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POWDERLESS ETCHING BATH COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Powderless etching bath additive compositions, especially for etching photoengraving plates of magnesium, zinc or alloys thereof, containing

(a) a water soluble or dispersible sulfonated fatty acid of from 8 to 24 carbon atoms, and
(b) at least one saturated or olefinically unsaturated monocarboxylic acid of from 8 to 24 carbon atoms,

and etching baths also containing nitric acid and water, gives good etching performance, particularly decreased lateral etching and better side wall protection of the resist.

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 results 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, there 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 the 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 mis-named. 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 visual appeal.

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

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

(a) From about 5 to 95 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 and

(b) From about 5 to 95 percent by weight of at least one saturated or olefinically unsaturated mono-carboxylic acid of from 8 to 24 carbon atoms.

While substantial advantages are secured by the use of component (a) alone, the resulting etching bath has been found not entirely satisfactory. Use of both components (a) and (b) according to the instant invention improves the etching characteristics, gives better side wall protection during the etching process and decreases lateral etching, compared to use of component (a) alone.

Apart from providing the additive compositions described above, the instant invention provides etching bath compositions comprising components (a) and (b) and, additionally, water and a mineral acid. In such a bath, component (a) is preferably contained in amounts of from 0.5 to 10, most preferably from 2 to 6, grams per liter of final bath. Component (b) is preferably contained in amounts of from 0.5 to 10, most preferably from 2 to 8, 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, capric, 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 stoichiometric amount of sulfur trioxide (see U.S. Patent 2,743,288 to Rueggeberg et al.). 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-sulfostearic 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. Truly sulfonated ricinoleic acid can also be obtained by sulfonation with acetyl sulfonic acid, which is itself obtained by reacting sulfur trioxide with glacial acetic acid or acetic anhydride.

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.

Examplary 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 hydrocarbon chains can also be used. Examples of such acids are ricinoleic, 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.

While the precise amount of sulfonated acid (a) relative to the amount of mono-carboxylic acid (b) to be used, within the ranges set forth above, for optimum results is readily determinable by the skilled artisan, it has been found that, when using the shorter alkyl chain monocarboxylic acids, less sulfonated acid (a) is required than when using the longer, e.g., 18 carbon atom and over, monocarboxylic acids. Generally, however, the total amount of monocarboxylic acid (which may be a mixture of acids) will be from, e.g., 0.5 to 10 times, by weight, the amount of sulfonated acid used. This ratio, and the total amount of components (a) and (b) used in the bath, will depend also on other factors, e.g., the amount of nitric acid employed. We have found that, most preferably from about 1 to 2 grams of sulfonated acid, and about 3 to 4 grams of monocarboxylic acid, are employed per liter of final etching bath.

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, they may desirably contain, in addition to the components (a) and (b) 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) and (b) above. In further aspect of the additive compositions contemplated herein, components (a) and (b) are combined with water, and, as a neutralizing agent, appropriate amounts of an alkali metal hydroxide such as potassium hydroxide. Such additive compositions, either non-aqueous 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 effects 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) and (b) 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 with 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
Water-immiscible organic liquid	0–2.0
Water	Balance

It will be understood that a certain amount of nitric acid needs to be supplied per part, by weight, of components (a)+(b), if one operates at preferred bath temperatures, e.g., 90 to 110° F. For instance, weight ratios of 30 to 100 parts of nitric acid per part of (a)+(b) are desirably maintained.

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 patent 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 bearing 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 are 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:

Da is the etch depth with additive
Dn is the etch depth without additive
Wa is the under cutting loss with additive
Wn 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 8% by weight of (pure) nitric acid, 0.05% by weight of 11-sulfo-oleic acid, 0.15% by weight of oleic acid 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 4 minutes at 100° F. in a bubble-etch machine conventional in the art as described above. The quality of the etched plates was good with little lateral etching or side wall erosion being observed. The etch factor ratio (EFR) was about 20.

EXAMPLE II

Example I was repeated but 16% by weight of nitric acid was used. The results were comparable to those obtained in Example I.

EXAMPLE III

Example I was repeated but using 0.15% by weight of caprylic acid, rather than oleic acid. The etched magnesium plates had comparable good quality and an EFR of about 20.

EXAMPLE IV

Example III was repeated with the nitric acid concentration raised to 16% by weight. The results were comparable to those obtained in Example III.

EXAMPLE V

Example I was repeated but using 14% by weight of nitric acid, 0.2% by weight of 11-sulfo-oleic acid, and 0.25% by weight of linoleic acid. The results were as in Example I.

EXAMPLE VI

Example I was repeated but using 22 percent by weight of nitric acid, 0.2 percent by weight of 11-sulfo-oleic acid, and 0.6 percent by weight of isostearic acid. The results were as in Example I.

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.

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. Etching bath for powderless etching of printing plates of magnesium, zinc or alloys thereof comprising water and from 30 to 300 grams of nitric acid, and

(a) from 0.5 to 10 grams of at least one water-soluble or water-dispersible sulfonated fatty acid of from about 8 to 24 carbon atoms, wherein the sulfur atom in the sulfonate group is directly bonded to a carbon atom, and

(b) from 0.5 to 10 grams of at least one saturated or olefinically unsaturated mono-carboxylic acid of from about 8 to 24 carbon atoms,

per liter of bath.

2. Etching bath as claimed in claim **1** wherein the said mono-carboxylic acid contains from 8 to 18 carbon atoms and is saturated.

3. Etching bath as claimed in claim **1** wherein the said mono-carboxylic acid is 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.

4. Etching bath as claimed in claim **1** wherein the said mono-carboxylic acid is a substituted acid wherein the substituent does not substantially affect the lipophilicity of the acid.

5. Etching bath as claimed in claim **1** wherein said carboxylic acid is a mixture of caprylic acid with isostearic acid.

6. Etching bath as claimed in claim **1** wherein the said mono-carboxylic acid is oleic acid.

7. Etching bath as claimed in claim **1** wherein the said mono-carboxylic acid is caprylic acid.

8. Etching bath as claimed in claim **1** wherein the said mono-carboxylic acid is linoleic acid.

9. Etching bath as claimed in claim **1** comprising water, from 30 to 300 grams of nitric acid, from 2 to 6 grams per liter of sulfo-oleic acid, from 2 to 8 grams per liter of a saturated mono-carboxylic acid of from 8 to 18 carbon atoms, per liter of bath, and wherein the total amount of mono-carboxylic acids is from 0.5 to 10 times by weight the amount of sulfo-oleic acid.

10. Etching bath as claimed in claim **1** consisting essentially of water, nitric acid, sulfo-oleic acid and isostearic acid.

11. Etching bath as claimed in claim **1** consisting essentially of water, nitric acid, sulfo-oleic acid and caprylic acid.

12. Etching bath as claimed in claim **1** consisting essentially of water, nitric acid, sulfo-oleic acid and a mixture of isostearic and caprylic acids.

13. Etching baht 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.

14. Etching bath as claimed in claim **1** also containing up to 2 grams per liter of a water-immiscible organic liquid.

15. Etching bath as claimed in claim **1** for etching photoengraving plates based on magnesium or alloys thereof.

16. Etching bath as claimed in claim **1** wherein components (a) and (b) are formed in situ in the bath.

17. Etching bath as claimed in claim **1** wherein about 30 to 100 parts by weight of nitric acid are present per part of [(a) plus (b)].

18. Method of etching a plate of magnesium, zinc, or alloys thereof which comprises bringing the plate into etching contact with an etching bath as claimed in claim **1**.

References Cited

UNITED STATES PATENTS

3,234,137 2/1966 Lemaire et al. ________ 252—79.4

FOREIGN PATENTS

1,074,979 4/1954 France ______________ 156—14

JACOB H. STEINBERG, Primary Examiner

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Disclaimer

3,728,180.—*Harold J. Messerschmidt*, Stockholm, *Karl Heyman*, Montclair, and *Bernadou W. Johnsen II*, Paterson, N.J. POWDERLESS ETCHING BATH COMPOSITIONS. Patent dated Apr. 17, 1973. Disclaimer filed July 10, 1973, by the assignee, *Mona Industries, Inc.*

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