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ALKALI ETCHANT COMPOSITION FOR ALUMINUM HAVING EXTENDED BATH LIFE

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Int. Cl. C23f 1/04
U.S. Cl. 252—79.5 2 Claims

ABSTRACT OF THE DISCLOSURE

An alkali etching composition for aluminum is comprised of an aqueous solution of alkali metal hydroxide, hexavalent chorium ion, chelating agent, and a minor proportion of fluoroalkyl surfactant. The composition provides more efficient alkali consumption and a longer bath life.

This invention pertains to compositions for the etching of aluminum and aluminum alloys. More particularly, this invention concerns an alkali composition which, as an aqueous alkali etching solution for aluminum, provides more efficient alkali consumption and longer bath life due to the incorporation therein of a specifically defined minor proportion of fluoroalkyl surfactant.

Industrial aluminum finishers usually process their product in an aqueous alkaline etching bath to remove surface imperfections and generally to enhance the appearance of the aluminum or aluminum alloy product. In such operations it is desirable for obvious economic reasons to produce good finishes with the smallest possible consumption of etching chamicals while endeavoring to employ the etchant baths over an extended period of time without the need for frequent costly dumping and recharging. The conventional, previously used, alkaline etching compositions suffer from deficiencies in these areas in the following respects. Conventional alkaline etchant systems, such as that disclosed in my U.S. Pat. 3,314,890, generally involve the removal of a relatively large amount of metal from the surface of the treated aluminum object to produce an acceptable finish. In accomplishing this metal removal, as much as 1.6 to 3.5 pounds of etchant composition are consumed for every pound of aluminum that is removed from the object's surface and thus solubilized. This high alkali consumption makes frequent replenishment of the etchant bath necessary. Moreover, the increasing concentration of dissolved aluminum in these baths causes an undesirable increase in density; accordingly, when the specific gravity of the alkali etchant bath reaches about 1.2, it must be disposed of because its use results in unacceptable finishes from etch defects such as "galvanized etch," "pin-burn" and "caustic-burn." In addition, the baths having high aluminum contents are very viscous resulting in a considerable "drag-out" of material from the bath. It is also difficult to get a good rinse-off of this residual, viscous etchant composition from the aluminum. The foregoing disadvantages are surprisingly and significantly alleviated by the use of the etchant composition of this invention.

The novel aqueous etching solution of this invention produces a desired architectural finish on aluminum and aluminum alloys that may be described as an etched finish, gray white to white in color, having a non-metallic appearance, having a low or matte reflectance, having a uniform fine grained appearance independent of any underlying aluminum grain boundaries and having what is known in the trade as an excellent hide, that is, all extrusion, die marks and scratches are completely hidden. In addition to the production of an aluminum finish of excellent quality employing this invention, the etchant

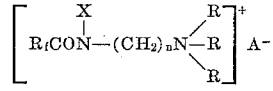
consumption is significantly reduced to the extent that there is about 10% to 25% less consumption of the etchant chemicals than that incurred using the conventional etching compositions to accomplish an equivalent amount of surface finishing. Moreover, the bath life is appreciably extended because the solution can be used without causing product surface defects until the specific gravity of the bath is increased by dissolved aluminum to a value of from about 1.35 to 1.50, compared to a specific gravity of 1.20 for the previously known baths at which point dumping would be required to avoid defective etching.

This invention provides an alkali etching composition for aluminum and aluminum alloys comprised of an aqueous solution containing (A) from 3.75 to 209 grams per liter of alkali metal hydroxide, (B) water-soluble hexavalent chromium ion ranging in amount of at least 0.035% by weight of the alkali metal hydroxide content and no greater than 11 grams per liter, (C) chelating agent ranging in amount of at least 3% by weight of the alkali metal hydroxide content and no greater than 44 grams per liter and (D) fluoroalkyl surface active agent ranging in amount of at least 0.0002% by wegiht of the alkali metal hydroxide content and up to 0.44 gram per liter. Since it is uneconomical and sometimes impractical to ship aqueous solutions for long distances, an embodiment of the invention comprises the solid granular compositions which are capable of forming the foregoing aqueous solutions by mixing in water. In the solid granular (dry blend) compositions the components are present in the following ranges in percents by weight: (A) from 80% to 95% of alkali metal hydroxide, (B) from 0.035% to 5% of water-soluble hexavalent chromium, (C) from 3% to 20% of chelating agent, and (D) from 0.0002% to 0.2% of fluoroalkyl surfactant, said percentages of (B), (C) and (D) based on the weight of the alkali metal hydroxide (A). The total of the four components will, of course, be 100%. The composition of this invention can also be conveniently handled as a liquid concentrate comprised of from 15 to 60 weight percent of the aforesaid granular composition and from 40 to 85 weight percent water.

Sodium hydroxide is the principal source of the alkali metal hydroxide because it is inexpensive as compared to potassium or lithium hydroxide. However, potassium hydroxide or other alkali metal hydroxides are equally efficient in these compositions. The source materials for the hexavalent chromium ion are one or more of the well-known water-soluble ionizable chromium containing compounds. They may be selected from the group which includes sodium dichromate, potassium dichromate, ammonium dichromate, sodium chromate, potassium chromate, chromic anhydride, sodium chrom glucosate and potassium chrom glucosate. The above sources of hexavalent chromium ion are all normally solid materials and of course are useful in preparing the solid granular concentrates which are used in making the etching solutions. The third component of the formulation which acts as a surface modifier with respect to the action of the alkali metal hydroxide etchant on aluminum and aluminum alloys is a special group of well-known surface modifyingg agents of the chelating type which combine with the hexavalent chromium to modify the attack of the caustic soda and to prevent precipitation of aluminum salts from solution. Suitable chelating agents include sorbital, mannitol, ascorbic acid, sorbose, tannic acid, ethylene diaminetetraacetic acid, diglycolic acid, picolinic acid, aspartic acid, dithiooxamide, 1-rhamnose, b-fructose, glycerol, maleic acid, mannose, succinic acid, sucrose, tartaric acid and the like.

It is, however, the incorporation of the previously prescribed small but effective amount of fluoroalkyl surfac-

tant in the etchant composition that provides the surprising results of reduced chemicals consumption and extended bath life. There are a large number of polyfluoroalkyl surface active agents available for use in the compositions embodied herein. Representative agents include the following classes of compounds: the acid R_fCOOH, where R_f is perfluoroalkyl of about 4 to about 16 carbon atoms, and the alkali metal and ammonium salts of said acid (see, for example, U.S. 2,567,011); the perfluoroalkyl quaternary nitrogen compounds, e.g., of U.S. 2,764,602 and U.S. 2,759,019,



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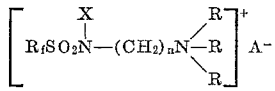
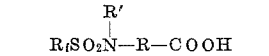


where n is 2 to 6, X is hydrogen or lower alkyl, the R groups are hydrocarbon groups and A is an anion; the acids and alkali metal and ammonium salts of the acids described in U.S. 2,809,990,



where R is an alkylene group and R' is hydrogen or alkyl; the acids and salts of U.S. 2,951,051, i.e.,

$$R_fCH_2RCH_2COOH$$

where R is alkylene; the fluoroalkyl phosphinic acids and salts such as described in U.S. 3,047,619; the fluoroalkyl carboxylic acids and salts described in U.S. 3,232,970; the fluoroalkyl amido carboxylic acids and salts described in U.S. 3,238,235, the fluoroalkyl acids and salts described in U.S. 3,311,566; the fluoroalkyl sulfonic acids and salts described in U.S. 2,732,398 and U.S. 2,950,317; and other like polyfluoroalkyl surfactants known in the art of surface-active materials.

In using the etching solutions of this invention, the aluminum or aluminum alloy is first cleaned with a conventional aluminum cleaner which may be of the alkaline or acid type to remove oxides and soil which might obstruct the etching action. After cleaning, the aluminum is rinsed with water, preferably warm, and is then immersed in or sprayed with the etching solution held at a temperature within the range of 150 to 200° F. However, at temperatures less than 150° F. the solutions are effective in preventing the unwanted effect known in the industry as "galvanizing." The preferred temperature range for securing the preferred architectural finish is within the range of 160° to 180° F. The metal workpiece is allowed to remain in contact with the etchant solution until the desired etch is obtained. Generally this will vary from one to 15 minutes depending on the concentration of the ingredients in the bath and the temperatures used. Suitable etching is often obtained in about 3 to 7 minutes.

Following etching the work piece is then rinsed at least once with water, preferably warm, and then the work piece is desmutted to remove the metal particles which are insoluble in the etching solution. Since the present etching solutions have a considerable concentration of chromium contained therein it is unnecessary to use a chromated desmutter, and in fact, a nonchromated desmutter is preferred.

The following examples are presented to illustrate the invention and not to limit its scope as described herein above and defined by the claims.

Etchant baths were prepared having the following compositions wherein the proportions are expressed in grams of ingredient per liter of aqueous solution and in weight percent based on a dry composition basis.

	Grams/ l.	Weight percent
Bath A, control:		
Sodium hydroxide	69.4	92.5
Sorbitol	3.75	5.0
Sodium chromate	1.875	2.5
Bath B, U.S. 3,314,890:		
Sodium hydroxide	67.4	90.0
Sorbitol	3.75	5.0
Sodium chromate	1.875	2.5
Sodium fluoride	1.875	2.5
Bath C, this invention:		
Sodium hydroxide	69.4	92.5
Sorbitol	3.75	5.0
Sodium chromate	1.875	2.5
$C_8F_{17}SO_2N(CH_3)CH_2CH_2N(CH_3)_3{}^+I^-$	0.0012	0.0015
$C_8F_{17}SO_2N(C_2H_5)(CH_2CH_2O)_4H$	0.0004	0.0005

Aluminum etchant studies were made with the above baths on 6063 alloy aluminum at 155–165° F. Concentrations were maintained during the tests by replenishment with fresh solution. Tests were continued until each etching efficiency required its disposal. In contrast, a Bath Bath A and Bath B were relatively very viscous compared to Bath C, resulting in defective etching characteristics for A and B while C bath remained operable. For a comparable amount of aluminum finishing, the consumption of etchant materials in Bath C was 18.9% and 19.7% less than in Baths A and B, respectively.

In production runs of aluminum finishing employing 7000 gallon etchant baths, a "Bath B" type composition was used for two weeks with appropriate replenishment before an unacceptable increase in viscosity and lack of etching efficiency required its disposal. In contrast, a Bath C composition was used for some nine weeks with appropriate replenishment before disposal became necessary.

The following representative fluoroalkyl surfactants were substituted for the surfactant of Bath C above, and the minimum effective concentration thereof was determined in order to obtain the maximum advantages of this invention.

Fluoroalkyl surfactant	Surfactant concentration, percent of weight of etchant composition
$C_8F_{17}SO_3K$	0.10
$C_8F_{17}COONH_4$	0.10
$C_8F_{17}SO_2N(C_2H_5)CH_2COOK$	0.0009
$C_8F_{17}SO_2N(CH_3)CH_2CH_2N(CH_3)_3{}^+I^-$	0.00079
$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OPO(OH)_2$	0.002
$C_8F_{17}SO_2N(C_2H_5)(CH_2CH_2O)_{14}H$	0.00026
$C_8F_{17}SO_2\underset{\displaystyle H}{\underset{\vert}{N}}CH_2CH_2CH_2N^+(CH)_3CH_2CH_2COO^-$	0.01
$CF_2Cl(CF_2)_7CONH(CH_2CH_2O)_{11}H$	0.00026

The foregoing data illustrate that extremely small quantities of the fluoroalkyl surfactant are needed to produce marked improvements in aqueous alkali etchant compositions. Thus, a particularly noteworthy feature of the invention is the remarkable economic benefits it affords by the incorporation of such small amounts of fluoroalkyl surfactant in the etchant composition.

I claim:

1. A composition for the etching of aluminum and aluminum alloys comprised of an aqueous solution of (A) from 3.75 to 209 grams per liter of alkali metal hydroxide, (B) water-soluble hexavalent chromium ion ranging in amount of at least 0.035% by weight of the alkali metal hydroxide and up to 11 grams per liter, (C) chelating agent ranging in amount of at least 3% by weight of the alkali metal hydroxide and up to 44 grams per liter and (D) fluoroalkyl surfactant ranging in amount of at least 0.0002% by weight of the alkali metal hydroxide and up to 0.44 gram per liter.

2. The solid granular composition capable of forming the aqueous etching solution of claim **1** comprised of (A) from 80% to 95% of alkali metal hydroxide, (B) from 0.002% to 0.2% of fluoroalkyl surfactant, hte precent- (C) from 3% to 20% of chelating agent and (D) from 0.0002% to 0.2% of fluoroalkyl surfactant, the percentages of (B), (C) and (D) being based on the weight of the alkali metal hydroxide (A).

References Cited

UNITED STATES PATENTS

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JACOB H. STEINBERG, Primary Examiner

U.S. Cl. X.R.

252—79.3; 156—18

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,557,000 Dated January 19, 1971

Inventor(s) Harold Vernon Smith

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

PAGE 3

on the weight of the alkali metal hydroxide 'A)."

should read

--0.035% to 5% of water-soluble hexavalent chromium, 'C) from 3% to 20% of chelating agent and 'D) from 0.0002% to 0.2% of fluoroalkyl surfactant, the percentages of 'B), 'C) and 'D) being based on the weight of the alkali metal hydroxide 'A).--.

Signed and sealed this 27th day of April 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER,
Commissioner of Pate