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ETCHING BATH AND PROCESS FOR PHOTOENGRAVED PLATES

Emile Lemaire, D 50 Quai St. Leonard, and Roger Lemaire, 24 Rue Morinval, both of Liege, Belgium

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The present invention relates to improved baths and processes for etching metals, especially zinc and its alloys, intended for use in the production of photoengraved plates and other etched metal surfaces. This application is a continuation-in-part application of our applications Serial No. 28,019, filed May 10, 1960, and Serial No. 100,008, filed April 3, 1961, which in turn are continuation-in-part applications of our application Serial No. 815,790, filed May 29, 1959 all of which are now abandoned.

In the usual process for preparing photoengraved (line, halftone or combination) plates by a photomechanical process, an acid-resistant coating sensitive to light is applied to the surface of a metal plate. The sensitized surface is exposed to light through a negative image, so as to reproduce the corresponding image. The exposed surface is then developed to provide areas of acid resistant coating in the form of the corresponding image. The remaining portion of the metallic surface which is not protected by the remaining areas of the developed resist is subjected to an acid etching bath. The metallic plate is a zinc and/or magnesium base alloy. The etching solution conventionally used is an aqueous nitric acid solution containing various additives. This acid solution etches or corrodes those parts of the surface that are not protected by the image coating. Such an etching process results in the formation of depressions and hollows, the depth and size of which is a function of the line or halftone negative, of the concentration of acid in the solution, of the temperature, and of the other bath and process variables which affect the dissolution of metal in the acid solution.

For accurate reproductions, the acid should not deleteriously attack the protected surface of the metal plate. Since the acid will attack all unprotected metal, the problem arises that, as depressions in the surface are formed by the etching action, the acid also attacks laterally against the newly formed sides or shoulders of the depressions. Sufficient lateral attack will cause the top surface to break down. The need still exists for aqueous acid baths which will etch the metal in the desired areas of the plate with minimal lateral attack.

It is one object of the present invention to provide improved baths and processes for the etching of photoengraving plates, including line, halftone and combination engravings.

It is another object of the present invention to provide novel compositions of matter, which, when diluted with hydrocarbon solvents and dissolved in aqueous nitric acid baths, provide such improved etching baths.

The additives which have heretofore been developed are primarily intended for use with plates of magnesium and their alloys, and while they have been used commercially for the etching of line, halftone and combination plates of zinc and its alloys, their results have been erratic and not completely satisfactory. The etching baths of the present invention, on the other hand, are especially useful with plates of zinc and its alloys and are useful under special conditions with plates of magnesium and its alloys.

Etching baths for photoengraved plates contain (1) nitric acid as the active etching agent; (2) organic compounds which function to form films on the lateral surfaces which are to be protected from attack by the etching

solution; and (3) small amounts of various other additives to control the emulsion of the water soluble and water insoluble film-forming constituents. We discovered that baths containing nitric acid and particular film producing agents together with particular surfactants useful for controlling the emulsion formed between the film producers and the aqueous bath are excellent etching baths.

The nitric acid (100% basis) is present in the bath in amounts between about 30–300 g./l.; and preferably between 50–150 g./l.

The nitric acid used in the process of the present invention is preferably the U.S.A. technical grade (42° Bé.) as distinguished from the usual photoengraving nitric acid (40° Bé.) which contains various contaminating impurities, and alum. The use of photoengraver's nitric acid in the process of the present invention leads to results which are far inferior to those obtained by the use of technical nitric acid which does not contain alum.

Film producing agents are present in the baths in amounts between 11 g./l. and 45 g./l., and preferably between 17 g./l. and 31 g./l. Two classes of film producing agents are present in etching baths. They are (a) oxygenated hydrocarbon compounds in amounts between 1 g./l. and 10 g./l. and, preferably, between 2 g./l. and 6 g./l.; and (b) liquid hydrocarbon solvents in amounts between 10 g./l. and 35 g./l. and, preferably, between 15 g./l. and 25 g./l.

Saturated carboxylic acids, esters of carboxylic acids, sulfated oils and sulfated unsaturated acids have been previously disclosed as being useful as constituents of powderless etching baths. However, none have utilized sulfurized unsaturated acids, partially sulfated polymeric ricinoleic acid, sulfated olefinic acids nor any of them in combination with alkyl phenolic compounds condensed with ethylene oxide, thus combining anionic and nonionic wetting agents.

We have discovered that a superior etching bath is provided when the bath contains a non-ionic, partially sulfated, polymerized olefinic acid such as sulfated polymerized ricinoleic acid in the aqueous nitric acid etching bath, in combination with the liquid hydrocarbon and a very small amount of an alkylbenzenepolyethylene oxide adduct.

The partially sulfated polymerized ricinoleic acid used in the specific examples herein is commercially available as "polymerized ricinoleic acid," but is to be carefully distinguished from the systematically named compound—polymerized ricinoleic acid—which is not sulfated and is not readily commercially available.

Superior etching baths utilizing relatively small quantities of the partially sulfated polymerized ricinoleic acid require much less of such a sulfated acid than is required with sulfated ricinoleic acid. The results are superior both with respect to the etch factor, as well as with respect to the tone rendition in the halftone areas of a combination plate.

Thus, the etching baths of the present invention contain from about 1 g./l. to about 25 g./l. by weight of a sulfated polymerized ricinoleic acid, preferably from 1.5 to 6.0 g./l. and more preferably from about 1.5 g./l. to less than 4.0 g./l. by weight of such an acid in the total etching bath. These percentage additions are calculated on the basis of commercially available sulfated polymerized ricinoleic acid which contains from about 36 to about 38% by weight of water, and has a degree of sulfation equivalent to about 6% —SO_3 based on the total non-aqueous portion of the sulfated polymerized ricinoleic acid. As the water content of the sulfated material is reduced, the quantity of this sulfated acid needed may be reduced, and as the degree of sulfation is increased the amount of sulfated acid used may be reduced to some ex-

tent. However, the formulae and percentages herein stated are based upon the commercially available material with its normal percentage of water content, and with its normal degree of sulfation.

Commercial partially sulfated polymerized ricinoleic acid normally contains about 36% of water, and is partially soluble in water at pH 6.4 to the extent of about 20% to 50%, but is completely soluble in water at higher temperatures than room temperature and is also completely soluble in water in solutions more alkaline than pH 6.4. It normally is supplied as a very viscous liquid material which is principally the sulfated polymeric condensation product of ricinoleic acid apparently occurring principally as the guadrimer, trimer and dimer, but on addition of water and heating and as actually used, it appears to be principally the partially sulfated dimer of ricinoleic acid.

The partially sulfated polymerized ricinoleic acid preferred for use in the present invention has an average molecular weight of about 750 to 810 and a sulfur content of about 2.3% and may be prepared from castor oil by the following process:

Castor oil is mixed with an excess of an aqueous solution of potassium hydroxide and boiled for 8 to 10 hours or until it is fully saponified.

After standing and cooling, dilute sulfuric acid is added with vigorous mixing while the mixture is held at about 80° C., and agitation is continued for about 2 hours. After standing several hours, the partially condensed ricinoleic acid separates and the sulfate-containing water layer is separated.

Boiling water to the extent of about 50% by volume of the partially condensed ricinoleic acid is added and vigorously mixed for 1 or 2 hours to wash the oily product.

After standing for several hours, the oily product is decanted and to the oily product is added about 5% by weight of 86% sulfuric acid. The acidified oily mixture is then heated for 14 to 16 hours at 80° to 90° C. so as to obtain a polymerized product which is a mixture of the dimer, trimer and quadrimer of the ester formed by reaction of the internal hydroxyl group with the terminal carboxylic groups and with some of the hydroxyl groups sulfated by the sulfuric acid.

This product is then diluted with about 30% water and is neutralized by successive additions of a dilute sodium hydroxide-water solution, until it shows a pH of from about 6.5 to 6.7 in dilute aqueous solution. Thereafter, the partially sulfated, polymerized ricinoleic acid is separated from the most of the water to yield a final product which has from 36 to 38% water, about 2% ash, and about 70 to 72% of alcohol soluble material.

It is such a material which is herein referred to as the partially sulfated, polymerized ricinoleic acid.

The etching bath also includes a long chain (12 to 20 carbon atoms) fatty acid or its glyceride, or more preferably an unsaturated aliphatic acid or fat, such as linoleic, palmitoleic, or oleic acid, preferably oleic acid and less preferably a glyceride of such unsaturated aliphatic acids. Alternatively, some or all of these fatty acids or their glycerides may be replaced by a sulfurized unsaturated aliphatic acid or its glyceride in which the double bond appears to have been eliminated and replaced by a double-bond sulfur atom. A preferable quantity of oleic acid is from about 1.0 to 5.0 g./l. in the etching bath. When sulfurized oleic is also used, it may also be present in the bath from 1.0 to 5.0 g./l.

Such a sulfurized oleic acid may be prepared by reacting oleic acid with sulfur dichloride, one molecule of sulfur dichloride being used for each molecule of oleic acid, or the oleic acid may be directly reacted with sulfur under prolonged heating. However, the sulfurized oleic acid, while useful, is not essential and may be omitted provided there is a suitable adjustment of the quantity of other olefinic acid employed in the etching bath.

In addition to the partially sulfated polymerized ricinoleic acid, the etching bath may contain a smaller amount of sulfated oleic acid, such as "Prestabit oil V" which is a partially sulfated oleic acid containing about 17% by weight of $—SO_3$, and in which from 40 to 50% of the "oil" is sulfated. Thus, optionally the etching bath may contain up to about .3 g./l. of such a sulfated oleic acid.

In addition to the sulfated polymerized ricinoleic acid and the olefinic acid, there is also provided a water-soluble, non-ionic surface active agent comprising an alkyl phenol which has been condensed with from 4 to 16 moles of ethylene oxide, of which the octyl and nonyl phenols condensed with an average of about 8 or 9 moles of ethylene oxide are preferred. From about 0.02 g./l. to about 0.7 g./l., preferably from about 0.08 g./l. to 0.4 g./l. of the alkyl phenol-ethylene oxide adduct are used per liter of etching bath.

The polyethyenoxy ethers of alkylphenols are prepared by condensing 4 to 16 moles (preferably averaging about 8 moles) of ethylene oxide with an alkylphenol, having from 4 to 18 carbon atoms in the alkyl radical, such as diamylphenol or, most preferably, octyl- or nonylphenol, and are sold commercially under the name "Igepal." "Igepal CO–610" is nonylphenol condensed with an average of 8 or 9 molecules of ethylene oxide.

The useful hydrocarbon solvents include various liquid derivatives of petroleum and coal having a boiling range from about 100° to 300° C. and preferably between 150° and 225° C. They also include synthetic alkylaryl hydrocarbons such as decylbenzene, dodecylbenzene, tetrapropylbenzene, octodecylbenzene, dodecytoluene, octodecylnaphthalene, amylnaphthalene, of which we prefer to use dodecylbenzene or tetrapropylbenzene in amounts in the etching bath between 1 g./l. and 20 g./l. and, preferably, between 3 g./l. and 8 g./l., together with sufficient hydrocarbon from petroleum or coal to bring the total hydrocarbon liquid up to 10 g./l. to 35 g./l., preferably 15 g./l. to 25 g./l.

The petroleum solvent may be any of the relatively high boiling range petroleum hydrocarbons, or such closely-cut, highly aromatic solvents as "Solvesso 150" (boiling range 187° to 211° C., 50% at 193°) or "Amscosolv G" (boiling range 183° to 216° C., 50% at 199.5°, 95% at 211.5°), may be substituted in whole or in part by other hydrocarbons such as diethylbenzene, or dodecylbenzene or other hydrocarbons boiling up to about 260° C. or somewhat higher.

The film producing agents are desirably in the aqueous bath in the form of a fine dispersion which is stable and, yet, which will break down at the new surfaces produced by the etching to deposit the necessary protective film. We discovered that a superior bath is prepared by utilizing two types of wetting (surface active) agents, (i) an anionic partially sulfated polymerized ricinoleic acid, and (ii) a nonionic polyethenoxy ether of alkylphenol.

We also prefer to use in combination with the aforementioned two wetting agents, at least one lower alkyl ether, "Butyl Cellosolve" (ethylene glycol monobutyl ether), propylene glycol, diethylethylene glycol or dibutylpropylene glycol. These are used in amounts between 0.03 g./l. and 5 g./l. and preferably between 0.1 g./l. and 1.5 g./l., and "Butyl Cellosolve" is preferred.

The aqueous nitric acid etching baths may be made up by adding the various bath components separately. For minimization of measurement errors and for better control, it is preferred to premix the various organic compounds of the bath to form a liquid concentrate, which is then added to the bath.

The concentration of acid and the preferred concentration of the other bath components is dependent upon the type of etching machine as well as the type of photoengraved plates to be etched. The concentrated additive mixture of organic compounds used to make up our preferred etching baths consists of between 30% and 85%

(percent by volume) of liquid hydrocarbon solvents, of which, preferably, at least 15% to 30% of the total additive is an alkylaryl compound; between 3% and 18% of at least one unsaturated acid; between 3% and 20% of polymerized partially sulfated ricinoleic acid, and between 0.1% and 2.0% of the polyethenoxy ether of an alkylphenol. The mixture, also, may contain between 1% and 5% of a lower alkyl ether of ethylene glycol or of propylene glycol, or an alkyl ether of an alkanol, preferably "Butyl Cellosolve."

A highly concentrated additive liquid may be prepared, which may be suitably diluted by the user before adding it to the nitric acid etching bath, and is preferably compounded in the following proportions:

Partially sulfated polymerized ricinoleic acid	ml	30 to 200
Oleic acid or olein	ml	30 to 180
Sulfurized oleic acid	ml	0 to 180
"Igepal CO–610"	ml	1 to 20
"Butyl Cellosolve"	cc	0 to 50
Sulfated oleic acid	ml	0 to 90

which is diluted with ½ to 4 times its volume with liquid hydrocarbon such as Amscosolv G or dodecylbenzene prior to being added to the nitric acid etching bath.

For the purpose of giving those skilled in the art a better understanding of our invention the following illustrative examples are given:

Example 1

A preferred nitric acid etching bath for the etching of zinc line engravings, zinc halftone plates and zinc combination (halftone and line) plates, comprises:

Nitric acid, technical grade 42° Bé.	liters	16.75
Partially sulfated ricinoleic acid (6.5% $—SO_3$, 25% water)	ml	377.6
Oleic acid	ml	262.0
Petroleum hydrocarbon solvent boiling from about 199° to 216° C.	ml	2332.0
Dodecylbenzene	ml	744.0
"Igepal CO–610"	ml	42.4
Sulfurized oleic acid	ml	185.5
"Butyl Cellosolve" (optional)	ml	0 to 56.8
Water to make 138 liters.		

Such an etching bath is used in the conventional manner, as in a Chemco powderless etching machine for the etching of zinc (or less desirably with magnesium plates) or in a Master's or other etching machine intended for similar use.

Preferably, the additive materials of Example 1 are mixed together, omitting the nitric acid and the water, and from 3 to 5 liters of such a mixture are added to the nitric acid and water and then diluted to make the 138 liters of etching bath required for loading a conventional type of etching machine.

Such a concentrated additive composition may comprise the ingredients in the following proportions which are given as percentages by volume:

Example 1–A

	Percent
Partially sulfated ricinoleic acid	9.45
Oleic acid	6.55
Sulfurized oleic acid	4.62
Dodecylbenzene	18.60
"Amscosolv G" or "Solvesso 150"	58.30
"Igepal 610"	1.06
"Butyl Cellosolve"	1.42

An even more concentrated additive mixture may be prepared, in which the Amsocosolv G or Solvesso 150 and/or the dedecylbenzene are omitted and are to be added by the user before or after the other ingredients have been added to and dissolved in the acid bath.

Example 1–B

Such a concentrated additive composition comprises, in its preferred form:

	Vol. percent
Partially sulfated polymerized ricinoleic acid	40.8
Oleic acid	28.4
Sulfurized oleic acid	20.0
"Igepal CO–610"	4.6
"Butyl Cellosolve"	6.2

This is first diluted for use with about 3 times its volume of petroleum hydrocarbons and dodecylbenzene or other aromatic hydrocarbon, after which preferably 4.0 liters, or from 3 to 5 liters are added to 138 liters of nitric acid etching bath containing about 8.5% nitric acid.

The aqueous nitric acid etching baths may be prepared by dissolving the mixtures of organic compounds noted in the Examples 1–A, 1–B, 2–A, 2–B, and 5 in aqueous solutions containing between 3% and 30% by weight of nitric acid, most preferably in an aqueous solution of technical 42° Bé. nitric acid, to produce a bath containing about 12% technical acid or 8.45% of 100% nitric acid.

The partially sulfated polymerized ricinoleic acid may be substituted in part by sulfated oleic acid or a salt thereof and for this purpose we prefer to use the sodium salt of sulfated oleic acid containing about 17% by weight of $—SO_3$ and being approximately 42.5% fully sulfated oleic acid, commercially available as "Prestabit oil V." This is water-soluble clear liquid which has a pH from abolut 5.5 to 7.5 in a 10% water solution.

Example 2

An excellent etching bath according to the present invention is prepared in accordance with the following formula:

Nitric acid 42° Bé.	liters	16.75
Partially sulfated polymerized ricinoleic acid	ml	298
Oleic acid	ml	373
"Amscosolv G"	ml	2470
Dodecylbenzene	ml	785
"Igepal CO–610"	ml	20
"Prestabit oil V"	ml	15
"Butyl Cellosolve"	ml	0–60
Water to make 138 liters.		

Example 2–A

For ease in preparing the bath, the additive may be compounded on the basis of the following formula:

	Vol. percent
Partially sulfated polymerized ricinoleic acid	7.4
Oleic acid	9.3
"Prestabit oil V"	0.4
"Amscosolv G"	61.3
Dodecylbenzene	19.6
"Igepal CO–610"	0.5
"Butyl Cellosolve" (optional)	1.5

This additive is diluted with from 27 to 46 volumes, preferably about 35 volumes, of aqueous solution containing from 3 to 30% of nitric acid, preferably from 6 to 10%, and most preferably about 8.5% nitric acid.

Example 2–B

In case it is desired to ship only the minor ingredients of the additive composition so that the user may add his own hydrocarbon liquid to the etching bath, the concentrated additive of this example comprises:

	Vol. percent
Partially sulfated polymerized ricinoleic acid	39.1
Oleic acid	48.5
"Prestabit oil V"	2.0
"Igepal CO–610"	2.6
"Butyl Cellosolve"	7.8

Example 3

A substantial proportion of the unsaturated fatty acid may be replaced with a quantity of sulfurized unsaturated acid, such as sulfurized oleic acid, and another illustrative example of such an additive is as follows:

	Vol. percent
Partially sulfated polymerized ricinoleic acid	9.45
Oleic acid	6.55
Sulfurized oleic acid	4.62
"Igepal CO–610"	1.06
"Amscosolv G"	58.3
Dodecylbenzene	18.6
"Butyl Cellosolve"	1.42

From 3 to 5 liters of this additive are added to an aqueous solution of nitric acid to form 138 liters of an etching bath having about 8.5% nitric acid.

Example 4

Another etching bath according to the present invention is prepared as follows:

	Grams
Partially sulfated polymerized ricinoleic acid	5
Butylricinoleate	1
Octylphenol condensed with an average of 8 moles of ethylene oxide	0.5
Butyl propylene glycol	1
Petroleum hydrocarbon liquid	12
Dodecylbenzene	5
Dehydrated ricinoleic acid	5
Nitric acid (42° Bé.)	100
Water to make 1 liter.	

In general quantities of the sulfated polymerized ricinoleic acid and other sulfated materials greater than about 0.3% in the etching bath are not as effective as etching baths containing smaller amounts, although the optimum quantities of the sulfated materials will depend upon the degree of sulfation, and upon the water-content of the sulfated material.

Also in general, the specific hydrocarbon liquids employed are not critical, but they are preferably relatively non-volatile so as to reduce loss by evaporation with the attendant fire hazard, while higher boiling hydrocarbons tend to be too viscous.

Example 5

Another etching bath additive producing excellent results in the etching of combination plates of zinc in either a Chemco or a Master etching machine, such as are commonly used in the powderless etching of such plates, comprises:

	Vol. percent
Partially sulfated polymerized ricinoleic acid	9.69
Oleic acid	9.00
"Igepal CO–610"	0.61
"Butyl Cellosolve"	1.45
"Amscosolv G"	60.10
Dodecylbenzene	19.15

From 3 to 5 liters of this additive (preferably about 4 liters) are dissolved in aqueous nitric acid to provide 138 liters of a solution containing about 8.5% by weight of nitric acid.

Example 6

Much larger quantities of the partially sulfated polymerized ricinoleic acid may be used by suitable adjustment of the quantity of oleic acid and petroleum solvent, and one such formula is as follows:

	Ml.
Partially sulfated polymerized ricinoleic acid	2180
Sulfurized oleic acid	100
Olein	390
Dodecylbenzene or tetrapropylbenzene	400
"Solvesso 150"	3400
"Igepal 610"	15
"Butyl Cellosolve"	30
Nitric acid 42° Bé. sufficient to make 85 liters.	

The invention in its broader aspects is not limited to the specific steps, processes and compositions shown and described but departures may be made therefrom within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

What is claimed is:

1. A method for powderless etching of plates of zinc, magnesium and their alloys which comprises impinging against the surface of the plate, portions of which are protected by a resist layer, an etching bath comprising, per liter of etching bath, from 30 to 300 grams of nitric acid, from 1 to 25 grams of a partially sulfated polymerized ricinoleic acid, having a molecular weight of from about 750 to about 810 and a sulfur content of about 2.3% from 10 to 35 grams of a liquid hydrocarbon, boiling within the range of from about 100° C. to about 300° C., from 1 to 5 grams of an unsaturated aliphatic acid selected from the group consisting of oleic acid, linoleic acid and palmitoleic acid and from 0.02 to 0.7 gram of a water-soluble, non-ionic surface active agent which is a polyethyleneoxy ether of an alkyl phenol having from 4 to 18 carbon atoms in the alkyl group, the ratio of ethylene oxide to alkyl phenol in the said ether being from 4 to 16 moles of ethylene oxide per mole of alkyl phenol.

2. A method as recited in claim **1** in which the nitric acid is derived from technical grade nitric acid.

3. A method as recited in claim **1** in which the etching bath also includes from 1 to 5 grams per liter of sulfurized oleic acid.

4. A method as recited in claim **1** in which the etching bath also includes up to 0.3 gram per liter of sulfated oleic acid.

5. An etching bath for powerless etching of plates of zinc, magnesium, and their alloys comprising, per liter of etching bath, from 30 to 300 grams of nitric acid, from 1 to 25 grams of a partially sulfated polymerized ricinoleic acid, having a molecular weight of from about 750 to about 810 and a sulfur content of about 2.3%, from 10 to 35 grams of a liquid hydrocarbon, boiling within the range of from about 100° C. to about 300° C., from 1 to 5 grams of an unsaturated aliphatic acid selected from the group consisting of oleic acid, linoleic acid and palmitoleic acid and from 0.02 to 0.7 gram of a water-soluble, non-ionic surface-active agent which is a polyethyleneoxy ether of an alkyl phenol having from 4 to 18 carbon atoms in the alkyl group, the ratio of ethylene oxide to alkyl phenol in the ether being from 4 to 16 moles of ethylene oxide per mole of alkyl phenol.

6. An additive composition to be diluted with liquid hydrocarbon boiling within the range of from about 100° C. to 300° C. and added to an aqueous solution of nitric acid for the powderless etching of plates, which comprises the following ingredients in the following proportions: about 30 to 200 ml. of partially sulfated polymerized ricinoleic acid, having a molecular weight of from about 750 to about 810 and a sulfur content of about 2.3%, about 1 to 20 ml. of a water-soluble, non-ionic, surface-active polyethyleneoxy ether of an alkyl phenol having from 4 to 18 carbon atoms in the alkyl group, the ratio of ethylene oxide to alkyl phenol in the ether being from 4 to 16 moles of ethylene oxide per mole of alkyl phenol and about 30 to 180 ml. of at least one unsaturated aliphatic selected from the group consisting of oleic acid, linoleic acid and palmitoleic acid.

7. An additive composition as recited in claim **6** in which there is additionally provided about up to 180 ml. of sulfurized oleic acid.

8. An additive composition as recited in claim **6** in which there is additionally provided up to 90 ml. of sulfated oleic acid.

9. An additive composition as recited in claim **6** in which the additive composition includes about 22.4 cc. of a liquid hydrocarbon boiling within the range of from about 100° C. to 300° C.

10. An additive composition to be added to an aqueous bath of nitric acid for the powderless etching of plates comprising from about 3% to 20% by volume of partially sulfated polymerized ricinoleic acid having a molecular weight of from about 750 to about 810 and a sulfur content of about 2.3%, from about 0.1% to about 2% by volume of a water-soluble, non-ionic surface-active agent which is a polyethylene oxyether of an alkyl phenol having from 4 to 18 carbon atoms in the alkyl group, the ratio of ethylene oxide to alkyl phenol being from 4 to 16 moles of ethylene oxide per mole of alkyl phenol, from about 30% to 85% by volume of liquid hydrocarbon boiling within the range of from about 100° C. to about 300° C. and from about 3% to 18% by volume of at least one unsaturated aliphatic acid selected from the group consisting of oleic acid, linoleic acid and palmitoleic acid.

11. An additive composition to be diluted with liquid hydrocarbon having a boiling point within the range from 100° C. to about 300° C. and added to an aqueous solution of nitric acid for the powderless etching of plates, which comprises water-soluble and water-insoluble components, said water-soluble component comprising sulfate-radical containing, polymerized ricinoleic acid, having a molecular weight of from about 750 to about 810 and a sulfur content of about 2.3% and a smaller amount of a water-soluble, non-ionic, surface-active polyethyleneoxy ether of an alkyl phenol having from 4 to 18 carbon atoms in the alkyl group, the ratio of ethylene oxide to alkyl phenol in the ether being from 4 to 16 moles of ethylene oxide per mole of alkyl phenol, and said water-insoluble component comprising at least one unsaturated aliphatic acid selected from the group consisting of oleic acid, linoleic and palmitoleic acid in an amount much smaller than the amount of liquid hydrocarbon with which the additive is to be used.

12. An etching bath for the etching of plates for use in photoengraving processes consisting essentially of, per liter of etching bath:

(a) nitric acid, from about 50 to about 150 grams;

(b) a partially sulfated, polymerized ricinoleic acid having a molecular weight of from about 750 to about 810 and a sulfur content of about 2.3%, from about 1.5 to about 4 grams;

(c) an unsaturated fatty acid selected from the group consisting of oleic acid, linoleic acid and palmitoleic acid, from about 1 to about 5 grams;

(d) a polyethyleneoxy ether of an alkyl phenol having from 4 to 18 carbon atoms in the alkyl group, the ratio of ethylene oxide to alkyl phenol in the ether being from 4 to 16 moles of ethylene oxide per mole of alkyl phenol;

(e) liquid hydrocarbon having a boiling point within the range from about 150 to 225° C., from about 15 grams to 25 grams, of which from about 3 grams to about 8 grams consists of a hydrocarbon selected from the group consisting of dodecylbenzene and tetrapropylbenzene;

(f) a glycol derivative selected from the group consisting of ethylene glycol monobutyl ether, propylene glycol, diethylethylene glycol and dibutylpropylene glycol; and

(g) water.

13. An etching bath as recited in claim 12 wherein the unsaturated fatty acid is oleic acid.

14. An etching bath as recited in claim 13 also including a sulfated oleic acid.

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JULIUS GREENWALD, *Primary Examiner.*

ALBERT T. MEYERS, *Examiner.*