously stated, the presence of the strontium ion has a substantially greater effect with respect to slowing down the etching rate than the effect produced for equivalent amounts of the barium and calcium ions. However, surprisingly the effectiveness of the barium and calcium ions can be substantially increased by having these two ions together, there apparently being a synergistic action resulting in a greater decrease of the etching rate than can be obtained through use of either alone in the equivalent molar amount used in their combination. However, where the calcium and barium are used together with an alkali etching solution containing sodium gluconate as the scale inhibitor, the effect is no greater than the barium would have if present alone.

The effect of the presence of metal ions of the group consisting of calcium, strontium and barium on the etching rate of a 4% sodium hydroxide aluminum etching solution is well illustrated by the following table:

Additive (to aqueous solution containing 40 grams of caustic)	G.	Aluminum		Rate, Grams removed/ sq. ft./min.
Sorbitol	.4	52 S	(98% Al)	1.81
Sorbitol	.4	52 S		
Magnesium chloride	.4			1.81
Sorbitol	.4	52 S		
Calcium chloride	.3			1.28
Sorbitol	.4	52 S		
Strontium chloride	.1			1.25
Sorbitol	.4	52 S		
Barium chloride	.3			1.40
Sorbitol	.4			
Barium chloride	.2	52 S		1.10
Calcium chloride	.2			
Calcium chloride	.2	52 S		
Mucic acid	.4			1.51
Calcium chloride	.2	52 S		
Gluconic acid	.4			1.72
Strontium chloride	.2	52 S		
Gluconic acid	.4			1.30
Barium chloride	.4	52 S		
Gluconic acid	.4			1.25
Calcium chloride	.2	52 S		
Sorbitol	.4			1.35
Sorbitol	.8	52 S		
Calcium chloride	.8			1.50
Sorbitol	.4	2 S	(99% Al)	1.60
Mucic Acid	.4	2 S		1.70
Sorbitol	.4	2 S		
Calcium chloride	.2			.86
Mucic Acid	.4	2 S		
Calcium chloride	.2			.73

The etching rates in the table were obtained by etching a series of panels 3" x 3" by 1/16" in a 4% sodium hydroxide solution at 150° F. for three minutes. The panels after etching were rinsed in water, desmutted in a nitric acid solution, again rinsed in water and then dried. The panels were weighed before and after this treatment.

In the table and throughout the specification and claims, when percent is given, the percent is percent by weight.

In co-pending application Ser. No. 474,036 inventors

Spring and Elliott, the metal ions calcium and barium are used in alkaline etching solutions in combination with ethylene diamine-tetraacetic acid, tartaric acid and aldehyde sugar for the prevention of scale formation. In the present application, however, the addition of these materials is not for the prevention of scale formation since the metals are used in combination with materials that in and of themselves, in the amounts used, will prevent scale and are not dependent for this action on the presence of the metal ions.

In practicing the present invention, the metal ions may be added in the form of any of their salts and are generally added as chlorides, the chlorides being the least expensive. As previously stated, they are also generally used together with a scale inhibitor. The strontium ion is effective in slowing down the etching rate of an alkaline aluminum etching solution when present in amounts as low as 3.0% of the scale inhibitor used. The strontium ion should not, however, be present in amounts greater than 83.0% of the scale inhibitor. Otherwise, there is a tendency for scale formation to occur. This is particularly true where the etching solution is operated under severe conditions to dissolve large amounts of aluminum. In the preferred practice of the present invention, the strontium ion is generally present in amounts of 4.0 to 33.0% as based on the scale inhibitor. Though the strontium ion is effective in slowing down the etching rate of a caustic bath containing no scale inhibitor, such baths are seldom used due to the tendency for scale formation. When used without a scale inhibitor, the strontium, as based on the caustic, is effective in amounts as low as .03% by weight.

Where the barium ion is employed to slow down the etching rate, it is found to be effective when present in amounts of 14 to 140% of the scale inhibitor used. In the preferred practice of the invention, however, the barium ion is generally used in amounts of 28.0 to 70.0% barium ion as based on the scale inhibitor present.

The calcium ion is found to be effective in slowing down the etching rate when present in amounts of 14.0 to 55.0% of the scale inhibitor used, the preferred amounts being within the range of 20.0 to 34.0% by weight calcium ion as based on the scale inhibitor. However, as previously stated, the scale inhibitor when using calcium should be selected from the group consisting of hydroxy alcohols of the formula $CH_2OH(CHOH)_nCH_2OH$ where n is 3 to 6 and hydroxy dibasic acids of the formula

$$COOH(CHOH)_nCOOH$$

where n is 3 to 6.

As previously stated, a substantially greater effect on the etching rate can be obtained by using the metal ions calcium and barium together than by using either alone. When used in combination, the combination is effective in total concentrations of 14 to 100% of the metal ions, as based on the scale inhibitor. The preferred concentrations are generally within the range of 15 to 70% as based on the scale inhibitor. When used together it is generally preferred that at least 25% of the combined ions be either calcium or barium.

In practicing the present invention, the etching compositions are generally prepared on a dry basis for addition to water in making up the aluminum etching solutions. Where such is the case, the composition would contain along with the etching alkali, sodium hydroxide being preferred, a scale inhibitor for the prevention of scale formation. Several inhibitors of this type are mentioned in the above referred to co-pending application Ser. No. 474,036. The scale inhibitor depending upon its effectiveness may be present in amounts varying from 0.8 to 6.0% based on the etching alkali used. One of the preferred dry formulations using the present invention comprises a mixture of sodium hydroxide, sorbitol and any of the metal ions heretofore mentioned in the preferred ranges indicated. The sorbitol in such a composition would be present in amounts of 1.5 to 4.0% of the sodium hydroxide.

The etching solutions used for the etching of aluminum, in practicing the present invention, generally contain 1 to 15% etching alkali, the preferred concentrations usually being in the order of 2.0 to 8.0% sodium hydroxide.

The following examples will help to better illustrate the practice of the present invention. These examples are given for purposes of illustrations, and the invention is not limited thereto.

Example 1

A mild steel tank was charged with 588 lbs. of sodium hydroxide, 12 lbs. of sorbitol and 2000 gallons of tap water. The solution was heated to 150° F. and then used for the etching of aluminum. In the etching process about 250 sq. ft. of aluminum surface were etched in the tank every 5 minutes. The aluminum articles were immersed in the solution for 5 minutes, after which they were removed and passed on to a water rinse. Additions of caustic soda containing 2% sorbitol were made periodically to maintain the concentration of the etching solution at 5 ozs. of caustic per gallon.

After several hours' operation the temperature of the solution, due to the heat of reaction, had risen from the initial starting temperature of 150° F. to a temperature of 170° F. (No external heat was applied to the solution during the etching process.) At the higher temperature drying occurred during transfer of the etched articles to the rinse tanks. This resulted in undesirable staining of the etched articles. Also, the reaction in the etching tank was so rapid that the hydrogen fumes given off during the etching contained substantial amounts of fine droplets of the etching solution with resulting irritation to workmen.

A fresh etching bath was prepared containing the same amount of caustic, water and sorbitol as the initial bath and differing therefrom only in the addition of 1½ lbs. of strontium chloride. During the etching operation strontium chloride was in the make-up in the same proportions with respect to the caustic and sorbitol in which it was present in the initial charge. The aluminum was passed through the etching bath at the same rate as previously. However, the action of the bath was sufficiently slowed that the temperature remained at about 150° F. throughout the etching operation, and the vapors resulting from the etching process were not nearly as irritating as when the bath was operating at the higher temperature.

Example 2

Aluminum extrusions were etched in a tank containing about 800 gallons of etching solution containing an initial charge of 250 lbs. of caustic soda, 2½ lbs. of sorbitol and approximately 1 lb. of calcium ion. The etching solution was maintained at a concentration of approximately 5 ozs. of caustic per gallon by the periodic addition of fresh amounts of caustic, sorbitol and calcium ion in the same proportions. The time required to obtain a satisfactory etch, when operating the bath at approximately 150° F., was about 8 minutes, the calcium acting to substantially slow down the etching rate.

In the specific examples given the only scale inhibitor illustrated is sorbitol and the only two metal ions illustrated as slowing down the etching rate are the metal ions of strontium and calcium. Other etching solutions containing barium as the metal ion and scale inhibitors other than sorbitol act in a similar manner. It is, therefore, not believed necessary for purpose of illustrating the invention to include still further specific examples containing these materials.

Having thus described my invention, I claim:

1. In the etching of aluminum involving the step of immersing aluminum in an aqueous alkaline etching bath containing from 1% to 15% of etching alkali maintained at a temperature of from 110° to 200° F. and containing from 0.8% to 6%, based on the weight of the etching alkali, of a scale inhibitor effective in preventing alkali

aluminates forming during the etching operation from depositing as a scale, the method of decreasing the etching rate comprising the step of including in said etching bath a metal ion selected from the group consisting of strontium, barium and calcium ions in amounts ranging from 3% to 140% based on the weight of the scale inhibitor.

2. A method in accordance with claim 1 in which the scale inhibitor is selected from the group consisting of polyhydroxy alcohols of the formula

$$CH_2OH(CHOH)_nCH_2OH$$

where n is 3 to 6, and polyhydroxy dibasic acids of the formula $COOH(CHOH)_nCOOH$ wherein n is 3 to 6.

3. A method in accordance with claim 1 in which said metal ion is strontium ion in amounts ranging from 3% to 83% by weight based on the weight of the scale inhibitor.

4. A method in accordance with claim 1 in which said metal ion is barium ion present in amounts ranging from 14% to 140% by weight based on the weight of the scale inhibitor.

5. A method in accordance with claim 1 in which said metal ion is calcium ion present in amounts ranging from 14% to 55% by weight based on the weight of the scale inhibitor.

6. A method in accordance with claim 1 in which said metal ion is a mixture of calcium and barium ions, the total weight of said ions ranging from 14% to 100% by weight based on the weight of the scale inhibitor, each of said ions making up at least 25% of the total weight of the mixture.

7. A composition providing in an aqueous solution a bath for the etching of aluminum consisting essentially of caustic, from 0.8% to 6% by weight, based on the weight of the caustic, of a scale inhibitor effective in preventing alkali aluminates forming during the aluminum etching operation from depositing as a scale, and a metal salt providing ions selected from the group consisting of strontium, calcium and barium ions, effective in decreasing the rate of aluminum etching, said metal salt

being present in amounts sufficient to yield from 3% to 140% by weight of said metal ions based on the weight of said scale inhibitor.

8. A composition in accordance with claim 7 in which said scale inhibitor is selected from the group consisting of polyhydroxy alcohols of the formula

$$CH_2OH(CHOH)_nCH_2OH$$

wherein n is 3 to 6, and polyhydroxy dibasic acids of the formula $COOH(CHOH)_nCOOH$ wherein n is 3 to 6.

9. A composition in accordance with claim 7 in which said metal salt is a salt of strontium yielding from 3% to 83% of strontium ion by weight based on the weight of said scale inhibitor.

10. A composition in accordance with claim 7 in which said metal salt is a salt of barium yielding from 14% to 140% of barium ion by weight based on the weight of said scale inhibitor.

11. A composition in accordance with claim 7 in which said metal salt is a salt of calcium yielding from 14% to 55% of calcium ion by weight based on the weight of said scale inhibitor.

12. A composition in accordance with claim 7 in which said metal salt is a mixture of barium and calcium salts yielding together from 14% to 100% by weight of a mixture of barium and calcium ions, each of said ions making up at least 25% of the total weight of the mixture.

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