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CHEMICAL COMPOSITION AND PROCESS FOR ALUMINUM ETCHING

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This invention relates to anti-scaling compositions for use in alkaline etching baths and to the utilization of such anti-scaling compositions in the etching of aluminum and aluminum base alloys. The term "etching" as used herein, both in the specification and claims, includes not only light surface etching, but chemical dissolution of substantial amounts of the metal treated as occurs when forming metal objects through controlled selective chemical dissolution, a process frequently referred to as "chem milling."

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 hydroxide, potassium hydroxide, sodium carbonate, trisodium phosphate, and the like, or with mixtures of these materials. The aluminum reacts with the alkaline etching materials, and where sodium hydroxide is used as the etchant, a solution of sodium aluminate is formed. However, when the concentration of alkali in the etching bath is reduced below a certain value, the sodium aluminate in the solution reacts with water and the end result of this reaction is the formation of a hard scale which is deposited on the sides and bottom of the tank containing the etchant and on heating coils or other equipment which may be submerged within the tank. This scale is primarily alumina, having the formula $Al_2O_3 \cdot 3H_2O$.

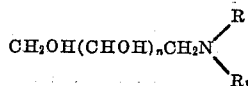
It has generally been believed that amines are unsuitable as additives to aluminum etching baths for the prevention or inhibition of scale formation. However, in co-pending application Ser. No. 474,036, a formulation is described in which ethylene diamine-tetra-acetic acid is used in conjunction with tartaric acid and preferably in conjunction with tartaric acid, glucose and certain metal ions to prevent scale formation.

Though ethylene diamine-tetra-acetic acid is effective for scale inhibition when used together with tartaric acid, glucose and certain metal salts in the proportions and manner described in co-pending application Ser. No. 474,036, the ethylene diamine-tetra-acetic acid is ineffective when used alone and in some instances actually promotes scale formation.

It has now been discovered that certain hydroxy amines have excellent scale inhibiting properties when added to caustic aluminum etching solutions. Furthermore, these amines are effective in and of themselves, it not being necessary to formulate these amines with other materials in order to inhibit the scale formation.

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The hydroxy amines referred to can generally be described by the empirical formula



where n is at least 2; R is hydrogen, another

$CH_2OH(CHOH)_nCH_2$ -radical

a normal alkyl radical containing not more than 4 carbon atoms, or an α or β carboxyalkyl group containing not more than 4 carbon atoms exclusive of the carbon in the carboxy group; and R' is similar to R but does not include the $CH_2OH(CHOH)_nCH_2$ -radical.

The relative effectiveness of hydroxy materials of this general type is well illustrated by the following table:

TABLE I

Additive	Concentration of Additive			
	.3 gram	.4 gram	.5 gram	1.0 gram
Crude glucamine	S	T	N	-----
Crude glucamine made in accordance with preferred condition	T	N	N	-----
Monoglucamine	S	T	N	-----
Diglucamine	T	N	N	-----
Sodium N-carboxymethyl-glucamine	N	N	N	-----
N' Ethyl glucamine	S	S	S	N
N' Butyl glucamine	S	S	S	N
N' Octyl glucamine	S	S	S	T

Code: S—scale; T—trace of scale; N—no scale.

(The data for this table was obtained as follows: Separate solutions were prepared containing 30 grams caustic soda, 600 ml. water and scale inhibitor in the amount indicated in the tables. These solutions were then heated to 150° F. at which temperature 18.5 grams of aluminum metal were dissolved in each solution. The solutions were then permitted to cool and stand for 18 hours after which time they were observed for scale formation.)

It will be noted from the different types of hydroxy amines of Table I that the least effective, in preventing scale formation, are the normal alkyl hydroxy amines where R or R' of the above general formula is a normal alkyl group. Why these amines are not as effective as the other hydroxy amines of this general type is not understood. However, they do have an appreciable effect in reducing or preventing scale formation and may be used where the etching bath is not subjected to severe operating conditions.

The hydroxy amines of Table I all have in common that they are prepared directly from monosaccharides by reductive amination (i. e. by reaction of monosaccharide with ammonia or an alkyl substituted ammonia and hydrogen under the influence of a hydrogenating catalyst such as nickel) or are products subsequently formed by reacting the initial products of the reductive amination with α or β halo fatty acids to form N— α or N— β carboxymethyl alkyl derivatives. These amines which constitute a class formed by the reductive amination of

monosaccharides are, for simplicity, referred to as "sugar amines," both in the present specification and claims.

When it is considered that the sugars, from which these amine products are made, are unsatisfactory for inhibiting scale formation in alkaline aluminum etching systems and that amines generally, as illustrated by Table II, do not have this property, it is indeed surprising that the amine derivatives of these sugars are such excellent scale inhibitors.

TABLE II

Additive	Concentration of Additive	
	1 gram	3 grams
Glutamic acid.....	S	S
Aspartic acid.....	S	S
Ethylenediamine.....	S	S
Ethylenediamine tetraacetic acid.....	S	S
Hexamethylenetetramine fluosilicate.....	S	S
Glucosamine.....	S	S
Diphenylamine.....	S	S
Triethylamine.....	S	S
Glucose.....	S	S
Monoethanolamine.....	S	S
Triethanolamine.....	S	S

(The data for Table II was obtained in the same manner as that for Table I, the conditions being the same, with the exception of the additive used.)

Though any of the reducing sugars may be employed in preparing the "sugar amines" for scale inhibition glucose is generally preferred because of its ready availability and low cost.

Of the glucamines, diglucamine is the most effective in preventing scale formation, it being preferred to the monoglucamine. In its preparation, however, a substantial amount of the monoglucamine is formed so that the crude product contains essentially a mixture of both the mono and diglucamine. It has been found that when the amination is carried out under certain conditions, the scale inhibiting properties of the crude is, in many instances, better than that of the monoglucamine and equal to that of the diglucamine which is excellent.

If the crude is prepared with a water content of about 10 to 15% by weight, the product is readily mobile at temperatures of about 50° C. and can readily be sprayed onto the caustic or other solid alkali while blending in preparing the final aluminum etchant composition. Furthermore, the physical properties of the crude are such that they prevent any dustiness in the final blend. This is of considerable advantage, since caustic formulations are frequently quite dusty, the dust causing irritation and frequently requiring the wearing, by workers, of protective garments and masks.

The crude glucamine compositions which are most effective in scale inhibition, are prepared in the following manner:

Glucose and ammonia, generally as aqueous ammonia, are added to a pressure reactor along with a hydrogenation catalyst such as nickel. Hydrogen is then introduced under pressure and the reactants heated, with agitation, at a temperature preferably below 75° C. until hydrogen uptake is substantially complete. If some caustic has been added to the reactor, hydrogen uptake will begin at about 52-54° C. However, without the caustic present, hydrogen absorption does not begin until about 67-70° C.

Towards the end of the reaction, the temperature is increased to complete hydrogen take-up. However, the temperature should preferably not exceed 100° C. since side reaction products tend to form at the higher temperatures which apparently adversely affect the scale inhibiting properties of the crude. Glucamine crudes having excellent scale inhibiting properties are obtained by employ-

ing mol ratios of ammonia to glucose of about 1.5:1 to 6.2:1. The preferred ratio is in the order of about 2.2 mol of ammonia to 1 mol glucose.

Though the ratio of ammonia to crude does not seem to greatly affect the scale inhibiting properties of the resulting product, particularly within the above limits, the hydrogenation pressure, i. e. the pressure at which the hydrogen uptake occurs, appears to have a substantial effect. Thus, crudes prepared at pressures of about 250 pounds per square inch gage are not particularly satisfactory unless an exceptionally large amount of hydrogenation catalyst is used. This is well illustrated in the following table:

TABLE III

Gram Mols NH ₃ /glucose	Ni Catalyst, wet basis	Pressure	Results	
			Mild test	Severe test
60/10.....	125	1,000	good.....	
30.9/13.9.....	250	800-520	good.....	good.....
30.9/13.9.....	815	250	good.....	fair.....
30.9/13.9.....	125	250	fair.....	poor.....
30.9/13.9.....	125	1,750		good.....
20.8/13.9.....	125	1,100		good.....
48/8.....	72	1,500		good.....
40/10.....	90	250		poor.....
27.8/13.9.....	125	500	good.....	fair.....

(In the above table, the nickel catalyst is given on a wet weight basis; on a dry basis the weight is about half the amount given. The data for Table III was obtained by using caustic solutions containing 30 grams caustic soda, 600 ml. water and .5 gram of crude glucamine. The aluminum was dissolved at a temperature of 150° C. and the solutions observed after 18 hours standing. In the mild test only 18 grams were dissolved. While in the severe test 18.5 grams of aluminum was dissolved. After 18.5 grams of aluminum has been dissolved, substantially all of the free caustic has been consumed and the solution is essentially incapable of dissolving more aluminum.)

After the hydrogen take-up is completed, the crude is removed from the reactor and filtered to remove the nickel catalyst. Sufficient water is then removed from the crude, preferably by heating under a vacuum, to give a product having a water content of about 10 to 15%.

Though the normal alkyl glucamines, such as normal ethyl glucamine and normal butyl glucamine, are not as effective scale inhibitors as either mono or diglucamine, the normal carboxy alkyl glucamines have excellent scale inhibiting properties.

For purposes of illustration, the following preparation of methyl carboxy glucamine is given:

Crude glucamine, in the amount of 210 grams, prepared as above described and representing 1 mol of nitrogen containing product, as shown by titrations (210 being the apparent molecular weight), was dissolved in 500 cc. of distilled water containing 106 grams (1 mol) sodium carbonate. To this was added 94.5 grams (1 mol) chloroacetic acid and the mixture refluxed for five hours.

This product was dried to a substantially anhydrous condition by evaporation of the water on a steam bath under vacuum. The product consisted primarily of methyl carboxy glucamine.

The normal alkyl glucamines appearing in Table I were prepared in much the same manner as the glucamines. The following description of the preparation of normal butyl glucamine will serve to illustrate the preparation of these materials. Butyl amine in an amount of 7.1 mols, and glucose in an amount of 3.2 mols were heated in a steam bath to a temperature of about 70° C. for 30 minutes, after which time a clear solution resulted. This solution, together with 3100 cc. of water and 188 grams

of drained Ranie nickel-catalyst (approximately 100 grams actual nickel content) were placed in a 2 gallon stainless steel autoclave of the stirrer type. Hydrogen was then introduced under a pressure of 1000 pounds per square inch gage over a period of 7 hours while the reactants were maintained at a temperature of 60 to 65° C. The reaction was then discontinued, the reaction mixture filtered to remove the nickel catalyst and then left to stand over night at room temperature. The crystalline product which formed was filtered from the mother liquor, washed and air dried. This product which melted at 130.2 to 134° C. was normal butyl glucamine.

In practicing the invention, the mono and diglucamines and the carboxy alkyl glucamines are preferably used with the caustic in amounts of 1.5% to 5% by weight based on the caustic soda. However, these materials will inhibit scale formation when concentrations of as little as 0.5% are used and may be used in such lower concentrations where the caustic etchant solution will not have severe working. However, for general operation, as stated, it is preferred to have these materials present in amounts of at least 1.5%. There appears to be no detrimental effect resulting from using these "sugar amines" in higher concentrations up to and above their saturation point.

The alkyl glucamines such as normal ethylglucamine, normal butyl glucamine etc., when used in concentrations of 3% tend to cause foaming. It is not clearly understood whether this foaming is a property of these alkyl glucamines or whether it is due to impurities present, such as decomposition products which may be formed in their preparation. However, where foaming is not a problem or where foam depressants are added to prevent or minimize the foaming, these alkyl glucamines may be employed at the concentrations indicated.

The etching of aluminum with compositions using these "sugar amines" as scale inhibitors is best illustrated by the following examples:

Example I

A blend was prepared of a glucamine crude, prepared in the manner above described and caustic soda, containing 2.2% of the glucamine crude and 97.8 of flake caustic soda. The glucamine crude used had a syrup-like consistency and contained 12% water.

450 pounds of the blended composition was charged to a 600 gallon tank of water. Titration showed that the concentration, after charging was 4.2 ounces of composition per gallon of water.

This solution was then used for etching aluminum parts on a production basis, the parts being etched for about five minutes at 150° F. The etching operation was continued for eight hours a day for five days during which time solution additions were made to maintain the concentration between 2 and 5 ounces of the caustic per gallon. At the end of the fifth day the viscosity of the etching solution, due to the sodium aluminate held in solution, had increased to a point where it was difficult to rinse the etched parts. The specific gravity of the solution, at this point, was 1.18 at 90° F. Because of this high viscosity the tank was emptied. Inspection of the tank showed that no alumina scale had formed. At the bottom of the tank, prior to emptying, about two inches of soft sludge was observed. This sludge was found to be made up of the alloying elements, such as copper, manganese and zinc, which were present in the aluminum parts that had been etched.

Example II

A caustic aluminum etching composition was prepared by blending glucamine syrup containing approximately 12% water and caustic soda to give a composition having 3% glucamine syrup and 97% caustic soda.

The resulting composition was added to 2500 gallons of warm water in the amount sufficient to give a concentration of 5 ounces per gallon. This solution was used

for etching aluminum articles, the solution being in use for two days during which time some additions were made to maintain the concentration at the 5 ounces per gallon level.

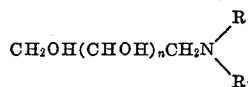
When the specific gravity of the etching solution had reached 1.195 at 90° F. the solution was dumped and the tank carefully observed. No scale formation was noted.

During the etching process a foam blanket about two inches thick was formed on the top of the etching solution. This blanket was particularly helpful in preventing caustic solution going into the air as fine spray, such sprays ordinarily being quite irritating to the workmen carrying out aluminum etching operations.

Though in the specific examples given, the sugar amines are employed in solutions of etching alkali wherein the alkali is present in amounts of about 5 ounces per gallon of solution, they are effective in any solution sufficiently alkaline to etch the aluminum. Etching solutions as used are generally within the concentration range of 1 to 15% by weight etching alkali.

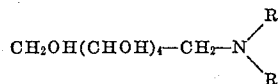
Having thus described our invention we claim:

1. The method of etching aluminum comprising treating said aluminum at an etching temperature with an aqueous solution of an etching alkali containing, in an amount sufficient to prevent scale formation, a hydroxy amine having the general empirical formula



wherein n is at least 2; R is any of the group consisting of hydrogen, another $\text{CH}_2\text{OH}(\text{CHOH})_n\text{CH}_2$ -radical, a normal alkyl radical containing not more than 4 carbon atoms, an α carboxyalkyl group containing not more than 4 carbon atoms and a β carboxyalkyl group containing not more than 4 carbon atoms exclusive of the carbon in the carboxy group and R_1 is any of a group similar to R with the exception that it does not contain another $\text{CH}_2\text{OH}(\text{CHOH})_n\text{CH}_2$ -radical.

2. The method of claim 1 wherein said hydroxy amine is a glucamine, having the general formula



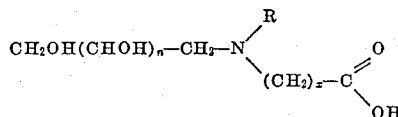
wherein R and R_1 represent the same substituents as in claim 1.

3. The method of claim 2 wherein said glucamine is diglucamine.

4. The method of claim 2 wherein said glucamine is monoglucamine.

5. The method of claim 2 wherein said glucamine is a glucamine crude obtained by hydrogenation of a mixture of glucose and ammonia in the presence of a hydrogenation catalyst at a pressure of at least 500 pounds per square inch gage.

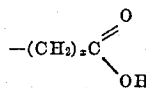
6. The method of claim 1 wherein said hydroxy amine is a carboxyalkyl hydroxy amine derivative having the general formula



where n is at least 2, x is a numeral of 1 to 3 and R is any of the group consisting of hydrogen, another



70 radical and another

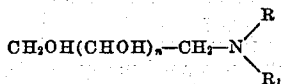


75 radical.

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7. The method of claim 6 wherein said carboxyalkyl hydroxy amine is sodium methyl carboxy glucamine.

8. A composition adapted for preparing aluminum etching solutions consisting essentially of an etching alkali and at least 0.5% by weight, based on the etching alkali, of a hydroxy amine having the general formula



wherein n is at least 2; R is any of the group consisting of hydrogen, another $\text{CH}_2\text{OH}(\text{CHOH})_n\text{CH}_2\text{---}$ radical, a normal alkyl radical containing not more than 4 carbon atoms, an alpha carboxy group containing not more than 4 carbon atoms and a beta carboxy alkyl group containing not more than 4 carbon atoms, exclusive of the carbon atom in the carboxy group, and R_1 is any of a group similar to R with the exception that it does not contain another $\text{CH}_2\text{OH}(\text{COCH})_n\text{CH}_2\text{---}$ radical.

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9. The composition of claim 8 wherein said etching alkali is primarily caustic soda.

10. The composition of claim 8 wherein said hydroxy amine is a glucamine.

11. The composition of claim 8 wherein said hydroxy amine is diglucamine.

12. The composition of claim 8 wherein said hydroxy amine is monoglucamine.

13. The composition of claim 8 wherein said hydroxy amine is a carboxy alkyl glucamine in which the alkyl group has not over 3 carbon atoms.

14. The composition of claim 13 wherein said carboxy alkyl glucamine is sodium methyl carboxy glucamine.

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