

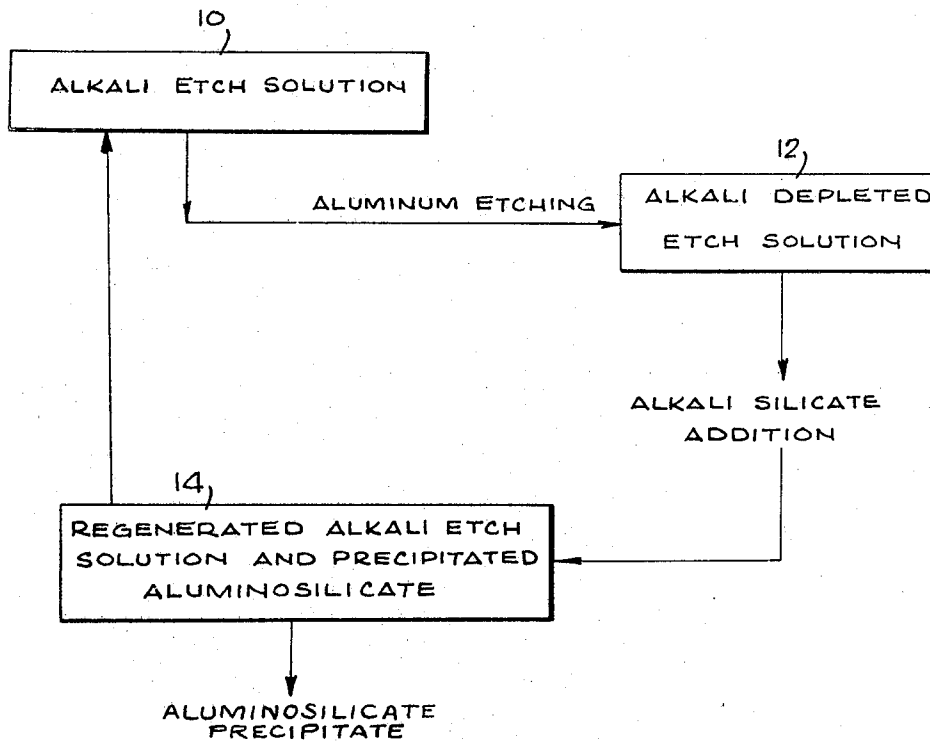
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METHOD FOR ETCHING ALUMINUM

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6 Claims

ABSTRACT OF THE DISCLOSURE

Regeneration of alkali depleted aqueous alkali etching solutions, e.g., sodium hydroxide, and precipitation of aluminate as aluminosilicate by the addition of an alkali metal silicate, e.g., sodium silicate.

This invention relates to a method for etching aluminum, and is more particularly concerned with a procedure for regenerating or rejuvenating solutions employed in the etching of aluminum.

The term "aluminum" as employed herein is intended to denote either substantially pure aluminum or any of the alloys of aluminum.

For the etching of aluminum, particularly to obtain a deep etch, for example, as practiced in the aircraft industry, it is known to employ hot alkali, usually sodium hydroxide, solutions for this purpose, and these solutions may contain additives such as sulfur or sulfur-containing compounds in the form, for example, of sodium polysulfide, to improve the etching operation or the properties of the etched aluminum surface which is produced.

In such etching operations, the alkali, e.g., sodium hydroxide, solution reacts with the aluminum surface to form sodium aluminate in known manner. After a period of etching, a substantial amount of such sodium aluminate is formed in the etching solution, and the alkali content of the solution is materially reduced. These conditions substantially reduce the effectiveness of the alkali etching solution for etching the aluminum surface and also adversely affect the quality of the etch obtained.

In large measure, it has been the practice heretofore to dump or discard spent alkali etching solutions containing substantial amounts of sodium aluminate, and to employ a fresh alkali solution. This practice substantially increases the cost of these operations. However, in order to regenerate such solutions and to overcome the effects of the accumulation of sodium aluminate in aluminum etching solutions and to remove or avoid the formation of excess amounts of sodium aluminate, various prior art procedures have been developed. Thus, for example, in U.S. Patent 2,975,041 spent etching solution containing alkali metal aluminate is cooled in the presence of solid hydrated alumina to precipitate an additional quantity of solid hydrated alumina, to regenerate the solution and increase the alkali metal hydroxide content of the solution, followed by separating the precipitated hydrated alumina. However, this procedure is time consuming and requires a substantial amount of equipment to carry out the procedure. In U.S. Patent 2,650,875, additives such as sodium gluconate are added to the alkali etching solution so as to prevent the reversion of the sodium aluminate to sodium hydroxide and alumina, or by controlling this reversion to produce a non-adherent alumina precipitate. However, to applicant's knowledge, there is lacking in the prior art any teaching of a simple direct inexpensive method in the chemical etching of aluminum employing alkali etching solutions such as sodium hydroxide, for regenerating the spent etching solution by simultaneously readily removing excess amounts of sodium aluminate from and increasing the alkali content of such solution, so as to pro-

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vide an efficient reuseable alkali etching solution for aluminum.

According to the invention, it has been found that alkali etching solutions for aluminum, e.g., caustic soda, can be simply and economically regenerated or rejuvenated by the addition of alkali metal silicate, preferably sodium silicate, to the spent etching solution containing alkali metal, e.g., sodium, aluminate. The sodium silicate reacts with the sodium aluminate to precipitate out the aluminate and to regenerate alkali, to thereby permit reuse of the solution for aluminum etching. The precipitates so formed is an aluminosilicate which tends to agglomerate in the form of small balls that fall to the bottom of the solution and can be removed.

The etching treatment for aluminum is generally carried out in a hot aqueous solution containing an alkali such as sodium or potassium hydroxide, trisodium phosphate, sodium carbonate, or the like, or mixtures thereof. Preferably, aqueous sodium hydroxide solutions are employed. Temperature of the solution during the etching process may range say from about room temperature up to about 212° F. Generally, a hot solution is employed with temperature maintained in the range from about 140° F. to about 210° F. during treatment. The alkali concentration of the etching solution can vary and such concentration may range from about 0.1 to about 10 normal, e.g., in the range from about 1 to about 3 normal.

In order to improve etching results, e.g., for producing etched surfaces which are smooth and fine grained, various additives can be incorporated in the etching solution. Thus, for example, a sulfur-containing additive such as an alkali metal sulfide, e.g., sodium sulfide, an alkali metal polysulfide such as sodium polysulfide, or sulfur can be incorporated in minor amounts, e.g., from about 0.1 to about 40%, by weight of the alkali, to improve the characteristics of the etched aluminum surface as noted above. However, it is understood that such additives are optional and need not be present in the alkali etching solution.

As previously noted, during the etching operation aluminum is dissolved from the aluminum body being etched and forms alkali metal aluminate in solution, e.g., sodium aluminate. As the etching reaction proceeds, the concentration of sodium aluminate progressively increases. The presence of small or moderate concentrations of sodium aluminate in the etching solution does not adversely effect to any appreciable extent the rate of etching or the quality of the etched surface. As a matter of fact, it has been found that it is preferable to maintain the presence of some aluminate in the etching solution during the etching process, provided the amount of such aluminate does not become deleterious from the standpoint of substantially reducing the etching rate or degrading the quality of the etched aluminum surface obtained. Thus, it has been found that the presence of sodium aluminate in small or moderate concentrations, e.g., not greater than about 6 ounces, preferably between about 3 and about 5 ounces, of sodium aluminate calculated as Al_2O_3 , per gallon of solution, is desirable in order to obtain a good high quality etch and to prevent intergranular pitting, "islanding," bad edges, and non-uniform surface of the etch.

Thus, when the amount of alkali metal aluminate, e.g., sodium aluminate, formed during the etching process increases to a point where the quality of the etch is reduced, and/or the etch rate substantially decreases, according to the invention alkali metal silicate, e.g., sodium or potassium silicate, is added to the etching solution, preferably in an amount to precipitate sufficient of the aluminate so as to reduce the alkali aluminate concentration in the etching solution to an amount preferably not greater than about 6 ounces of aluminate, calculated as Al_2O_3 , per

gallon of solution, and more desirably between about 3 and about 5 ounces of such aluminate, calculated as Al_2O_3 , per gallon. For this purpose, the alkali silicate, e.g., sodium silicate, added to the etching solution, is preferably in the form of an aqueous solution such as a solution of water glass, which is a commercially available 37% solution of sodium silicate. In preferred practice, and to produce an aluminosilicate precipitate which does not tend to adhere to the tank walls and which readily drops to the bottom of the tank for easy removal therefrom, relatively dilute sodium silicate solutions are employed, e.g., sodium silicate solutions having a concentration of about 3 to about 10%, e.g., about 5%, sodium silicate. Such solutions can be readily provided by suitably diluting the commercially available 37% water glass (sodium silicate) solution.

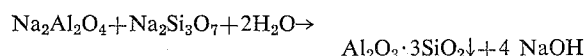
Generally, about 0.1 to about 10 ounces of alkali metal silicate, e.g., sodium silicate, can be employed, per gallon of spent alkali etching solution containing alkali aluminate, and usually about 0.5 to about 2 ounces of such alkali metal silicate is employed, per gallon of spent etch solution. Hence, the aqueous sodium silicate solution preferably employed is utilized in amounts sufficient generally to provide alkali metal, i.e., sodium, silicate in the above ranges. Larger amounts of alkali metal silicate within the above ranges are employed where the amount of aluminate in the solution is relatively large, e.g., substantially above 6 ounces per gallon of aluminate, calculated as Al_2O_3 . Smaller amounts of alkali metal silicate within the above ranges are employed where the amount of aluminate in solution is relatively small, e.g., of the order of about 6 ounces per gallon of aluminate or somewhat lower or higher. It will be understood that the alkali metal silicate can be added at intervals to the alkali etching solution during a period of etching, or the silicate added following a period of etching, to reduce the aluminate concentration and to increase the alkali concentration by regeneration, to desired levels.

The reaction between the aluminate present in the spent alkali etching solution, and the alkali silicate produces a white aluminosilicate precipitate, usually in the form of small diameter balls, e.g., of the order of about $\frac{1}{8}$ inch in diameter, which tend to drop to the bottom of the etching vessel. The exact composition of the aluminosilicate precipitate formed is not known to me, but is believed to be of a complex nature. As an example, a sample of such a complex aluminosilicate precipitated from a spent alkali etching solution according to the invention contained about 44.5% Al_2O_3 , and about 26.3% SiO_2 , the balance being largely water of crystallization. However, it is to be understood that the term "aluminosilicate" employed herein is intended to designate the precipitated reaction product of the reaction of alkali metal, e.g., sodium, aluminate and alkali metal, e.g., sodium, silicate, produced by the addition of such silicate to a spent etching solution containing such aluminate, according to the invention, regardless of the exact chemical composition of such aluminosilicate.

The aluminosilicate precipitate thus formed in the etching solution during regeneration thereof according to the invention can be readily removed by any suitable means, such as by mechanical means, or by centrifuging, or by siphoning out a portion of the spent etching solution containing such aluminosilicate precipitate. Simultaneously with removal of the aluminosilicate precipitate, small amounts of any other precipitate such as copper sulfide, zinc sulfide and magnesium hydroxide which may be formed during the etching process, where the corresponding metals are present, e.g., as alloying constituents in the aluminum being etched, and the etching solution contains a sulfur-bearing additive, such as sulfur per se, can also be removed.

Upon addition of the alkali silicate, e.g., sodium silicate, to the spent alkali etching solution containing sodium aluminate, at least a portion of the alkali, e.g., sodium hydroxide, consumed in the etching reaction is regenerated

simultaneously with production and precipitation of the aluminosilicate. A typical reaction mechanism is set forth below but is not intended as limitative of the invention:



Thus, by the procedure according to the invention, not only is the excess aluminate removed from the solution in the form of aluminosilicate precipitate, but additional alkali is produced to increase the alkali concentration of the spent solution. This permits the regenerated solution to be reused for further chemical etching of aluminum, without addition of fresh alkali, although if desired, some fresh alkali can be added to increase the alkali content to a desired concentration.

It is noteworthy that the addition of alkali silicate, e.g., sodium silicate, to a spent chemical etching solution including the above noted sulfur or sulfur-containing additive such as sulfur, sodium sulfide or sodium polysulfide, does not adversely affect the function of such additives when the regenerated solution is again employed for etching an aluminum body.

The flow diagram shown in the accompanying drawing illustrates the process of the invention whereby an alkali etching solution, indicated at 10, which becomes alkali depleted after a period of aluminum etching, as indicated at 12, is regenerated by addition of alkali silicate which also simultaneously causes precipitation of aluminosilicate, as indicated at 14. The regenerated etch solution is then further used to etch aluminum.

The following are examples of practice of the invention.

EXAMPLE 1

A 7075 aluminum body is etched in a hot alkali etching solution maintained at about 190° F. The initial etching solution has the following composition.

Components:	Ounces per gallon
Sodium hydroxide	21.3
Sulfur	7

The etching reaction takes place for a period of about 30 minutes, after which the etching solution contains a concentration of sodium aluminate equivalent to about 7 ounces Al_2O_3 per gallon of solution and the caustic concentration is reduced to 17.2 ounces of sodium hydroxide per gallon of solution. At this point, the rate of the etching reaction is substantially decreased and the quality of the etch is visibly diminished, e.g., as to smoothness of etch, and other important etch properties noted above.

To the black hot spent etching solution is added 1.2 ounces of sodium silicate, as a 37% sodium silicate solution, commercially available as water glass, per gallon of etching solution. A white precipitate forms in the nature of small balls which drop to the bottom of the etching vessel. Such precipitate is readily removed from the etching tank and the regenerated alkali etching solution is found to contain the following proportions of sodium hydroxide and sodium aluminate:

Components:	Ounces per gallon
Sodium hydroxide	18.6
Sodium aluminate calculated as Al_2O_3	4.43
Specific gravity	1.1932 at 25° C.

It is seen from the above composition of the spent alkali solution treated according to the invention, that the aluminate concentration based on Al_2O_3 is reduced from 7 ounces Al_2O_3 per gallon in the spent alkali solution to 4.43 ounces Al_2O_3 per gallon in the regenerated solution, and the caustic or sodium hydroxide content is increased from 17.2 ounces per gallon in the spent alkali etching solution to 18.6 ounces per gallon in the regenerated solution.

The regenerated alkali etching solution noted above is reused for the etching of additional bodies of 7075 alu-

minum to produce a high quality etched aluminum surface at good etching rates.

EXAMPLE 2

The procedure of Example 1 is carried out except that the 37% solution of sodium silicate employed is diluted seven times so that the concentration of sodium silicate in the silicate solution added to the spent alkali solution is about 5%.

It is observed that the aluminosilicate precipitate formed after addition of the diluted sodium silicate solution to the spent alkali etching solution, more effectively drops to the bottom of the tank and substantially none of such precipitate adheres to the side walls of the tank. Substantially all of the aluminosilicate precipitate, which is located at the bottom of the tank, is readily removed leaving practically no residue of aluminosilicate scale on the tank walls.

EXAMPLE 3

Pieces of 2024 and 7075 aluminum are etched in a hot aqueous sodium hydroxide etching solution at about 185° F. until the alkali content of the solution is reduced to 15.6 ounces sodium hydroxide per gallon of solution and the alkali aluminate content has reached about 9 ounces of sodium aluminate, calculated as Al_2O_3 , per gallon of solution.

Sodium silicate (in the form of water glass) is then added to the alkali etching solution in an amount of about 2 ounces of sodium silicate per gallon of etch solution. A precipitate of aluminosilicate forms, which is removed from the etching tank. The concentration of aluminate in the etching solution is thus reduced to about 5 ounces per gallon, and the alkali concentration is increased to about 17.3 ounces per gallon of solution.

The regenerated solution is employed to etch additional pieces of 2024 and 7075 aluminum at good etch rates and with production of a good quality etch on the aluminum parts.

From the foregoing, it is seen that the invention provides a simple and economical procedure for readily and rapidly regenerating or rejuvenating spent alkali etching solutions, by addition of alkali silicate to precipitate out excess aluminate in the form of aluminosilicate, and to increase the alkali concentration of the spent solution, and permit its reuse for etching additional aluminum bodies.

While I have described particular embodiments of my invention for the purpose of illustration, it should be understood that various modifications and adaptations thereof may be made within the spirit of the invention, as set forth in the appended claims.

I claim:

1. A method of etching aluminum which comprises contacting said aluminum with a hot aqueous alkali solution for a period sufficient to etch said aluminum and to form alkali metal aluminate in said solution and reducing the concentration of said alkali, and adding an alkali metal

silicate to the resulting etching solution to precipitate aluminate in the form of an aluminosilicate, and to regenerate alkali in said solution.

2. A method as defined in claim 1, said alkali solution being an aqueous sodium hydroxide solution, said alkali metal aluminate being sodium aluminate, and said alkali metal silicate being in the form of an aqueous sodium silicate solution.

3. A method as defined in claim 2, the sodium aluminate content of said etching solution following said period of etching being greater than about 6 ounces calculated as Al_2O_3 , per gallon of solution, and the amount of aqueous sodium silicate solution added to said etching solution being sufficient to precipitate an amount of aluminosilicate to reduce the concentration of the sodium aluminate in said etching solution to not greater than about 6 ounces calculated as Al_2O_3 , per gallon of said solution.

4. A method of etching aluminum as defined in claim 1, which includes contacting said aluminum with a hot aqueous sodium hydroxide etching solution for a period to etch said aluminum and to form sodium aluminate in said solution and reducing the concentration of sodium hydroxide, adding an aqueous sodium silicate solution to the resulting etching solution in an amount sufficient to provide from about 0.1 to about 10 ounces sodium silicate per gallon of etching solution, to precipitate aluminate in the form of an aluminosilicate, and to increase the sodium hydroxide concentration of said solution, and reducing the concentration of sodium aluminate to not greater than about 6 ounces calculated as Al_2O_3 , per gallon, removing said precipitated aluminosilicate, and contacting aluminum with the separated sodium hydroxide solution to etch said last mentioned aluminum.

5. A method as defined in claim 4, the amount of sodium silicate solution employed furnishing about 0.5 to about 2 ounces of sodium silicate per gallon of etching solution.

6. A method as defined in claim 4, said sodium hydroxide solution being a 0.1 to about 10 normal solution, and said sodium silicate solution having a concentration of about 3 to about 10% sodium silicate.

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134—10; 156—22