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3,689,417

POWDERLESS ETCHING BATH

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U.S. Cl. 252—79.3

5 Claims

ABSTRACT OF THE DISCLOSURE

An improved powderless etching bath for etching aluminum or an aluminum-base alloy comprising (a) an acid aqueous solution containing sulfuric acid, (b) metal ions of a metal having an ionization tendency less than that of aluminum, (c) a water-immiscible organic liquid, (d) a phosphate ester anionic surfactant, and (e) a nonionic surfactant.

This invention relates to an improved powderless etching bath for etching aluminum or an aluminum-base alloy.

Powderless etching technique has been well known per se. Generally, in the technique of powderless etching to make such objects as a photoengraving printing plate, a flat or cylindrical plate of an acid-soluble metal is coated with a light-sensitive coating or enamel. The coated surface is exposed to light through a negative having an image thereon so as to produce a corresponding image on the coating. The exposed coating surface is developed, forming an acid-resistant coating in the form of the image produced by the exposure. This acid resistant coating is further hardened by heating and the final acid-resistant image is called the "resist." The image-bearing surface of the plate is then subjected to etching by an acid to produce the image in relief. It is necessary in carrying out the etching process that techniques be employed to reduce lateral etching, so-called "side-etch," which undercuts the resist and/or relief side-walls causing a weakening, distortion, or complete loss of the image. The etching bath employed usually consists of a major amount of an aqueous solution of an acid as the etching agent and a minor amount each of a water-immiscible organic liquid and a filming agent. The filming agent is composed of an anionic surface active material having both hydrophobic and hydrophilic properties, such as sulfated or sulfonated organic compounds or phosphate esters. These compounds in fact act to reduce the side-etch of the resist, although a theory relating to their functional mechanism has not yet been fully established. Etching of little side-etch and high precision is rated by an "etch factor." The etch factor is defined as the ratio of the depth of the etch adjacent to a line of resist divided by one-half of the total loss in width, i.e. side-etch, of metal immediately beneath the resist.

Powderless etching of zinc, magnesium or their respective metal-base alloys and various etching baths used in such etching are known, for instance, by U.S. Pats. 2,640,763, 2,640,764, 2,763,536, 2,979,387, 3,023,138, and 3,337,462. It is currently a wide practice to etch the zinc, magnesium, or their alloys using etching baths containing an aqueous solution of nitric acid as an etching agent. Aluminum or an aluminum-base alloy cannot be etched with such nitric acid aqueous solution. In our co-pending application Ser. No. 783,717 filed Dec. 13, 1968, now U.S. Pat. No. 3,607,484. It is described that aluminum or an aluminum-base alloy is etched with advantage by using an etching bath comprising an aqueous solution

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of sulfuric acid containing metal ions of a metal having an ionization tendency less than that of aluminum and halogen ions, a water-immiscible organic liquid and a phosphate ester surface active agent. The present invention is an improvement over the invention of the co-pending application.

As regards printing plates, aluminum or its alloy is less expensive than zinc, magnesium or their alloys hitherto employed, and lends itself to easier handling as it is lighter in weight than zinc. In addition, it has a marked advantage of prolonging the life of a printing machine. But the etching bath to be used should not corrode an acid resistant coating and should have a practical rate of etching aluminum and a high etch factor. It is also desired that the etching bath should be easily handled, not evolve noxious gases such as nitrous oxide and should be readily emulsified. The etching bath for aluminum or its alloy used in the present invention meets all of these requirements.

Accordingly, an object of the present invention is to provide an improved bath for powderless etching of aluminum or an aluminum-base alloy.

The powderless etching bath for etching aluminum or aluminum-base alloy comprises:

- (a) an acid aqueous solution of the normally of 0.8 N to 10 N, said acid being sulfuric acid or a mixture of sulfuric acid and at least one other inorganic acid where more than one-half of said normality value is due to the sulfuric acid present,
- (b) a metal or its compound soluble in ingredient (a), said metal having an ionization tendency less than that of aluminum,
- (c) a water-immiscible organic liquid,
- (d) a phosphate ester anionic surface active agent, and
- (e) a nonionic surface active agent,

the proportion of the ingredients in the bath being one liter of (a), 0.01–7 gram ion (b) as the metal, 10–100 milliliters of (c), 0.5–80 grams of (d), and 0.05–24 grams of (e) where the amount of (e) is in the range of 10–30% by weight of (d).

The etching method of the present invention comprises providing the etching bath described in claim 1, bringing the etching bath to a well emulsified condition, and impinging the etching bath upon the metal surface to be etched.

Metals to be etched by the etching bath of the present invention are pure aluminum, industrially pure aluminum and aluminum-base alloys. By the aluminum-base alloy, used herein, is meant an alloy containing at least 80% by weight of aluminum. When it is desired to produce printing plates, an alloy containing at least 90% by weight of aluminum and the balance being zinc and/or tin is usually used and the etching bath of the present invention is suitable for application to such alloys. The aluminum and aluminum-base alloys will hereinafter be referred to simply as aluminum.

The ingredients used to prepare the etching bath of the invention will be described.

The acid aqueous solution employed as ingredient (a) is a predominant component for etching aluminum, and the acid consists mainly of sulfuric acid. An aqueous nitric acid solution conventionally employed to etch zinc or magnesium does not etch aluminum at all, but an aqueous solution of sulfuric acid etches aluminum at a practical rate. Aqueous sulfuric acid solutions of 0.8–10 N (corresponding to about 3.8–38% by weight of H_2SO_4) are used. Good results are obtained with the normality of 1.5 N to 3 N. Together with sulfuric acid, a minor amount of an aqueous solution containing other inorganic acids can be used. As the inorganic acids, hydrochloric acid, hydrofluoric acid, nitric acid and phos-

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phoric acid are used with especially favorable results. The other inorganic acids to be mixed act to accelerate the rate of etching aluminum with sulfuric acid. The ratio of such inorganic acid to be mixed should not exceed one-half of the normality of the acid aqueous solution (0.8–10 N). For example, when the acid aqueous solution has a normality of 2 N, it is necessary that at least one N should be based on the sulfuric acid.

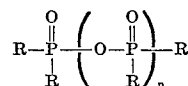
Ingredient (b) is a metal or its compound soluble in ingredient (a), an acid aqueous solution, said metal having an ionization tendency less than that of aluminum. The ingredient (b) is dissolved in ingredient (a) to become metal ions, and acts to accelerate the rate of etching aluminum. Metals having an ionization tendency less than that of aluminum are well known, and included within such metals are zinc, chromium, iron, cadmium, cobalt, nickel, tin, copper, mercury, and antimony. Of these, ions of Cu, Ni, Co and Fe have proved to have an especially marked effect of promoting the rate of etching aluminum. It has been found that the ions of Cu and Ni not only contribute to an increased etching rate, but also ensure the formation of a smooth etched surface and the achievement of a high etch factor. The elemental metals themselves may be used as component (b) if they are soluble in component (a). Usually, however, the metal compounds more readily soluble in ingredient (a) are used with preference. Examples of such compounds include inorganic acid salts of metals, such as the sulfates, nitrate, halides, phosphates and carbonates; organic acid salts of the metals, such as the formates, acetates and salts of higher fatty acids, and oxides and hydroxides of the metals. The amount of the ingredient (b) is 0.01–7 gram-ions, preferably 0.05–1 gram-ion, calculated as the metallic ion based on one liter of the ingredient (a).

The water-immiscible organic liquid used as ingredient (c) acts to reduce the side etch of a metal substrate to be etched. This is an essential component of all of the powderless etching baths heretofore known, and the various usable organic liquids are known. All of such known compounds are applicable in the present invention. The examples of these compounds include aliphatic, aromatic or naphthenic hydrocarbons (for instance, xylene, cumene, kerosene); hydrocarbon-type lubricant oils; aromatic solvents (for instance, Solvesso of Esso, U.S.A. and Swasol of Maruzen Oil Co., Japan); aliphatic solvents (for instance, Victoria Oil of Shell Oil, U.S.A.); terpene; liquid paraffin; machine oil; chlorinated hydrocarbons (for instance, liquid chlorinated paraffins and chlorinated diphenyl); unsaturated higher fatty acids; and natural oils and fats. Because of heat of reaction, the etching bath attains a maximum of 70 to 80° C. during etching; therefore, the organic liquid used ordinarily has a boiling point above 90° C. In order to minimize the loss owing to volatilization, those having a boiling point of above 150° C., especially 180 to 390° C., are used with preference. The amount of ingredient (c) is usually 10–100 milliliters, preferably 20–70 milliliters, per liter of ingredient (a).

The phosphate ester anionic surface active agent used as ingredient (d) has both hydrophobic and hydrophilic properties, and has an action of emulsifying and dispersing the ingredient (c), organic liquid, in ingredient (a), acid aqueous solution, forming a film on relief side-walls of the metal to be etched in cooperation with the organic liquid, and thus reducing the side-etch. Such surfactants are usually called filming agents. Typical examples of the known filming agents are sulfated or sulfonated organic compounds and phosphate ester compounds. The latter compounds are disclosed in U.S. Pat. No. 3,337,462. It has now been found that in etching aluminum, phosphate ester surfactants give especially good results as filming agents. The phosphate ester compounds used in

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the invention are phosphate esters or polyphosphate esters expressed by the general formula



wherein n is 0, 1 or an integer of usually up to 10, and R is a group $\text{A}-\text{O}-(\text{C}_2\text{H}_4\text{O})_a-(\text{C}_3\text{H}_6\text{O})_b-$, in which A is a hydrogen atom or a hydrocarbon radical, and a and b are 0, 1, or an integer of usually up to 9; the R's may be the same or different and A in at least one R is hydrocarbon radical. Within the hydrocarbon radical expressed by A are included saturated or unsaturated alkyl groups, aryl groups, alkaryl groups and aralkyl groups. Preferred are hydrocarbon radicals having 6–18 carbon atoms. Examples of particularly preferred hydrocarbon radicals are octyl group, nonyl group, decyl group, dodecyl group, oleyl group, myristyl group, naphthyl group, nonyl phenyl group and dodecyl phenyl group. When A represents hydrogen, it may be in the form of a salt or adduct. Of course, these phosphate ester compounds may be in the form of a mixture. The amount of ingredient (d) is 0.5–80 grams, preferably 1–10 grams, per liter of the ingredient (a).

The nonionic surface active agent as ingredient (e) is not used in the conventional etching baths. This is one of the characteristic ingredients used for the first time in the present invention. It has been found that the addition of a small amount of the nonionic surface active agent to an etching bath results in a marked reduction in the side-etch of the resist. This is more surprising in view of the fact that unlike anionic surfactants, nonionic surfactants are hardly capable of forming a film of the organic liquid when used singly. The nonionic surfactant used in the invention assists the emulsifying capability of the phosphate ester anionic surfactant to produce a well emulsified etching bath with ease, and ensures a stable and smooth etching operation. Accordingly, the nonionic surfactant has the advantage of replacing a part of the phosphate ester surfactant which is relatively expensive. This makes it possible to save about 10–20% of the amount of phosphate ester to be used which is required when the nonionic surfactant is not added. Thus, the nonionic surfactant and the phosphate ester are considered to exhibit a synergistic effect.

The amount of the nonionic surfactant is chosen within the range of 0.05–24 grams, preferably 0.07–16 grams, per liter of ingredient (a), and it is proper that the amount is 10–30%, preferably 14–20%, based on the weight of ingredient (d).

A number of nonionic surface active agents have been known heretofore. All of such known compounds can be used in the invention if they are substantially stable in the presence of the acid in the bath. Examples of various types of nonionic surfactants used with good results in the present invention are ethers such as polyoxyethylene cetyl ether, and polyoxyethylene nonyl phenyl ether, esters such as sorbitan monolaurate, sorbitan trioleate, polyoxyethylene sorbitan monostearate, polyethylene glycol distearate and saccharose ester, pluronic types such as an oxyethylene-oxypropylene block copolymer, condensed amines or amides such as polyoxyethylene lauryl amine, and polyoxyethylene stearylamine, and polyethylene imines such as polyethylene imine oleyl ether.

The anionic phosphate ester surfactants as ingredient (d) are prepared from nonionic surfactants. In this case, it is possible to leave some of the nonionic surfactant in the product without completing the esterification reaction. If such phosphate ester surfactants containing unreacted nonionic surfactant are used, the nonionic surfactant contained there can be utilized as ingredient (e) and it is not necessary to add ingredient (e) separately. In any case, the requirement is that the ingredients (d) and (e) should be contained in the etching bath in the proportions specified above. A combined amount of ingredients (d) and (e)

may be as small as less than one gram per milliliter of the organic liquid employed as ingredient (c).

The etching bath of the present invention consists of the above-mentioned ingredients. For convenience of storage or transportation before application to the etching operation, it is possible to prepare a concentrated mixture of ingredients (a) and (b) and a mixture of ingredients (c), (d) and (e) separately and mix and dilute them prior to use.

The method of etching aluminum or an aluminum-base alloy of the present invention is practised by using the above-described etching bath. The operation of etching may be the same as the conventional powderless etching process. Impinging the etching bath upon the metal surface to be etched can be effected by spray jetting the bath or splashing it by means of a paddle.

The rate of etching aluminum or an aluminum-base alloy achieved by using the etching bath of the present invention is substantially equal to that previously known with respect to the etching of zinc or magnesium. The depth of etching required of printing plates is usually 0.4–0.5 mm. According to the present invention, this depth can be attained generally in 4 to 15 minutes. The method of the present invention is also applicable to the production of name plates, templates, print-wiring and the like.

Specific examples of the invention will be given below.

EXAMPLE 1

A 72S aluminum alloy (Alcoa standards) plate having a thickness of 1 mm., a length of 50 mm. and a width of 50 mm. was coated with an acid-resistant light-sensitive coating, and an image of two lines each having a width of 0.2 mm., 0.4 mm., 0.6 mm., 0.8 mm. and 1 mm., respectively drawn at intervals of 3 mm. was exposed, and developed to prepare test pieces.

Ten grams of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 10 g. of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in one liter of an acid aqueous solution containing 2 N H_2SO_4 and 1 N HCl , followed by addition of 40 ml. of a mixture of 85% by volume of Swasol-1800 (product of Maruzene Oil Co., Japan) and 15% by vol-

ume of liquid paraffin as the organic liquid. Phosphoric ester of polyethylene lauryl ether as the filming agent and polyethylene lauryl ether as the nonionic surfactant were then added in the proportions indicated in Table 1 to prepare an etching solution.

The test piece was mounted in a small-sized paddle-type etching machine, and etched at a temperature of 28° C. with the number of rotation of the paddle maintained at 1,500 r.p.m. for the time indicated in Table 1. The etched piece was withdrawn, washed with water, and dried. The etch factor and the etch depth were measured with respect to each test piece. The results are shown in Table 1.

TABLE 1

Amount of phosphoric ester (g.)	Amount of nonionic surfactant (g.)	Etching time (minutes)	Etch factor	Depth of etch (mm.)
4.0*	0	8	22	0.58
4.0	0.1	8	30	0.51
3.9	0.2	8	37	0.50
3.6	0.4	8	46	0.48
3.2	0.6	8	50	0.40
2.9	0.8	10	47	0.32
2.5	1.1	10	52	0.20

EXAMPLE 2

The same procedure as set forth in Example 1 was repeated using aluminum or aluminum-base alloy of the following composition.

Samples:

- A ----- 2S (Alcoa standards).
- B ----- 17S (Alcoa standards).
- C ----- 72S (Alcoa standards).
- D ----- 0.5% Zn, the balance Al.
- E ----- 0.5% Zn, 0.1% Sn, the balance Al.
- F ----- 1% Zn, 0.2% Sn, the balance Al.
- G ----- 1.5% Zn, the balance Al.

The results obtained are given in Table 2.

TABLE 2

Run No.	Acid solution		Filming agent and nonionic surfactant compound (g./acid soln., 1 l.)	Organic water-immiscible liquid compound (ml/acid. soln., 1 l.)	Plate alloy	Etching condition		Etching results	
	Acid (normality)	Metal salt (g./acid soln., 1 l.)				Time (min.)	Temp. of bath (° C.)	Depth (mm.)	Etch factor
1	H_2SO_4 (2.5)	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (20), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (20).	Lauryl oxyethylene phosphate (4), sorbitan mono-laurate (0.4).	Solvesso-150 (40)	C	10	28	0.30	52
2	H_2SO_4 (2.5), HCl (0.5).	FeCl_3 (10)	oleyl oxyethylene phosphate (5), oleyl oxyethylene ether (0.5).	Solvesso-100 (50)	F	15	30	0.21	55
3	H_2SO_4 (4), HCl (0.35).	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (10)	Octylphenol phosphate (5), pluronic type surfactant (1).	Kerosene (30), toluene (40).	E	5	28	0.50	30
4	H_2SO_4 (2.5), HCl (1), HNO_3 (0.05), H_3PCl_4 (1).	$\text{Cu}(\text{CH}_3\text{COO})_2$ (15), SnCl_4 (1).	Tridecyl oxyethylene propylene phosphate (5), glycerin mono-oleate ester (1.5).	Solvesso-150 (45), liquid paraffin (5).	G	8	28	0.42	51
5	H_2SO_4 (2.5), HCl (1), HF (0.2).	$\text{Cu}(\text{OH})_2$ (10), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (10), FeCl_3 (5).	Tridecyl polyphosphate (5), lauryl oxyethylene ether (0.6).	Solvesso-150 (45), castor oil (5).	C	4	28	0.50	23
6	H_2SO_4 (2.5), HCl (1).	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (10), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (10).	Phosphate ester of polyoxyethylene lauryl ether containing 15% of the unesterified ether (8).	Victoria oil (50)	C	8	28	0.45	50
7	H_2SO_4 (2.5), HCl (1).	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (8), Fepowder (5).	Lauryl oxyethylene pyrophosphate (8), lauryl oxyethylene ether (0.2).	n-Paraffin (50)	C	8	28	0.40	34
8	H_2SO_4 (3), HCl (1).	$\text{Zn}(\text{OH})_2$ (100), SnCl_4 (0.1).	Polyphosphate ester of the mixture of lauryl polyoxyethylene ether and lauryl polypropylene ether (5), oleylphosphate (1), lauryl amine-ethylene oxide adduct (0.9).	Solvesso-100 (25), xylene (25).	C	8	28	0.50	45
9	H_2SO_4 (5), HCl (3).	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (20)	Dodecyl oxyethylene phosphate (10), polyoxyethylene stearyl amide (1).	Solvesso-100 (50)	A	8	28	0.25	43
10	H_2SO_4 (2.5), HCl (2), HNO_3 (0.05).	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (20)	Dodecyl oxypropylene phosphate (10), dodecyl oxyethylene ether (1).	Swasol-1800 (50)	B	8	28	0.30	40
11	H_2SO_4 (2.5), HCl (2).	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (20).	Phenyl oxyethylene phosphate (15), polyethylene imine stearyl ether (2).	Liquid paraffin (90)	B	8	28	0.31	40

TABLE 2—Continued

Run No.	Acid solution		Filming agent and nonionic surfactant compound (g./acid soln., 1 l.)	Organic water-immiscible liquid compound (ml/acid. soln., 1 l.)	Plate alloy	Etching condition		Etching results	
	Acid (normality)	Metal salt (g./acid soln., 1 l.)				Time (min.)	Temp. of bath (° C.)	Depth (mm.)	Etch factor
12.....	H ₂ SO ₄ (2.5), HCl (2).	NiCl ₂ ·6H ₂ O (20)	Phosphate ester by esterifying triethylene glycol mono-laurate ether with an equimol phosphorus oxychloride followed by adding 3 mol ethylene oxide (15), sucrose acetic ester (2).	Diphenyl chloride (3), Solvesso-150 (27).	C	8	20	0.38	38
13.....	H ₂ SO ₄ (7), HCl (1).	CuCl ₂ ·2H ₂ O (10)	Dodecyl oxyethylene phosphate (15), nonylphenol oxyethylene ether (5).	Methylethyl ketone (70).	D	8	28	0.50	29
14.....	H ₂ SO ₄ (1), HCl (0.5).	CuCl ₂ ·2H ₂ O (5), NiCl ₂ ·6H ₂ O (10).	Octylphenol oxyethylene phosphate (10), octylphenol oxyethylene ether (2).	Solvesso-150 (50)	C	8	30	0.42	48

What we claim is:

1. A powderless etching bath for etching aluminum or an aluminum-base alloy which comprises:

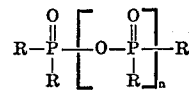
- (a) an acid aqueous solution of the normality of 0.8–20 10 N, said acid being selected from the group consisting of sulfuric acid and a mixture of sulfuric acid and at least one inorganic acid selected from hydrochloric acid, hydrofluoric acid, nitric acid and phosphoric acid, more than one-half of said normality value being based on the sulfuric acid present, 25
(b) a metal ion having an ionization tendency less than that of aluminum,
(c) a water-immiscible organic liquid,
(d) a phosphate ester anionic surface active agent, and 30
(e) a nonionic surface active agent,

the proportions being 0.01–7 gram-ions of (b), 10–100 milliliters of (c), 0.5–80 grams of (d), and 0.05–24 grams of (e) where the amount of (e) is in the range of 10–30% by weight of (d) per one liter of (a).

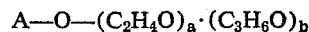
2. The bath of claim 1 wherein the metal ion of (b) is an ion of a metal selected from Cu, Ni, Co and Fe.

3. The bath of claim 1 wherein said water-immiscible organic liquid (c) is selected from the group consisting of aliphatic hydrocarbons, aromatic hydrocarbons, naphthenic hydrocarbons, hydrocarbon lubricant oils, terpene, liquid paraffin, chlorinated hydrocarbons, unsaturated higher fatty acids, and natural fats, said organic liquid having a boiling point higher than 80° C. 40

4. The bath of claim 1 wherein the phosphate ester of (d) is expressed by the formula



wherein n is 0 to 10, and each R is a group



in which A is selected from a hydrogen atom and a hydrocarbon radical, and a and b are 0 to 9, A in at least one R being a hydrocarbon radical.

5. The bath of claim 1 wherein the combined amount of (d) and (e) does not exceed one gram per milliliter of (c).

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156—14, 22; 252—79.4