United States Patent Office 3,725,158
Patented Apr. 3, 1973



3,725,158

# MULTI-COMPONENT POWDERLESS ETCHING BATH ADDITIVE

Harold J. Messerschmidt, Jr., Stockholm, Karl Heyman, Montclair, and Bernadou W. Johnsen II, Paterson, N.J., assignors to Mona Industries, Inc., Paterson, N.J.

No Drawing. Filed Mar. 29, 1972, Ser. No. 239,340
Int. Cl. B44n 3/02; C23g 1/26
U.S. Cl. 156—14 33 Claims

## ABSTRACT OF THE DISCLOSURE

Improved powderless etching bath additive compositions, especially for etching magnesium photo-engraving plates, containing:

(a) at least one water-soluble or water-dispersible sulfonated fatty acid of from 8 to 24 carbon atoms, wherein the sulfur atom in the sulfonate group is directly bonded to a carbon atom;
(b) at least one saturated or olefinically unsaturated mono-carboxylic acid of from 8 to 24 carbon atoms;
(c) at least one lower mono-carboxylic acid of from 2 to 6 carbon atoms and/or poly-carboxylic acid of from 2 to 10 carbon atoms;
(d) at least one polyhydric alcohol of from 2 to 10 carbon atoms or an ether derivative thereof, and
(e) at least one alkylaryl sulfonate having from 6 to 12 carbon atoms in the aryl moiety and having from 8 to about 18 carbon atoms in each alkyl moiety,

and etching baths containing such compositions and nitric acid and water, give outstanding etching performance, particularly improved definition of the printable area of the plate, depth of the half-tones, side wall smoothness, and, particularly, control of side wall slope and substantial elimination of hooking at print line points.

This invention relates to powderless etching and is more specifically concerned with improved additive compositions, both anhydrous and water based, for use in powderless etching baths. In further aspect, the invention relates to etching baths as such, particularly for chemically dimensioning photoengraving plates, and with a method of etching such plates, especially magnesium-based plates.

To make photoengraving plates a flat or cylindrical plate of an acid-soluble metal such as magnesium, zinc or one of their alloys, is coated with a light sensitive coating or "enamel." This coated surface is exposed to light through a negative having an image thereon so as to produce an image on the coating. The exposed coated surface is then developed to form an acid-resistant coating corresponding to the image produced by exposure. This coating may be further hardened by heating and the final acid-resistant image is called the "resist." Subsequently, the image bearing surface of the plate is subjected to etching by an acid to remove the metal which is not under the resist and thus to produce the image in relief.

In carrying out this etching process, techniques are employed to reduce lateral etching which undercuts the resist and/or the relief side walls, which undercutting may cause a weakening, distortion or complete loss of image.

A common method which the art formerly used for minimizing lateral etching consisted of powdering the sides of the relief with an acid-resistant powder, but this was a difficult and time-consuming operation which had to be repeated a number of times during the etching of each plate.

In recent years so-called "powderless" etching has been introduced and expanded. In this technique the etching bath is so formulated that the non-resist portion of the plate can be removed without the need for powdering the side walls.



Powderless etching is now a well-known, widely practiced technique. It is used to etch photoengraving plates and other similar shaped articles. Zinc, magnesium and alloys based thereon are generally used as the photoengraving plate metals.

In the growth of this art, it has been discovered that etching baths made up of aqueous solutions of nitric acid and one or more surfactants are quite suitable for powderless etching of zinc and/or magnesium. Many technological contributions have been made to this art, such as for example in U.S. Pats. 2,640,673; 2,640,764 and 2,640,766, according to which the aqueous nitric acid etching baths are modified by the incorporation therein of aliphatic acids, or esters of aliphatic acids with polyhydric aliphatic alcohols, or sulfonates of succinic acid diesters.

One characteristic of these etching baths is their tendency to permit localized defilming on relief side walls. This resuglts in a chipped surface which, in aggravated situations, causes poor printing plates. Another problem stems from the inability of these same baths to quickly form a protective film in the initial stage of etching that will protect the resist from lateral etching beneath it. Further, as the etching action of the acid penetrates to greater depths, here is a problem of preventing lateral etching of relief side walls. Another problem of great importance is the capacity of the etching bath to produce proper depths of etch in all areas of a combination plate, i.e., a plate having both line and half tone image areas. This latter problem, for example, is most vexing because the use of filming additives which may be expected to increase or stabilize the filming tendency of the etching bath usually also results in the production of lesser depths of etch in half tone areas of combination plates. On the other hand, while the use of smaller amounts of the filming additives might be expected to provide deeper etching in half tone areas, such modifications also tend to cause excessive etching and undercutting in open line areas of the same plate. These problems are often sufficiently serious to make the poor products which result therefrom readily apparent to even the casual observer, particularly as evidenced by a chewed appearance of the plate.

Many attempts have been made to remedy the situation and to formulate etching baths which will give acceptable etching speeds and good quality production. Thus, in more recent patents than those set forth above, newer and improved formulations have been disclosed, which employ a water-immiscible organic liquid. Thus the modern etching bath technology is generally based on aqueous nitric acid, a water-immiscible organic liquid and a surfactant. These modern etching baths have reached a high degree of commercial success and are in wide use throughout the world. Unfortunately, these modern etching baths still have a problem in that they are ecologically undesirable. The water-immiscible organic liquid, which is generally a petroleum solvent, is a serious pollutant. It is therefore desirable to eliminate this component from etching bath compositions or at least to reduce the level thereof as much as possible.

The most commonly commercially used surfactant in the powderless etching art is a material which is usually referred to in the trade as sulfonated castor oil. This is a commercially available material which is chemically misnamed. The material referred to is actually a *sulfated* castor oil, mainly the sulfate ester of ricinoleic acid (that is, the hydroxyl group of ricinoleic acid is esterified with sulfuric acid to add a sulfate group thereon). Other surfactants which have been recommended in the patent literature in combination with the water-immiscible organic liquid are sulfosuccinates, petroleum sulfonates, alkylaryl sulfonates, sulfated alcohols, sulfated fats and

oils other than sulfated castor oil, phosphates, esters, polyether non-ionic surfactants, and alkylaryl ether sulfonates.

It is, therefore, an object of this invention to provide a novel etching bath for zinc or magnesium based shaped articles such as photoengraving plates.

It is another object of this invention to provide an improved etching bath having markedly improved filming capacity and giving better side wall protection and decreased lateral etching.

It is a further object of this invention to provide a novel additive for use in aqueous nitric acid etching baths.

Other objects of this invention are to provide a novel etching bath capable of producing desired depths of etch in all kinds of image areas of combination plates, to provide an etching bath capable of forming a stable protective film to prevent or retard lateral etching and chipping of relief side walls and a smooth, uniform side wall permitting easy release from a matrix, besides having a visual appeal.

A still further object of this invention is to provide an improved etching bath for producing name plates, metal patterns, templates and the like.

In accordance with this invention there is provided an additive composition comprising:

(a) from about 0.5 to 90 percent by weight of at least one water-soluble or water dispersible anionic aliphatic sulfonated carboxylic acid containing at least one hydrophobic hydrocarbon group of from 8 to 24 carbon atoms attached to the carboxyl group and at least one sulfonate group attached to a carbon atom in said hydrophobic hydrocarbon group,

(b) from 0.5 to 90 percent by weight percent of at least one saturated or olefinically unsaturated monocarboxylic acid of from 8 to 24 carbon atoms,

(c) from 0.5 to 90 percent by weight of at least one saturated or olefinically unsaturated

(i) lower mono-carboxylic acid of from 2 to 6 carbon atoms and/or

(ii) lower poly-carboxylic acid of from 2 to 10 carbon atoms;

(d) from 5 to 95 percent by weight of at least one polyhydric alcohol of from 2 to 10 carbon atoms or an ether derivative thereof; and

(e) from 2 to 40 percent by weight of at least one alkylaryl sulfonate having from 6 to 12 carbon atoms in the aryl moiety and having from 8 to about 18 carbon atoms in each alkyl moiety,

optionally in the additional presence of a neutralizing amine.

While compositions containing components (a) through (d) as identified above show outstanding and substantial improvement relevant to prior art etching additives and bath compositions, the addition of component (e) appears to even further significantly improve and, in fact, permit, control of the slope of the side wall of the printable area surface of the plate and to also control, or substantially eliminate, erosion of, e.g., arrow points, ends of lines and similar configurations on the printable surface. The latter erosion phenomenon is referred to in the art as "hooking" or "chipping" and is only difficultly controlled with conventional additives or baths. The fact that use of component (e) in the instant invention actually reduces shoulder is particularly surprising because alkylaryl sulfonates have been conventionally used in the art in etching baths to achieve the opposite effect, i.e., to build up and widen the shoulder or side wall of the printing character. For instance, U.S. Pat. 2,979,387 to Easley et al. teaches the use of an alkylaryl sulfonate for a purpose which is diametrically opposed to one of the functions this component serves in the instant invention.

Apart from providing the additive compositions described above, the instant invention provides etching bath compositions comprising components (a) and (e) and, additionally, water and a mineral acid. In such a bath component (a) is preferably contained in an amount of from 0.5 to 10, most preferably from 2 to 6, grams per liter of final bath. Component (b) is preferably contained in an amount of from 0.5 to 10, most preferably from 2 to 8, grams per liter of final bath. Component (c) is preferably contained in an amount of from 0.5 to 100, more preferably from 1 to 60, and most preferably from 2 to 30, grams per liter of final bath. Component (d) is preferably contained in an amount of from 1 to 200, more preferably from 2 to 100 and most preferably from 5 to 70, grams per liter of final bath. Component (e) is preferably contained in an amount of from 0.2 to 10, more preferably from 0.5 to 8, and most preferably from 1 to 6, grams per liter of final bath.

The mineral acid of an etching bath is generally nitric acid, although mixtures of nitric acid and small quantities of sulfuric, hydrochloric or acetic acids can be beneficial. Suitable amounts of mineral acid range from about 30 to 300 grams per liter of bath with a preferred range from about 70 to 250 grams per liter of bath. The mineral acid component of the powderless etching bath of this invention is per se known.

The sulfonated carboxylic acids used as component (a) in this invention are true sulfonates as distinguished from the so called sulfonated oils like sulfonated castor oil which products are actually sulfates or esters of sulfuric acid. The true sulfonates of this invention differ from the sulfates by the fact that, in the sulfonate, sulfur is directly linked to a carbon atom rather than through an intermediary oxygen atom as in the sulfate.

Examples of fatty acids which in their sulfonated condition are useful in this invention are, for example, caprylic, caproic, lauric, myristic, palmitic, stearic, isostearic, behenic, lignoceric acids, undecylenic, myristicoleic, palmitoleic, oleic, linoleic, linolenic eleo-stearic, arachidonic acids and the like. Saturated and unsaturated fatty acids which have substituents on their hydrocarbon chains can also be sulfonated to add a sulfonate substituent bonded to a carbon atom thereof. Examples of such acids are ricinoleic, 9,10-dichlorostearic acids, beta-phenylpropionic, 10-phenylundecanoic and 9,10-dibenzylstearic acids. In many cases the esters, amides and nitriles, chlorides and/or anhydrides of these fatty acids can be sulfonated with ease, and the sulfonation products thus produced are applicable in this invention provided there is a sulfur-carbon bond and provided they hydrolyze in an aqueous acid etching bath into the corresponding sulfonated carboxylic acids. The sulfonated acids of this invention can be based on pure fatty acids or can be mixtures of fatty acids and/or esters or other derivates thereof such as occur naturally in vegetable, animal or marine oils, fats and waxes or in synthetic fatty acids derived from petroleum, bituminous coal and natural gas. Where mixtures of sulfonated fatty acids are to be used, sulfonation of the fatty acids can be accomplished before and after mixing.

The sulfonation of fatty carboxylic acids is a well established procedure and can be accomplished by different means as the occasion demands. Saturated fatty acids can be sulfonated directly in the alpha-position by reaction thereof with chlor-sulfonic acid or sulfur trioxide, which may be dissolved in sulphur dioxide, dioxane or chlorinated hydrocarbons. Alpha-sulfonations can also be accomplished less directly by the Strecker reaction of an alpha-bromo fatty acid with sodium sulfite. Side chain sulfonation of phenylalkanoic acids like 4-phenylcaproic, 10-phenylundecanoic, phenylstearic and 9,10-dibenzylstearic acids can be performed with a dioxane-sulfur trioxide complex. The same method is used for the alpha-sulfonation of hydroxystearic and 9,10-dihydroxystearic acid. Mono- and polyunsaturated fatty acids having hydrocarbon chains in the range of 8 to 24 carbon atoms can be sulfonated with sulfur trioxide dissolved in sulfur dioxide to yield truly sulfonated carboxylic acids e.g., oleic acid yields predominantly 8-, 9-, 10-, or 11-sulfo-oleic and 9-hydroxy-10-sulfostearic acids when reacted with a stoichio-

metric amount of sulfur trioxide. (See U.S. Pat. 2,743,288 to Rueggeberg et al.)

Truly sulfonated ricinoleic acid can also be obtained by sulfonation with acetyl sulfonic acid, which is itself obtained by reacting sulfur trioxide with glacial acid or acetic anhydride. As taught in the Rueggeberg et al. patent, the sulfo group attaching to the fatty acid, e.g., oleic acid, may attach on one or more different positions; thus, in the case of the sulfo-oleic acid produced according to Rueggeberg et al., the reaction product appears to be a mixture of predominantly 8-, 9-, 10-, or 11-sulfo-oleic acid (as well as some 9-hydroxy-10-sulfosteraic acid). For convenience hereinafter the term "11-sulfo-oleic acid" is sometimes used; in using this term we intend to refer to the mixed product obtained by following the teachings of the art.

The mono-carboxylic acids used as component (b) in this invention may be straight-chain, linear, or branched-chain and preferably contain from 8 to 18 carbon atoms. Preferably, said acids have melting points below 50° C. and, most preferably, they are liquids at room temperature.

Exemplary of the mono-carboxylic acids which may be used are both saturated acids and unsaturated acids such as caprylic, capric, lauric, myristic, palmitic stearic, isostearic, behenic, lignoceric acids, undecylenic oleic linoleic, linolenic, eleostearic, arachidonic acids and the like. Thus, it can be seen that the acids operative as component (b) are generally the same as those used, in sulfonated form, as component (a). Thus, saturated and unsaturated fatty acids which have substituents on their hydrogen chains can also be used. Examples of such acids are ricinoelic, 9, 10-dihydroxystearic, 10-chloro- or 9,10-dichlorostearic acids, beta-phenylpropionic, 10-phenylundecanoic and 9, 10-dibenzylstearic acids. Of the saturated acids, isostearic, caprylic and capric acids are particularly preferred, based on their melting point, ease of handling, outstanding performance in etching compositions and, of the unsaturated acids, oleic and linoleic (one olefinic double bond) and linolenic (two double bonds) are preferred.

While we generally prefer to use unsubstituted acids, it will be understood by those skilled in the art that operative acids may include one or more substituents which do not essentially alter the lipophilicity of the acid molecule; thus, halogenated mono-carboxylic acids, such as bromo-, chloro, or fluoro-substituted acids, may be employed.

It has been found useful, even preferable to use mixtures of two or more acids, e.g., the combination of caprylic and oleic acids, or of caprylic and isostearic acids as component (b) herein.

Component (c) as contemplated herein is at least one saturated or olefinically unsaturated (i) lower mono-carboxylic acid of from 2 to 10 carbon atoms and/or a (ii) lower poly-carboxylic acid of from 2 to 10 carbon atoms.

The mono- or poly-carboxylic acids operative as component (c) herein are, optionally substituted, saturated or olefinically unsaturated mono-carboxylic acids of from 2 to 6 carbon atoms or poly-, especially di and tri-, carboxylic acids of from 2 to 10 carbon atoms.

Thus, within the compass of the component (c) definition, there are simple saturated mono-carboxylic acids, preferably of from 2 to 4 carbon atoms, such as acetic and butanoic, but also hexanoic acids, as well as unsaturated monocarboxylic acids such as acrylic, crotonic or isocrotonic (butenoic) acid, and saturated or unsaturated mono-acids also containing a substituent, e.g., halogen, such as chloro, fluoro, bromo, or iodo, or hydroxy or sulfo- or cyano, which preferably does not substantially decrease the water-solubility of the molecule; thus, chloro-acetic is illustrative. For instance, glycolic acid, $OHCH_2$—COOH, may be employed and, interestingly, we have found that less of the hydroxy-substituted acid is needed to give the same results as the corresponding unsubstituted acid, i.e., acetic acid, although the same final result could be achieved by use of greater amounts of the acetic acid.

Of the poly-carboxylic acids within the compass of component (c), we prefer the di- and tri-carboxylic materials of 2 to 10, preferably 4 to 6, carbon atoms and we prefer the tri- over the di-acids. In addition, we prefer the tri- and di-materials over the mono-carboxylic acids because of the particularly excellent results achieved by use of the poly-acids. Illustrative of the dicarboxylic acids are oxalic acid, malonic, succinic acid, glutaric acid, adipic acid, suberic acid, azaleic acid, and sebacic acid; hydroxy-malonic acid and malic acid (which are hydroxy substituted); tartaric acid (which is a di-OH acid); and maleic acid and itaconic acid (which are unsaturated di-acids). Also included are, e.g., 2-hydroxy-hex-3-en-1,6-dioic acid, i.e., molecules having substitution and unsaturation. Of the tri-carboxylic acids, there may be mentioned as illustrative citric acid, and aconitic acid (which is unsaturated) and 4-hydroxy-1,2,6-hexatrioic acid. The unsaturation and substitution described above for the mono-acids is thus also applicable to the di- and tri-acids of component (c).

The acids of component (c) may, of course, be supplied in the form of salts thereof, e.g., sodium or other alkali metal salts, or ammonium or amine salts, thereof; these are then split to the free acid in the ultimate bath composition. Thus, there are contemplated as within the compass of inventive component (c) sodium succinate or ammonium itaconate, or where the acid is substituted, e.g., sodium sulfosuccinic acid and tri-sodium sulfo-itaconate.

While the specific optimum amount, within the range above set forth, of component (c) in a particular use application is readily determinable by the skilled artisan, we find that, as indicated above, in the range of 0.5 to 100 of component (c) per liter of final bath. In general, more of the mono-acid is needed for the same results as of the di-acid, and more of the di-acid than of the tri-acid except when substitutions, e.g., —OH substitution, lessens the amount required, as noted above. In relation to components (a) and (b), above, few hard-and-fast generalizations may be made but we have found that, as the amount of component (a) or (b) is increased, the amount of component (c) must also be increased, assuming other factors, especially nitric acid concentration, are constant. An increased nitric acid content generally requires use of less carboxylic acid, assuming a constant concentration of components (a) and (b), for similar results.

The water-soluble or water-dispersible polyhydric alcohols or ether derivatives thereof operative as component (c) herein may be saturated or olefinically unsaturated, and the ether portion, in the case of the ether derivatives, may be aliphatic (e.g., alkyl), cycloaliphatic, or aryl; the ether portions preferably do not decrease the water-solubility of the molecule to such an extent that it would no longer be soluble in the bath at the concentrations and conditions set forth herein as preferred.

The polyhydric alcohols usable herein are preferably di- or tri-hydric but may contain more —OH groups (as in sorbitol) and are preferably water-soluble over the range of 0.5 to 100 grams per liter. We prefer alcohols of from 2 to 10 carbon atoms, most preferably from 2 to 6 carbon atoms and also those alcohols whose carbon chain is interrupted by ether functions, i.e. oxygen atoms, as in certain (ether) glycols. Illustrative of operative alcohols under this invention are ethylene glycol, diethylene glycol, propylene glycol, triethylene glycol, dexylene glycol, di- and tri-propylene glycol, glycerine, and the like. As noted the ether glycols are preferred.

As set forth above in the definition of component (d), there are also embraced herein ether derivatives of the aforementioned polyhydric alcohols, i.e. wherein one or more of the —OH groups of the alcohols are replaced with an —OR group where R is typically an aliphatic radical of up to, e.g., 12 carbon atoms, preferably from 1 to 8 carbon atoms, e.g. alkyl or substituted alkyl radi-

cals. The mono-ether derivatives of the polyhydric alcohols, or more precisely, molecules in which at least one OH— function is etherified *and* at least one is not etherified, i.e., where there is partial etherification, are in fact preferred for use herein, relative to the alcohols per se, and ether derivatives in which the total number of carbon atoms in the ether, (i.e., —OR) groups is from 1 to 4 for every etheric oxygen interrupting the carbon chain of the alcohol, are most preferred. Thus, e.g., a mono-ether derivative of diethylene glycol (which contains one internal ether oxygen) preferably contains up to 4 carbon atoms in each of the ether (R) group:

R—O—C—C—O—C—C—ON

as in, e.g., diethylene glycol mono-ethyl or mono-butyl ether.

As noted above the ether moiety of the polyhydric alcohol or of the ether derivatives of the polyhydric alcohols contemplated herein may be cycloaliphatic or aromatic as well aliphatic. Illustrative of suitable aromatic ethers are those wherein the ether moiety is benzene, naphthalene and higher aryls and substituted aryl moieties such as the alkylaryl, e.g., alkylbenzene (for instance tolyl) groups; other substituents on the aryl ring may be alkoxy, halogen, e.g., chloro or bromo, nitro, cyano, sulfo and the like. The term "cycloaliphatic" as used herein is intended to embrace not only the usual, e.g., cycloalkyl radicals such as cyclobutyl, cyclopentyl, or cyclohexyl, but also cyclic moieties containing a hetero atom, e.g., a nitrogen atom as in pyrrolidinyl or oxygen atoms as in tetrahydrofuryl. The cycloaliphatic moieties contemplated herein may, of course, be substituted with the substituents envisioned above for the aryl moities. Thus, within the compass of component (d) there are monocyclobutyl ethers of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol and butylene glycol, it having been found that those ethers wherein the ether moiety is relatively bulky are preferably ethers of glycols, as opposed to polyhydric alcohol having no internal oxygen atom. The same can be said of the aryl ether, i.e., there are embraced herein the monophenyl ethers of the aforementioned glycols, e.g., monophenyl Cellosolve and monophenyl Carbitol, which are commercially available products.

Generally the amount of component (d) in the final bath compositions contemplated herein will range from 1 to 200 grams per liter of bath as noted above and it can readily be appreciated that optimum amounts will depend on many factors, e.g., nitric acid content, and the amount and identity of components (a) and (b) used, and is readily determinable by those skilled in the art.

Component (e) as set forth above is an alkylaryl sulphonate of certain carbon atom content. More specifically, there are contemplated herein alkylbenzene sulfonates wherein the alkyl portion contains from 8 to 18 carbon atoms and the alkylnaphthalene sulfonates wherein the alkyl portion contains from 3 to 18 carbon atoms, as exemplified in the formula

$$RA—SO_3X$$

in which R is an alkyl radical having from 3 to 18 carbon atoms inclusive, A is an aromatic nucleus, e.g., benzene, naphthalene, and X is H or a salt forming ion, e.g., an alkali metal or alkaline earth metal or amine. Specifically illustrative of typical alkylaryl sulfonates that may be employed are sodium decylbenzene sulfonate, sodium dodecylbenzene sulfonate, sodium tetradecylbenzene sulfonate, sodium propylnaphthalene sulfonate, sodium amylnaphthalene sulfonate, sodium diamylnaphthalene sulfonate and sodium dodecylnaphthalene sulfonate. In the above illustrations, sodium can be replaced by, e.g., an amine to provide amine salts. The alkyl substituent or substituents are preferably such that the total number of carbon atoms in all of the alkyl radicals taken together does not exceed about 12. The particular position of the alkyl radical on the aryl, e.g., benzene, ring, can also be varied; thus, *ortho,* alkylaryl sulfonates, *para* alkylaryl sulfonates, and *meta* alkylaryl sulfonates are contemplated.

It will be understood by those skilled in the art that, with regard to the additive compositions which are one aspect of this invention, i.e., those compositions not containing the mineral acid and water used in the final etching bath, may desirably contain, in addition to the components (a) to (e) set forth above, a neutralizing agent such as a basic amine, e.g., diethanol amine, monoisopropanol amine and the ethylene glycol amines, for the purpose of neutralizing the acidic components included within (a) to (e) above. In further aspect of the additive compositions contemplated herein, components (a) to (e) are combined with water, and, as a neutralizing agent appropriate amounts of an alkali metal hydroxide such as potassium hydroxide. Such additive compositions either nonaqueous or aqueous, can be transported per se as articles of commerce and constitute an embodiment of this invention different from the ultimate etching bath compositions which also contain a mineral etching acid, e.g., nitric acid, which is a separate composition claimed herein.

It will also be understood that a number of additional ingredients may desirably be incorporated into either the additive compositions or the ultimate bath compositions envisioned herein. Thus, e.g., foam suppressants such as "Triton CF 21" may desirably be added, certain mineral oils may be added as cleansing agents but care must be taken that any "water immiscible" organic liquid be added only in amounts of less than two grams per liter of final bath because use of greater amounts deleteriously affects etching performance when using the compositions of the instant invention. In fact, it appears that, as regards the instant invention, so-called "water-immiscible" organic liquids are desirably only added at concentration ranges at which such liquid is in fact miscible, i.e., at very low concentrations. When used in such very small amounts it has been found that the liquid in question, e.g., white mineral oil, actually mixes with the final bath and thus can no longer be regarded as a "water-immiscible" organic liquid.

It is truly surprising that when a typical aqueous solution of nitric acid, in a concentration which is conventionally used for zinc or magnesium plate etching, is modified by the admixture thereof with the composition comprising components (a) to (e) as set forth herein, the resultant etching bath is suitable for use with no "water-immiscible organic liquid" required in the composition which liquids are called for in certain prior art compositions. Although very small amounts of such liquid may be added, e.g., up to about 2 grams per liter of the final bath, use of greater amounts deleteriously affects etching performance.

In accordance width one aspect of this invention, etching baths are provided having the following composition:

| | Grams per liter |
|---|---|
| Nitric acid (100%) | 30–300 |
| Sulfonated fatty acid [component (a)] | 0.5–10 |
| Monocarboxylic acid [component (b)] | 0.5–10 |
| Carboxylic acid [component (c)] | 0.5–100 |
| Polyhydric alcohol or ether [component (d)] | 1–200 |
| Alkylarylsulfonate [component (e)] | 0.2–10 |
| Water-immiscible organic liquid | 0–2.0 |
| Water—balance. | |

In etching with the baths of the present invention it has been found to be desirable to impinge the bath against the surface to be etched, as by splashing. In theory at least, the etching bath forms a partially acid-resistant film on the resist-free metal surfaces, and when the bath is impinged against the surface to be etched in a direction normal to that surface, the film is broken. On the other hand when the bath hits the sides of the relief, the film is generally not broken because of insufficient striking

force and etching of the sides (or under-cutting) is substantially reduced.

An etching machine of the type disclosed in U.S. Pat. No. 2,669,048, issued Feb. 16, 1954, and entitled, "Etching Machine" or the so-called "bubble-etch" machines as described in, e.g., U.S. Pats. Nos. 3,227,166; 3,136,323; 3,136,671; (all to C. Martz) can be used. In the machine described in the above patents, U.S. 2,669,048, elongated paddles dipping into the bath composition intermittently throw, by splashing, the etching bath composition in sheets upwardly against the image bearinng side of the object being etched, e.g., a plate. The bubble-etch machine described in the latter group of three U.S. patents comprises a manifold having multiple orifices in the manifold pipes immersed in the etching bath wherein compressed air is forced through the manifold to produce bubbles which then rise upwards through the etching bath into which the plate to be etched is immersed and rotated. Other types of etching machines known to the art also applicable.

As used in this specification, the terms "etch factor ratio" (EFR) is defined as the ratio of (1) the depth of the etch adjacent to a line of resist divided by one half of the loss in width of metal immediately beneath the resist using a particular additive to (2) the depth of the etch adjacent to a line of resist divided by one half of the loss in width of metal immediately beneath the resist when only nitric acid is used in the exact concentration as was used with the particular additive:

$$EFR = \frac{\frac{Da/Wa}{2}}{\frac{Dn/Wn}{2}}$$

where:
D*a* is the etch depth with additive
D*n* is the etch depth without additive
W*a* is the under cutting loss with additive
W*n* is the under cutting loss without additive

The following examples are given to illustrate the present invention, but are not to be construed as limiting thereon.

## EXAMPLE I

An etching bath was made up consisting of the following components:

| Component: | Grams per liter of bath |
|---|---|
| Nitric acid (42° Bé.) | 120 |
| 11-sulfo-oleic acid | 1.5 |
| Caprylic acid | .5 |
| Isostearic acid | 3 |
| Malic acid | 1.5 |
| Butyl Carbitol | 4 |
| n-Hexyl Cellosolve | 1.5 |
| Dodecyclbenzene sulfonate isopropanolamine | 1.5 |
| Foam suppressant | .5 |
| White mineral oil | .25 |

and the balance water.

This bath was used to etch magnesium printing plates having a typical representative resist image thereon. Etching was carried out for four minutes at 100° F. in a bubble-etch machine conventional in the art as described above and, in a second run in a paddle-type machine. The quality of the etch plates was excellent with substantially no lateral etching, side wall erosion or "hooking" being observed in either run. The quality of the printable area was outstanding as was the clarity and clean appearance of the overall plate. The etch factor ratio (EFR) was about 300.

## EXAMPLE II

Example I was repeated but using oleic acid (4.5 grams) in place of the caprylic and isostearic acids used in Example I. The results were comparable to those in Example I.

## EXAMPLE III

Example I was repeated but using citiric acid (1 gram) in place of the malic acid used in Example I. The results were comparable to those in Example I.

## EXAMPLE IV

Example III was repeated but the white mineral oil was left out of the composition. The results were comparable to those in Example I.

## EXAMPLE V

Example I was repeated but using diethyleneglycol instead of the Carbitol and Cellosolve used in Example I; the diethylene glycol was used in the same amount as the combined amount of Cellosolve and Carbitol used in Example I. The quality of the etched plates was good with little lateral etching observed and no hooking observed. The etch factor ratio (EFR) was about 80.

## EXAMPLE VI

Example I was repeated but the concentration of dodecylbenzene sulfonate isopropanolamine was lowered to 0.1 gram per liter. The etched plates exhibited a wider shoulder than those etched in Example I and substantial hooking was observed. The etch factor ratio (EFR) was about 40–50.

## EXAMPLE VII

An etching bath was made up consisting of the following components:

| Component: | Grams per liter of bath |
|---|---|
| Nitric acid (42° Bé.) | 220 |
| 11-sulfo-oleic acid | 1.5 |
| Caprylic acid | 0.5 |
| Isostearic acid | 6 |
| Citric acid | 2 |
| Butyl Carbitol | 4 |
| n-Hexyl Cellosolve | 1.5 |
| Dodecylbenzene sulfonate isopropanolamine | 2 |
| Foam suppressant | .5 |

and the balance water.

This bath was used to etch magnesium printing plates as in Example I. The quality of the etched plates was comparable to that of the plates of Example I but the etch factor ratio (EFR) was in the high hundreds.

It is particularly noteworthy that the compositions of the instant invention, while providing outstanding etching performance, do not pose any pollution hazard, contrary to certain conventional compositions. Thus, our compositions are biodegradable as demonstrated in actual tests in which samples containing the components of this invention were tested according to standard techniques ["Standard Methods for the Examination of Water and Waste Water," 13th edition (1971), published by the American Public Health Association; tests conducted by the Bridgeport Testing Laboratory, Inc.] and it was found that such compositions were 91% biodegradable after 30 days of being in the test water.

The formulations disclosed herein are capable of producing etching rates higher than any obtainable by conventional compositions and equipment. The capacity of the instant bath compositions, in terms of ability of the bath to absorb quantities of magnesium while remaining effective as an etching bath, is also superior to any bath composition heretofore known.

It will be understood that the specification and examples are illustrative but not limitative of the present invention and that other embodiments within the spirit and scope of the invention will suggest themselves to those skilled in the art.

What is claimed is:

1. Powderless nitric acid etching bath additive composition for printing plates of zinc, magnesium or alloys thereof comprising:

(a) from 0.5 to 90 percent by weight of a watersoluble
(a) from 0.5 to 90 percent by weight of a water-soluble or water-dispersible sulfonated fatty acid of from 8 to 24 carbon atoms, wherein the sulfur atom in the sulfonate group is directly bonded to a carbon atom;
(b) from 0.5 to 90 percent by weight of at least one saturated or olefinically unsaturated monocarboxylic acid of from 8 to 24 carbon atoms,
(c) from 0.5 to 90 percent by weight of at least one lower mono-carboxylic acid of from 2 to 6 carbon atoms and/or poly-carboxylic acid of from 2 to 10 carbon atoms;
(d) from 5 to 95 percent by weight of at least one polyhydric alcohol of from 2 to 10 carbon atoms or an ether derivative thereof; and
(e) from 2 to 40 percent by weight of an alkylaryl sulfonate having from 6 to 12 carbon atoms in the aryl moiety and having from 8 to 18 carbon atoms in each alkyl moiety;

based on the total additive composition.

**2.** Composition as claimed in claim **1** additionally containing a neutralizing amount of an amine.

**3.** Powderless nitric acid etching bath additive composition for printing plates of zinc, magnesium or alloys thereof comprising water and, dissolved or dispersed therein, an additive comprising:
(a) from 0.5 to 90 percent by weight of a water-soluble or water-dispersible sulfonated fatty acid of from 8 to 24 carbon atoms, wherein the sulfur atom in the sulfonate group is directly bonded to a carbon atom;
(b) from 0.5 to 90 percent by weight of at least one saturated or olefinically unsaturated monocarboxylic acid of from 8 to 24 carbon atoms;
(c) from 0.5 to 90 percent by weight of at least one lower mono-carboxylic acid of from 2 to 6 carbon atoms and/or polycarboxylic acid of from 2 to 10 carbon atoms;
(d) from 5 to 95 percent by weight of at least one polyhydric alcohol of from 2 to 10 carbon atoms or an ether derivative thereof; and
(e) from 2 to 40 percent by weight of at least one alkylaryl sulfonate having from 6 to 12 carbon atoms in the aryl moiety and having from 8 to about 18 carbon atoms in each alkyl moiety;

based on total additive.

**4.** Composition as claimed in claim **3** additionally containing a neutralizing quantity of an alkali metal hydroxide, and wherein the composition contains at least about 50 percent by weight of water.

**5.** Composition as claimed in claim **4** wherein said hydroxide is potassium hydroxide.

**6.** Composition as claimed in claim **3** additionally containing a neutralizing amount of an amine and the composition contains at least about 5 percent by weight of water.

**7.** Composition as claimed in claim **1** wherein the fatty acid moiety of said sulfonated fatty acid component (a) and the mono-carboxylic acid of component (b) are individually selected from the group consisting of caprylic, capric, lauric, myristic, palmitic, stearic, isostearic, behenic, lignoceric, undecylenic, myristoleic palmitoleic, oleic, linoleic, linolenic, eleostearic, arachidonic, ricinoleic, 9,10-dihydroxystearic, 10-chlorostearic, 9,10-dichlorostearic, betaphenylpropionic, 10-phenylundecanoic, or 9,10-dibenzylstearic acid.

**8.** Composition as claimed in claim **1** wherein the carboxylic acid of component (c) is selected from the group consisting of acetic acid, lactic acid, glycolic acid, oxalic acid, malonic acid, succinic acid, malic acid, maleic acid, glutaric acid, adipic acid, sebacic acid, itaconic acid, and citric acid.

**9.** Composition as claimed in claim **1** wherein the polyhydric alcohol or ether derivative of component (d) is selected from the group consisting of polyhydric ether alcohols of from 2 to 10 carbon atoms and ether derivatives thereof, wherein the ether moiety is alkyl of from 1 to 12 carbon atoms.

**10.** Composition as claimed in claim **1** wherein component (e) is an alkylaryl sulfonate wherein the total number of carbon atoms in all of the alkyl moieties are not more than 12.

**11.** Composition as claimed in claim **1** wherein component (e) is an alkylbenzene sulfonate having a single alkyl moiety thereon containing from 8 to 12 carbon atoms.

**12.** Composition as claimed in claim **1** wherein component (e) is dodecylbenzene sulfonate.

**13.** Composition as claimed in claim **1** wherein said component (e) constitutes from 5 to 20 percent by weight of the total composition.

**14.** Composition as claimed in claim **3** wherein component (e) is present in an amount of 5 to 20 percent by weight of said additive.

**15.** Composition as claimed in claim **1** wherein component (a) is 11-sulfo-oleic acid, component (b) is at least one member of the group consisting of oleic acid, isostearic acid and caprylic acid, component (c) is at least one member of the group consisting of acetic acid, lactic acid, glycolic acid, oxalic acid, malonic acid, succinic acid, malic acid, maleic acid, glutaric acid, adipic acid, sebacic acid, itaconic acid, and citric acid, component (d) is at least one member selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, hexylene glycol and mono-alkyl ethers thereof where each alkyl group contains from 1 to 8 carbon atoms.

**16.** Etching bath for etching printing plates of magnesium, zinc or alloys thereof comprising water and from 30 to 300 grams of nitric acid,
(a) from 0.5 to 10 grams of water-soluble or water-dispersible sulfonated fatty acid of from 8 to 24 carbon atoms, wherein the sulfur atom in the sulfonate group is directly bonded to a carbon atom;
(b) from 0.5 to 10 grams of at least one saturated or olefinically unsaturated monocarboxylic acid of from 8 to 24 carbon atoms,
(c) from 0.5 to 10 grams of at least one lower mono-carboxylic acid of from 2 to 6 carbon atoms and/or polycarboxylic acid of from 2 to 10 carbon atoms;
(d) from 1 to 200 grams of at least one polyhydric alcohol of from 2 to 10 carbon atoms or an ether derivative thereof; and
(e) from 0.2 to 10 grams of at least one alkylaryl sulfonate having from 6 to 12 carbon atoms in the aryl moiety and having from 8 to about 18 carbon atoms in each alkyl moiety,

per liter of bath.

**17.** Etching bath as claimed in claim **16** wherein the fatty acid moiety of said sulfonated fatty acid component (a) and the mono-carboxylic acid of component (b) are individually selected from the group consisting of caprylic, capric, lauric, myristic, palmitic, stearic, isostearic, behenic, lignoceric, undecylenic, myristoleic, palmitoleic, oleic, linoleic, linolenic, eleostearic, arachidonic, ricinoleic, 9,10-dihydroxystearic, 10-chlorostearic, 9,10-dichlorostearic, beta-phenylpropionic, 10-phenylundecanoic, or 9,10-dibenzylstearic acid.

**18.** Etching bath as claimed in claim **16** wherein the carboxylic acid of component (c) is selected from the group consisting of acetic acid, lactic acid, glycolic acid, oxalic acid, malonic acid, succinic acid, malic acid, maleic acid, glutaric acid, adipic acid, sebacic acid, itaconic acid, and citric acid.

**19.** Etching bath as claimed in claim **16** wherein the polyhydric alcohol or ether derivative of component (d) is selected from the group consisting of polyhydric ether alcohols of from 2 to 10 carbon atoms and ether derivatives thereof, wherein the ether moiety is alkyl of from 1 to 12 carbon atoms.

20. Etching bath as claimed in claim **16** wherein component (e) is an alkylaryl sulfonate wherein the total number of carbon atoms in all of the alkyl moieties are not more than 12.

21. Etching bath as claimed in claim **16** wherein component (e) is an alkylbenzene sulfonate having a single alkyl moiety thereon containing from 8 to 12 carbon atoms.

22. Etching bath as claimed in claim **16** wherein component (e) is dodecylbenzenesulfonate.

23. Etching bath as claimed in claim **16** wherein said component (e) constitutes from 0.5 to 8 grams per liter.

24. Etching bath as claimed in claim **16** wherein component (e) is present in an amount of 1 to 6 grams per liter.

25. Etching bath as claimed in claim **16** wherein component (a) is 11-sulfo-oleic acid, component (b) is at least one member of the group consisting of oleic acid, isostearic acid and caprylic acid, component (c) is at least one member of the group consisting of acetic acid, lactic acid, glycolic acid, oxalic acid, malonic acid, succinic acid, malic acid, maleic acid, glutaric acid, adipic acid, sebacic acid, itaconic acid, and citric acid, component (d) is at least one member selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, hexylene glycol and mono-alkyl ethers thereof where each alkyl group contains from 1 to 8 carbon atoms.

26. Etching bath as claimed in claim **16** essentially consisting of the following:

| Component: | Grams per liter of bath |
|---|---|
| Nitric acid (42° Bé.) | 80–300 |
| 11-sulfo-oleic acid | 1–2 |
| Caprylic acid, isostearic acid, and/or oleic acid | 2–10 |
| Malic and/or citric acid | 0.5–3 |
| Alkyl ether of ethylene glycol, diethylene glycol and/or triethylene glycol | 3–7 |
| Alkyl benzene sulfonate and/or salt thereof | 1–2 |

and the balance water.

27. Etching bath as claimed in claim **1** wherein component (a) is the reaction product obtained when sulfonating oleic acid with sulfur trioxide in such a manner that a carbon-to-sulfur bond is obtained in at least one of the reaction products.

28. Etching bath as claimed in claim **27** wherein sulfur trioxide and oleic acid are reacted in stoichiometric amounts.

29. Etching bath as claimed in claim **16** also containing up to 2 grams per liter of a water-immiscible organic hydrocarbon liquid.

30. Etching bath as claimed in claim **16** for etching photoengraving plates based on magnesium or alloys thereof.

31 Etching bath as claimed in claim **16** wherein at least one of components (a) to (e) are formed in situ in the bath.

32. Etching bath as claimed in claim **16** wherein about 30 to 100 parts by weight of nitric acid are present per part of [(a) plus (b)].

33. Method of etching a magnesium plate which comprises bringing the plate into etching contact with an etching bath as claimed in claim **16**.

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J. H. STEINBERG, Primary Examiner

U.S. Cl. X.R.

96—32; 252—79.4