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2,739,883

PROCESS OF ETCHING ALUMINUM

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This invention relates to methods for etching aluminum and aluminum base alloys in which aluminum is the major constituent. Such alloys are well known and are employed in the decorative arts and as structural and machine parts and include, for example, the wrought, sand casting, permanent mold casting and die casting aluminum alloys. The various alloying elements employed in such alloys include Cu, Mg, Si, Mn and Zn. In some special purpose alloys Ni, Sn, Pb, and Bi are added as alloying elements, and in cast and wrought alloys Ti and Cr are sometimes added.

It is well known that aluminum and its alloys may be corroded, that is, dissolved by reaction with aqueous alkaline solutions of alkali metal hydroxides, such as sodium and potassium hydroxide and other alkali metal and salt solution of alkaline pH, for example, sodium and potassium carbonate and trisodium phosphate and tripotassium phosphate.

These reagents and particularly caustic soda, when used to etch aluminum and aluminum alloys, produce a hard scale on surfaces of tanks in which the etching process is employed. If the tanks are heated by coils as in the process of my invention this hard scale deposits on the coils and also on the surfaces of the etching tanks. Additionally, by depositing on the walls the scale reduces the volumetric capacity of the tank and if allowed to continue will fill the tank.

Various theories have been advanced by workers in this field to explain the formation of the scale in the etching of aluminum and its alloys by caustic soda. It has been said that the scale results from the hydrolysis of the aluminate which is formed in the etching of the aluminum by alkaline solutions. In order to prevent or reduce the formation of hard adherent scale in such process, it has been proposed to add to the alkaline etching solution, an agent which is said to have the property of keeping the aluminum compound, formed in the etching process, in solution or colloidal dispersion in the etching solution while others have used agents which are said to prevent the reversion of the aluminate to form the aluminum hydroxide and alumina and to cause the precipitate which is formed to be granular and non-adherent. In selecting the agents which are to be employed for these purposes these workers have selected those which have the property of holding the aluminum in a dissolved or colloiddally dispersed condition in the solution and which inhibit the precipitation of the aluminum hydroxide scale for prolonged periods of time.

I have found that I may avoid the deleterious effect of scale formation in etching aluminum and aluminum alloys with alkaline solutions by altering the nature of the precipitates formed rather than trying to retard or inhibit the formation of these precipitates.

It is, therefore, an object of my invention to etch aluminum and its alloys with an etching solution of the character which causes the aluminum, which is removed by the etching solution from the aluminum object which is being etched, to be precipitated in the form of a com-

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pound of aluminum, which is non-adherent in form and character.

I have discovered that citric acid has the property of modifying the character of the etching reaction to produce precipitates which are not adherent in form.

Citric acid has been rejected by the prior art (See U. S. Patent No. 2,650,875) as of any utility in preventing or inhibiting the formation of hard scale in etching process employing caustic soda. This patent which uses reagents which act to prevent or control the reversion of aluminate in order to retard the formation of scale, reports that citric acid has but a negligible effect on the time of formation of scale as compared with the use of caustic soda alone. Others (see U. S. Patent 2,653,860) have found citric acid to be inoperative to prevent the formation of adherent hard scale in such procedures.

Contrary to this teaching, I have found that citric acid has a material and beneficial effect on the formation of precipitates resulting from the reaction of the aluminum and its alloys with caustic soda solution containing citrate ions.

I have found that when employing a solution containing citrate ions having a weight rate (calculated as citric acid) to caustic soda in the solution of more than 2 parts of citric acid $(\text{COOH})\text{CH}_2\text{C}(\text{OH})(\text{COOH})\text{CH}_2\text{COOH}$ to 98 parts of caustic soda (NaOH), that is a mol ratio of more than 1 mol of citrate ion to about 230 mols of free NaOH, i. e. OH ion equivalent, the aluminum compound or complex, of a complex chemical composition unknown to applicant, precipitates after saturation of the caustic solution, in the form of a non-adherent sludge. Since the citric acid is neutralized, the result is sodium citrate equivalent to the citric acid added and the free caustic is reduced stoichiometrically to 96.8 parts by weight of free NaOH. In fact, if the percentage of citrate ion is increased by about 35%, that is, if 2.7 parts of citric acid is added to 97.3 parts of caustic in the solution, no adherent sludge is formed and all of the precipitate is found in the bottom of the vessel with none of the sludge adhering to the sides of the vessel or any exposed surface in the tank. When the tank is cleaned out the sludge may be readily flushed with a hose to give a clean tank surface.

I have also found that as the reaction progresses, caustic soda is used up so that the concentration of caustic in the bath employed decreases. However, observation indicates that if the original bath contained more than two parts of citrate ion (calculated as citric acid) to 98 parts of caustic soda (i. e., more than 2.69 parts sodium citrate to 96.8 parts free NaOH) then the bath will continue to etch aluminum without formation of any adherent scales notwithstanding that the caustic concentration will eventually become exhausted as is evidenced by exhaustion of its etching capacity and cessation of liberation of hydrogen gas.

While I do not wish to be bound by any theory of the procedure, I believe that the fact that notwithstanding the exhaustion of the caustic in the process, that the activity of the citrate ion remains that the caustic and the citrate radical are both removed from solution in some ratio such that the ratio of citrate ion and caustic soda in the solution are always in the proportion which I have found to be necessary, i. e., above about 1 mol of citrate ion to 230 mols of free caustic soda. This, I believe, indicates that the citrate radical forms a complex with the aluminum, and perhaps sodium, which complex by mechanical admixture or by chemical combination with other aluminum compounds, forms a sludge whose physical properties are essentially different from the sludge formed either without the citrate ion or when the citrate ion is used in insufficient amount.

The above theory includes the concept that citrate

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ion in my process is not relied on to hold in solution or colloidal dispersion, the aluminum compound formed when the aluminum is etched, nor that it affects the reversion of the sodium aluminate.

It is, therefore, another object of my invention to etch aluminum with a caustic soda solution containing citrate ion (calculated as citric acid) equal to more than 2 parts of citric acid by weight to about 96.8 parts of free NaOH by weight.

In carrying out my process, I preferably employ aqueous solutions of caustic soda containing a weight ratio of from about 2.7 parts to 10 parts by weight of citrate ion calculated as citric acid to about 96.8 to 83.34 parts by weight of free NaOH. I obtain these solutions conveniently by dissolving citric acid in caustic soda solution, using about 2.7 parts to 10 parts by weight of citric acid to 97.3 to 90 parts by weight of NaOH dissolved in water. The citric acid is neutralized by NaOH and the solution is thus reduced in causticity. Instead of NaOH, I may use other alkaline etching agents, for example, NH_4OH , KOH , or salts of these bases which give highly caustic solutions within the range indicated, such as basic salts of these bases, that is, trisodium or tripotassium phosphate, sodium or potassium carbonate either used separately or in admixture with the above bases, adjusting the ratio of the alkali material to the citrate ion to give the mola equivalents of hydroxide ions in solution to citrate ions in solution chemically equivalent to the ratios given above in connection with the use of NaOH and using the combination to give a hydroxyl concentration equivalent to from .1 to 10 normal as specified for NaOH. Instead of citric acid I may use an equivalent amount of citrate salts such as sodium citrate, potassium citrate and ammonium citrate adjusting the causticity to give the above ratios.

These water solutions are conveniently used at concentrations in the neighborhood of about $4\frac{1}{2}\%$ or lower by weight of the above mixture in water and I may use concentrations up to about 40% by weight of the mixture dissolved in water. The range of caustic soda or equivalent alkali or alkali salt is such that the free alkali, that is, hydroxide, concentration ranges from about .1 to about 10 normal and pH employed is in excess of 10.

Such solutions containing the citric acid in the proportion used above are preferably employed at elevated temperatures in order to etch the aluminum, and are preferably employed at temperatures varying from 120 degrees to 210 degrees F. Preferred temperatures are in the range of 140 to 180 degrees F.

Upon such conditions, the concentration employed will also depend on the degree of agitation involved in the process, the greater the agitation or circulation by which fresh solution is brought to the surface to be etched the lower the concentration which may be employed in which case NaOH as low as .01% by weight solution may be employed. The following examples are given as an illustration of the effect of concentration of citrate ion on the production of soft and hard sludges in my process:

Example 1

A number of aluminum parts composed of 24 ST wrought strips of aluminum alloy having the composition (91.4% Al; 4.5 Cu and 0.6% Mg) were etched in a vessel containing caustic soda solution made up by dissolving a mixture composed of 98 parts by weight of granular caustic soda and two parts by weight of granular citric acid in water in amounts sufficient to give a concentration of 5 parts by weight of the mixture in 95 parts by weight of water at a temperature of 140 degrees F. Parts were etched in the solution and removed therefrom when etched and new parts immersed until the etching power of the solution was practically exhausted as is observed by the fact that substantially no observable gas generation occurred.

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It was observed that the solution remained clear for a period at the beginning of the process but then there appeared dispersed in the solution a black precipitate which was maintained suspended because of the evolution of hydrogen gas.

The exhausted bath after removal of the aluminum parts was allowed to stand at ordinary temperature for 24 hours.

It was observed that the precipitate had settled to the bottom of the vessel and was composed of a black layer covered with a crust which was hard and that such a hard scale had formed on the vessel walls. The scale could not be flushed out and had to be scraped and brushed out to clean the sides of the vessel.

Example 2

The procedure of Example 1 was repeated using a ratio of 97.3 parts by weight of granular caustic soda and 2.7 parts by weight of granular citric acid. After standing over night, a considerable soft precipitate was formed in the bottom of the tank, no scale adhered to the sides of the vessel. The precipitate on the bottom of the tank could be flushed out readily.

Example 3

The procedure of Example 1 was repeated using a ratio of 97 parts by weight of granular caustic soda and 3 parts by weight of granular citric acid. The sludge is softer and more readily rinsed than that in Example 2.

Example 4

The procedure of Example 1 was followed using separately 4 parts of citric acid to 96 parts of granular caustic soda and in a separate test using five parts of granular citric acid to 95 parts of NaOH. In each case the sludge was somewhat softer and more readily dispersible in flushing with water as the citric acid to NaOH ratio was increased.

Experience has shown that for practical purposes no significant improvement in ease of removal of the sludge is obtained by increasing the citric acid ratio to caustic above 4 parts of citric to 96 parts NaOH. It is however, then possible to permit the dilution of the citrate ion by increasing the ratio of the caustic to citrate ion by addition of caustic during the process, provided preferably that the ratio be at least 2.7 and preferably more than 2.7 parts of citrate ion calculated as citric acid to caustic soda in balance to give 100 parts. The higher concentration of citric acid results in larger consumption of caustic used in neutralization requiring the increase and use of caustic soda to establish the proper causticity, that is, caustic soda concentration.

For practical operations, it has been found that a solution produced by dissolving 4 parts by weight of granular citric acid to about 96 parts by weight of granular NaOH, used in amounts equal to a weight concentration of at least $4\frac{1}{2}\%$ by weight of the mixture of caustic and citric acid in water solution when used in a tank into which the aluminum parts are immersed or the mixture is used in concentrations about $1\frac{1}{2}\%$ to 2% by weight of the mixture based on the water solution when the solution is sprayed on the aluminum part may be employed without deposit of sludge when the solution is used for periods of several months operations.

In carrying out my process, the part to be etched is suitably prepared by cleaning and if portions only of the aluminum body are to be etched, then with the remainder of the article suitably protected by a protective mask such as a paint or film or other suitable protective medium to prevent access to the alkali of the part which it is not desired to etch. As a specific example of the procedure which may be followed, the following example is given by way of illustration but not as a limitation of my invention.

Example 5

The aluminum body is immersed or sprayed with a solution composed of 7% by weight of a mixture of NaOH and citric acid (96 parts of granular NaOH and 4 parts of granular citric acid) or NaOH and sodium citrate to give equivalent concentration of NaOH and citrate ion. The solution is heated to 180 degrees F. and the etch procedure is continued until the desired depth of etch is obtained, for example, using 24 ST aluminum (91.4% Al; 4.5% Ca; 0.6% Mg) will etch at the rate of approximately .060 inches per hour in depth into the exposed surface. When the desired depth of etch is obtained the part is removed from contact with the alkali and thoroughly rinsed with plain water.

It will be observed that the mixture of the granular citric acid and granular caustic forms a convenient composition of matter or use in this procedure. I may make a mixture suitable for such use by mixing the granular citric acid in the range of about 2.7 parts to 10 parts of granular citric acid to 97.3 to 90 parts by weight of granular NaOH, for example, 96 parts by weight of granular NaOH to 4 parts by weight of citric acid. Instead of NaOH, I may use granular KOH or granular trisodium phosphate, tripotassium phosphate, potassium carbonate, sodium carbonate in amounts chemically equivalent to the amounts of NaOH given above. Instead of citric acid, I may use a granular sodium or potassium citrate or ammonium citrates in amounts chemically equivalent to the amounts of citric acid specified above. The mixtures may be separately made and packaged and form a convenient way of making the etching solutions specified above. The mixture may be admixed with other reagents as desired so long as these other reagents do not interfere with the essential nature of the mixture to produce the alkaline solutions containing the citrate ion as explained above.

It will be observed that the surface of the aluminum etched with the above reagents is coated with a black "smut." Such smut is formed whenever an alkali material is used to etch aluminum alloys containing alloying metals such as Cu.

The smut may be removed by the procedure disclosed in my copending application, Serial No. 448,775 filed August 9, 1954.

While I have described a particular embodiment 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 bodies of aluminum and aluminum base alloys which comprises treating said aluminum bodies with an aqueous alkaline solution which contains citrate ions and alkali hydroxide, said citrate ions being present in a ratio to the alkali hydroxide chemically equivalent to at least about 2.7 percent of the combined

weight of the citrate calculated as citric acid and alkali hydroxide calculated as NaOH, and etching the said aluminum bodies by said treatment and forming a precipitate in said container.

2. A method of treating bodies of aluminum and aluminum alloys which comprises treating said aluminum bodies in a container with an aqueous alkaline solution containing free alkali in concentration ranging from about .1 to 10 normal and citrate ion, said citrate ion being present in a ratio to the alkali chemically equivalent to at least about 2.7 percent of the combined weight of the citrate calculated as citric acid and alkali calculated as NaOH, and etching the bodies and forming a precipitate in said container.

3. A method of treating bodies of aluminum which comprises forming an aqueous solution by dissolving an alkaline etching agent taken from the group consisting of NH_4OH , NaOH, KOH, and alkali salts of said bases and a compound taken from the group consisting of citric acid, ammonium citrate, potassium citrate and sodium citrate, the ratio of said compound and said alkaline etching agent being chemically equivalent to from about 2.7 parts to about 10 parts by weight of citric acid to from about 97.3 parts to about 90 parts by weight of NaOH, said alkaline etching agent being present in amount sufficient to establish a concentration of hydroxyl ions within the range of about .1 normal to 10 normal and contacting said bodies with such a solution in a vessel and forming a precipitate in said solution.

4. An etching bath consisting essentially of an aqueous solution of an alkali material in concentration having an hydroxyl ion concentration chemically equivalent to a range of from about 0.1 to 10 normal NaOH, and citrate ion, said citrate ion being present in a ratio to the alkali chemically equivalent to at least about 2.7 percent of the combined weight of the citrate calculated as citric acid and alkali calculated as NaOH.

5. An etching bath consisting essentially of an aqueous solution of an alkaline etching agent taken from the group consisting of NH_4OH , NaOH, KOH, and alkali salts of said bases, and a compound taken from the group consisting of citric acid, ammonium citrate, potassium citrate, and sodium citrate, the ratio of said compound to said alkaline etching agent being chemically equivalent to from about 2.7 parts to about 10 parts by weight of citric acid to from about 97.3 parts to about 90 parts by weight of NaOH, said alkaline etching agent being present in amounts sufficient to establish a concentration of hydroxyl ion equivalent to the range of about 0.1 to 10 normal NaOH.

References Cited in the file of this patent

UNITED STATES PATENTS

2,650,875 Dvorkovitz ----- Sept. 1, 1953