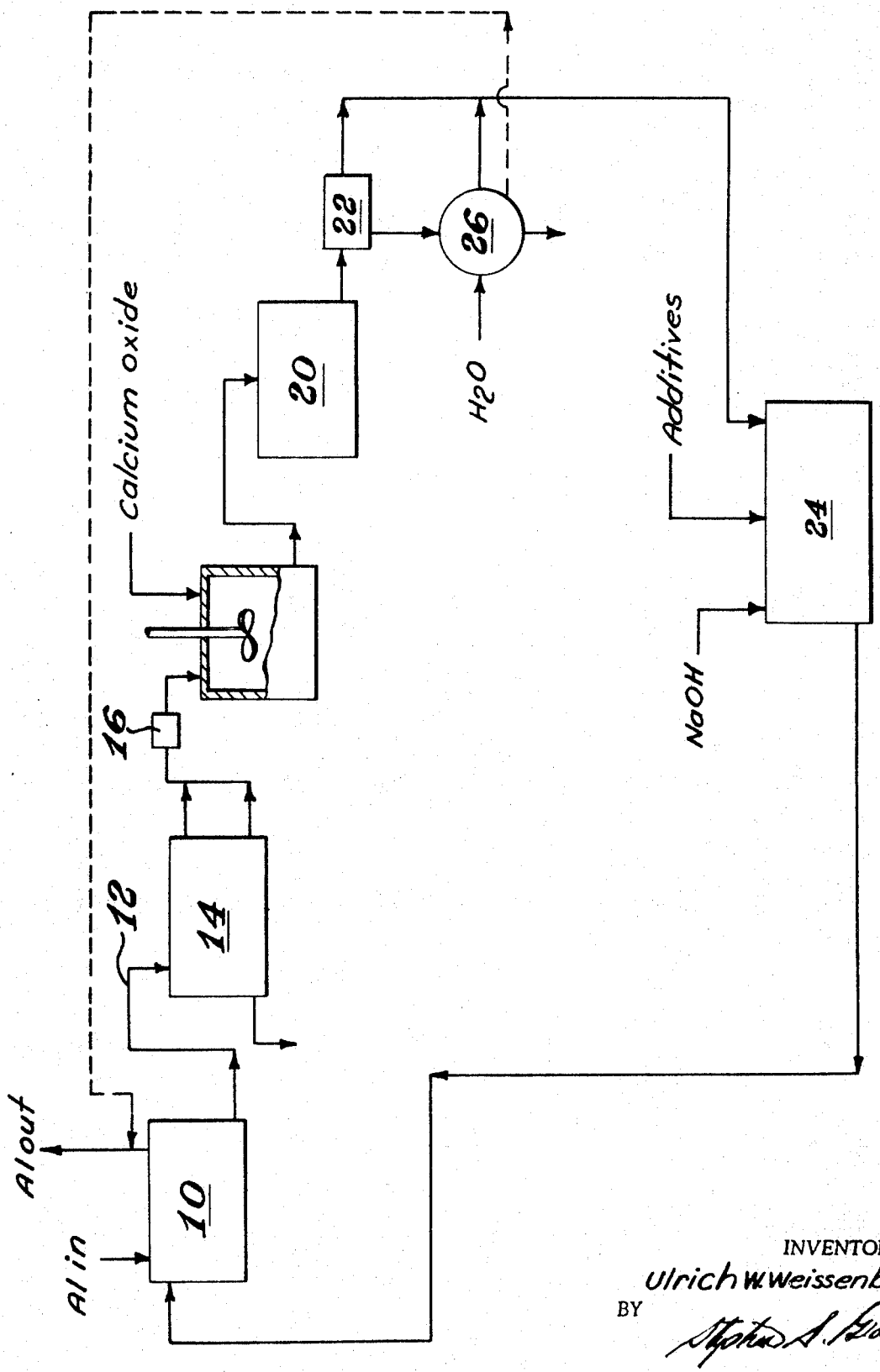
Jan. 23, 1973 U. W. WEISSENBERG 3,712,838

REGENERATION OF CAUSTIC LIQUOR FOR ETCHING ALUMINUM

Filed March 17, 1971



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United States Patent Office 3,712,838 Patented Jan. 23, 1973

3,712,838

REGENERATION OF CAUSTIC LIQUOR FOR ETCHING ALUMINUM

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Continuation-in-part of abandoned application Ser. No. 591,538, Nov. 2, 1966. This application Mar. 17, 1971, Ser. No. 125,086

Int. Cl. C23g 1/36

U.S. Cl. 156—19 8 Claims

ABSTRACT OF THE DISCLOSURE

The present invention is a process for regenerating spent caustic etching solutions resulting from reacting aluminum with aqueous solutions containing free alkali metal hydroxide. In particular a spent caustic etching liquor, ordinarily at the etching bath temperature, is contacted with calcium oxide to precipitate aluminum values present in the spent liquor and regenerate hydroxyl ions. The precipitate is removed from the regenerated solution.

This application is a continuation-in-part of Ser. No. 591,538, filed Nov. 2, 1966 now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to the etching of aluminum and more particularly is concerned with a novel process for regenerating spent caustic etching liquors used in the etching of aluminum bodies.

The term "aluminum" as used herein is meant to include aluminum and aluminum alloys having a minimum of about 70 weight percent aluminum.

Commercially, as is well understood in the art, aluminum objects are etched or chemically milled by alkaline solutions, primarily hot aqueous solutions containing free alkali metal hydroxide, e.g., aqueous sodium hydroxide solutions, to shape or alter the dimensions of such objects. Such solutions are referred to hereinafter as "caustic etching solutions," "caustic etch liquors" or "caustic etchants." In the etching operation, ordinarily aluminum is contacted with an aqueous caustic (NaOH) solution at a temperature of from about 100° F. up to the boiling point of the solution. Commonly, a solution containing about 10 weight percent NaOH and at a temperature of from about 190° F. up to the boiling point of the solution is used as the etchant.

During the etching process, aluminum goes into solution, probably in the form of an aluminate anion which in turn with the sodium values in the bath forms a complex hydrated sodium oxide·aluminum oxide.

As the etching of the metal proceeds, the free alkali, i.e., the hydroxyl ions not combined with the aluminum in salt formation, decreases and the concentration of the aluminum salt in solution increases. These changes in bath composition in turn lead to a decrease in the rate of etching. Also, as the aluminate concentration builds up in the etching bath, this reaches a point where the solubility limit is exceeded and precipitation of objectionable quantities of an alumina-containing sludge can occur in the bath. Such etching baths, therefore, heretofore have had to be dumped and replaced in order that satisfactory etching of aluminum can be carried out.

U.S. Pat. 2,975,041 alleges an etching process for aluminum which also provides for at least partial regeneration of spent caustic etching solutions. This process comprises contacting aluminum with an alkaline solution to etch or mill the metal. In this conventional operation, the free alkalinity of the etching solution is reduced and the

aluminum values in solution are increased. A principal teaching of this patent is to cool the spent etching solution so as to precipitate hydrated alumina therefrom. If an insubstantial amount of solid phase hydrate alumina is formed to effect precipitation, a sufficient amount of solid phase hydrated alumina is added to the spent etching solution to cause a thorough contact between the solution and the dispersed solid alumina hydrate. The resulting cooled solution is allowed to stand for an extended period of time whereby hydrated alumina precipitates therefrom and the supernatant solution is separated by settling of the solids and decanting of the clear solution. According to this patent, "the solution shows an increase in the free alkali and a decrease in the amount of the aluminate in solution." This process for regenerating spent aluminum etching solution suffers from the disadvantages that the solution must be cooled, many times undesirable solids must be added to the etching bath, lengthy storage times must be utilized and there is no real control of the degree and quality of the regenerated bath.

It is a principal object of the present invention to provide a novel method for regenerating spent caustic etching solutions.

It is another object of the present invention to provide a process for regenerating spent caustic etching solutions wherein the solution is treated at its normal operating conditions.

It is a further object of the present invention to provide a process for regenerating spent caustic etching solutions where the bath being treated need not be cooled during the treatment but wherein the regenerating process itself provides positive heat in situ and thereby overcomes natural heat losses accompanying the etching operation.

It is also an object of the present invention to provide a means for positively controlling the aluminate and hydroxyl ion concentrations of a caustic etching bath during operation without changing operating conditions and thereby provide for in situ regeneration of such a bath during etching with no down time.

It is an object of the present invention to provide a process for regenerating spent caustic etching solutions which also gives substantially constant control of the etch rate of the bath.

It is another object of the present invention to provide a method for regenerating spent caustic etching solutions which simultaneously produces a useful solid product.

It is a further object of the present invention to provide a novel method for regenerating spent caustic etching solutions which produces a solid product suitable for use as an aluminum source material which product is more soluble in aluminum metal producing processes than naturally occurring aluminum based ores.

It is another object of the present invention to provide a novel method for regenerating spent caustic etching solutions which simultaneously gives control of the bath concentration and no bath dilution.

It is a further object of the present invention to provide a process for regenerating spent caustic etching solutions which process also can be utilized to provide control of the froth which ordinarily is present, both with respect to total amount of froth present and the separation of froth from aluminum not being subjected to the etching process thereby preventing undesirable etch patterns.

It is a further object of the present invention to provide a novel process for regenerating spent caustic etching solutions which provides a substantially aqueous insoluble innocuous product which does not contain appreciable hydroxyl ions and which, if not utilized, can be disposed of by conventional disposal means, e.g., dumping or piling, since it does not have a detrimental effect on the pH of streams, ground water and the like water sources.

These and other objects and advantages readily will become apparent from the detailed description presented hereinafter when read in conjunction with the accompanying drawing.

The figure of the drawing is a schematic flow diagram illustrating one embodiment of the present novel process.

In general, the present invention comprises contacting a spent caustic etching solution with calcium oxide to precipitate aluminum values from solution and regenerate hydroxyl ions and separating the precipitate from the regenerated caustic liquor. The calcium oxide reacts substantially quantitatively with the aluminate values in the spent caustic solution to provide a substantially insoluble, readily removable solid, calcium aluminate precipitate. Surprisingly, in addition to aluminate removal, the present method also regenerates the hydroxyl ion concentration in the caustic solution. This is felt to be due to the calcium oxide reacting with the soluble anions in the spent solution to form an insoluble calcium salt and free hydroxyl ions. These anions are introduced into the solution during the etching operation. The solids are removed from the solution and the regenerated caustic values ordinarily returned to the etching process for reuse. The term "spent caustic etching solution" as used herein, is meant to include any caustic solution which has been contacted with aluminum, primarily for purposes of etching or chemically milling the aluminum, wherein any portion or all of the hydroxyl values have been depleted by reaction with the aluminum, and which contains one or more soluble anions, e.g., sulfate, carbonate, sulfide or sulfite, which react with calcium oxide to form an insoluble calcium salt.

More particularly as shown in the embodiment of the figure of the drawing ordinarily in carrying out the present process calcium oxide, for example burnt lime, is introduced in finely divided form into a stream of spent caustic etching liquor taken from an etching bath **10**.

In most operations, as shown, the present process is practiced by treating a by-pass stream **12** of spent caustic liquor which is removed either on a continuous or intermittent basis from an etching bath **10** during the etching operation. Ordinarily, this stream **12** is first sent to a settling and storage tank **14** and a filter **16** to remove solid material therefrom prior to treatment in the present process although this prefiltering is not critical to operation of the present invention. Removal of etching bath produced solids prior to treatment usually is practiced in order to assure a more rigid bath control. However, it is to be understood that a caustic etching bath **10** can be treated directly by the practice of the present invention. Generally, as is well understood by one skilled in the art, it is not desirable to increase the solid contents of a working bath. Therefore, the use of a by-pass stream **12** serves not only to provide for bath control but to maintain the etching bath in a "clean" conditions.

The calcium oxide is introduced into the stream ordinarily with agitation at the operating temperatures of the bath in a tank or reactor **18**. The resulting slurry of regenerated caustic and precipitated solids of calcium aluminate, primarily in the form of hydrogrossularite ($Ca_3Al_2(OH)_{12}$), and calcium salt from reaction with the soluble anion are transferred to a settling tank **20** and the solid product removed by a filter **22** or other liquid-solid settling techniques.

The regenerated caustic, usually is returned to a caustic make-up tank **24** for reuse in subsequent etching operations. The solids **26** can be sent to waste disposal or, as indicated hereinbefore, can be utilized as an aluminum source material in aluminum metal producing operations.

Ordinarily, as shown, the solids product **26** is washed to remove occluded caustic values therefrom and the resulting caustic wash liquor also sent to the make-up tank. Alternatively, if desired, the caustic wash water solution can be transported directly back to the etch tank and used to wash aluminum work pieces as they are removed from the bath thereby to further recover caustic values which otherwise would be lost by adhesion to the work pieces. In this latter embodiment, the dilute caustic wash usually is directed against the work piece near the surface of the bath. This gives the additional utility of serving to control foaming by breaking of foam at the bath surface through differences in the surface tension of the wash water and the foam itself as well as prevents undesirable etching of that part of the work piece above the bath surface which could occur with contact of the work piece by the foam.

Although the present process of caustic solution regeneration ordinarily is carried out at the temperature of the etching bath, the regeneration can be carried out at lower temperatures. However, as indicated hereinbefore, it is an unexpected advantage of the present invention that it is not necessary to reduce the bath temperature prior to carrying out the present process thereby providing for bath and etch factor control on a continuous basis during operation.

The reaction between the dissolved aluminate values and the calcium oxide is substantially quantitative. Ordinarily, in actual caustic etching of aluminum, the etch bath compositions are predetermined so as to contain hydroxyl ions and aluminate ions within controlled ranges to assure the maintenance of a given etch rate. By treating a stream of a caustic etching bath as disclosed herein, positive control of hydroxyl ion and aluminate ions in the bath can be realized on a continuous basis.

The present process also provides an additional advantage in that different etch rates can be provided for different stages of etching with a given work piece. This is achieved by reacting predetermined quantities of the calcium oxide with a stream of spent liquor from the etching bath to remove controlled quantities of aluminate values and regenerate hydroxide thereby to vary in a controlled manner the etch rate of the bath during etching. This has not been possible in caustic etching processes practiced heretofore.

The actual reaction time employed at a minimum is that sufficient to effect reaction between the calcium oxide and the aluminate and anion values in the bath. Usually, a reaction period of from about several minutes to one-half hour or more is employed. Ordinarily contact times of from about 5 to about 20 minutes and preferably from about 10 to 15 minutes are used. In most operations to assure rapid and complete reaction within the indicated time periods, a finely divided, i.e. powdered alkaline earth metal oxide source material, is added to the caustic stream with agitation. For optimum reaction in the indicated reaction times, particulate calcium oxide having a maximum size so as to pass a 200 mesh U.S. Standard Sieve are utilized and preferably finely divided powdered materials passing at least a 325 mesh sieve or more, preferably passing a 400 mesh sieve, are utilized.

The reaction between the calcium oxide and the spent caustic is exothermic and thus can increase the temperature or recycle stream. As this stream is fed back into the bath, this heat energy serves to offset bath heat losses generally associated with elevated temperature operations as well as the secondary heat losses resulting from evaporation, frothing, surface agitation and the like encountered during etching.

Since certain useful additives, e.g., those containing soluble anions, may be removed during the regeneration of the caustic values, if necessary, additional quantities of these can be incorporated back into the bath in the make-up tank.

The following examples will serve further to illustrate the present invention but is not meant to limit it thereto.

EXAMPLE I

Spent caustic etching liquor from a commercial aluminum milling operation was obtained and used in a

series of regeneration studies. This material was filtered and analysis of the filtrate indicated this liquor contained about 0.07 gram OH^-/gram of the filtered liquor (equivalent to about 0.16 gram NaOH/gram of liquor) and about 0.027 gram dissolved aluminum (expressed as Al^{+3} ion) per gram of liquor. This solution thus had a caustic concentration of about 16 percent NaOH.

Three separate 500 gram samples of the filtered spent liquor were taken and each treated with a predetermined quantity (10, 20 or 40 grams) of powdered calcium oxide. In these studies, the calcium oxide powder was added under rapid agitation to the spent liquor solution which was maintained at a temperature of from about 190–212° F. Little or no overboiling was noticed in any of the runs during the calcium oxide addition. The resulting slurry was agitated for about 20 minutes although all visible evidence indicated the reaction to be substantially complete at about the time the last quantity of calcium oxide was introduced into the solution.

The resulting slurry was filtered under a reduced pressure through a Buchner funnel, the solid cake collected and sucked dry. A small sample of this cake was taken for analysis. This was found to be substantially calcium aluminate of hydrogrossularite structure.

The filter cake was reslurried wth 100 milliliters of water, this slurry refiltered and the filter cake washed with an additional 50 milliliters of water. The combined wash waters were added to the original filtrate and this solution analyzed for aluminum ion and hydroxyl ion concentration.

Table 1 summarizes the results obtained from each of these runs.

TABLE

Product	CaO reactant (grams) 10	20	40
1. Original filter cake (dry weight grams)	24.7	54.4	132.0
(a) Al in cake (expressed as Al^{+3}), grams	3.3	6.3	12.2
(b) Grams CaO added per g. Al^{+3} removed	3.04	3.17	3.28
(c) OH^- in cake, grams	6.15	11.92	23.07
2. Filtrate plus total wash, grams liquid recovered	618.5	593.7	543.8
(a) Al^{+++} in solution, grams	10.44	7.40	1.50
(b) OH^- in solution, grams	33.74	33.10	33.55
(c) Filtrate concentration, expressed as percent NaOH	12.8	13.1	14.5

These studies clearly establish the effective operability of the present process and particularly show that by practicing the present invention predetermined control of dissolved aluminum values and caustic values can be maintained in a caustic etching bath.

EXAMPLE II

500 grams of a 17.7 wt. percent NaOH solution containing about 4.3 wt. percent Al^{+++} was contacted with 31.5 grams of powdered CaO. The CaO was admixed at 190° F. and stirred at temperature for about 20 minutes. The precipitate formed was filtered, sucked dry, washed, sucked dry again and air dried at 50° C. The product was identified by X-ray diffraction as chiefly $Ca_3Al_2(OH)_{12}$. An anlysis of the precipitate, filtrate and wash water showed that about 45% of the Al^{+++} was removed.

For comparison the same procedure was carried out only this time the NaOH solution was contacted with 23.5 grams of MgO, the mole equivalent of the amount of CaO added above. The product was identified by X-ray diffraction as chiefly, $Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$ (hydrotalcite). Analysis showed that only about 17% of the Al^{+++} was removed.

What is claimed is:

1. A process for etching an aluminum or its alloy with an aqueous solution of sodium hydroxide which includes replenishment and recycling of spent etchant comprising:
   (a) contacting the spent liquor with calcium oxide to react the calcium oxide with aluminum and soluble anion values present in the spent liquor thereby to precipitate said aluminum values and regenerate hydroxyl ions; and
   (b) separating the resulting precipitate from the regenerated caustic etching liquor.

2. The process as defined in claim 1 and including the step of transporting the regenerated caustic etching liquor to a caustic make-up tank for reuse in a subsequent aluminum etching operation.

3. The process as defined in claim 1 and including the step of removing solids in said spent caustic etching liquor prior to contacting said liquor with calcium oxide.

4. The process as defined in claim 1 wherein a stream of said spent caustic etching liquor from an etching bath is treated at about operating bath temperature.

5. The process as defined in claim 1 and including the step of washing the separated precipitate and recycling the resulting hydroxyl-containing wash water to caustic make-up tank.

6. The process as defined in claim 1 and including the step of washing the separated precipitate and transporting the resulting hydroxyl-containing wash water to an etching bath and rinsing with said wash water an aluminum work piece being removed from said etching bath.

7. The process as defined in claim 6 wherein the wash water is directed against the aluminum work piece being removed from the etching bath at about the surface of said bath.

8. The process as defined in claim 1 wherein the calcium oxide has a maximum particle size of about 200 mesh U.S. Standard Sieve.

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U.S. Cl. X.R.

156—22; 252—79.5