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POWDERLESS ETCHING BATH

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ABSTRACT OF THE DISCLOSURE

In a method of powderless etching an etchable magnesium base metal plate in an etching machine in which a powderless etching bath, while at a temperature of about 65 to 85° F., is repeatedly impinged against said etchable plate, the bath comprising (A) from about 10 to about 15 volume percent of nitric acid, (B) from about 5.0 to about 12.5 grams per liter of bath of an ionic sulfonated ar-monochloro - ar' - dodecyl - diphenyl oxide consisting of at least about 70 percent by weight of the monosulfonate and the balance the disulfonate, (C) from about 18 to 64 grams of organic hydrocarbon solvent per liter of bath, and (D) the balance water, and as etching proceeds with the etching of successive plates in said bath, replenishing the nitric acid consumed and adding, to the bath, increments of an extender mixture of a petroleum sulfonate and of sodium monochlorododecyldiphenyl oxide disulfonate dissolved in an aqueous glycol ether, the improvement which comprises: utilizing as the organic hydrocarbon solvent a liquid organic mixture consisting essentially of (1) an aromatic naphtha characterized by a mixture of aromatics from C_8 to C_{12} in a concentration of at least about 80 percent, and a Kauri Butanol value range of from about 100 to 110, and (2) an alkyl benzene branched chain hydrocarbon liquid characterized by a boiling range at 5 percent recovery of about 525 to about 545° F. and 95 percent recovery at about 550 to 575° F. and a Kauri Butanol value range of from about 40 to about 50, said aromatic naphtha being employed in an amount of from about 9 to about 46 grams per liter of bath, said aliphatic substituted benzene being employed in an amount of from 9 to about 18 grams per liter of bath; and maintaining in the bath, per gram of metal plate dissolved in the bath, as etching proceeds on successive plates, from about 0.058 to about 0.104 gram of petroleum sulfonate, from about 0.04 to about 0.07 gram of sodium ar-monochloro-ar'-dodecyldiphenyl oxide disulfonate, and from about 0.715 to about 1.195 grams of an aromatic naphtha solvent, said aromatic naphtha solvent being characterized by a Kauri Butanol value of from about 100 to about 130, by being substantially unreactive with the acid component of the etching bath, and by containing substantially no terminal functional groups but rather a preponderance of carbon and hydrogen atoms.

This invention relates to the powderless etching of metals, and more particularly relates to a novel powderless etching method having a consistent high etch rate capability and high capacity for dissolving metal in the preparation and consistent obtention of quality etched products.

Prior to approximately 1953, most engraving of magnesium and zinc was done, primarily in the photoengraving art, by a so-called powder process, which process was used without significant improvements for a period of many decades before. With the advent of the powderless etching process, representatively disclosed in U.S. Patents 2,640,763 through 2,640,767, 2,828,194, 3,023,138, 3,152,083 and 3,251,777, the old powder technique of etching in photoengraving has been substantially discarded, particularly with zinc and magnesium metals, since powderless etching produces a vastly superior product in a fraction of the time required to "powder etch" a plate.

While sporadic etch rates, in conventional powderless etching baths and methods, up to about 0.004 inch per minute may occasionally be obtained while making a high quality plate, such high etch rates are substantially not reproducible under production conditions while also obtaining consistently high quality results. Conventionally, high quality powderless etched plates can consistently be obtained over a series of plates from an etching bath with an average etch rate, over all, of from about .0015 inch to 0.0020 inch. High etch rates from any conventional powderless etching bath can be obtained, by for example, increasing the acid concentration and paddle speed, but normally the images are severely undercut and exhibit, among other defects, severe loss of halftone and highlight dots. Such plates are totally unacceptable and unusable for commercial purposes.

A primary object of the present invention is to provide a novel method for increasing the etch rate and capacity for dissolving metal in producing magnesium base metal plates in powderless etching bath, while consistently obtaining high quality in substantially every plate etched thereby.

A further object of the invention is to provide an increased capacity powderless etching bath having a high etch rate capability for producing quality etched products characterized by a more uniform and desirable shoulder profile.

Other objects and advantages of the invention for general use in powderless etching as well as in photoengraving will become apparent from the following detailed description thereof.

The novel method of the present invention comprises: in an etching machine; (1) impinging a powderless etching bath at a temperature within the range of from about 65° to about 85° F. against a magnesium base metal plate having an acid resistant coated image pattern thereon, at a maximum force of impingement while yet avoiding detrimental undercutting and loss of halftone and highlight dots, said powderless etching bath consisting essentially of (A) aqueous nitric acid, (B) a filming agent, (C) one or more organic liquids, and, as optional additional ingredients, (D) film controlling agents, (2) admixing with said bath after completion of the first and each successive plate etched, a bath extender composition comprising, by addition into the bath, from about .058 to .104 gm., per gram of dissolved base metal, of a petroleum sulfonate, from about .04 to .07 gm., per gram of dissolved base metal, of sodium ar-monochloro-ar'-dodecyldiphenyl oxide disulfonate, and from about .715 to 1.195 gms., per gram of dissolved base metal, of an aromatic solvent.

The powderless etching bath composition employed in the present novel method consists essentially of the following components and amounts.

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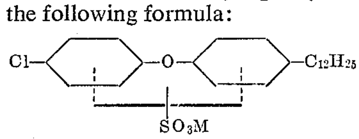
(A) Acid component

The acid component is essentially nitric acid. Operable amounts of nitric acid range from about 10 to about 15 percent by volume (142 to 213 grams per liter) (based on 42° Bé. nitric acid, technical grade), and preferably about 10 to 12 percent (142 to 170 grams per liter). A particularly preferred amount is 12 percent by volume.

(B) Filming agent component

The filming agent employed herein is principally sulfonated ar-monochloro-ar′-dodecyldiphenyl oxide corresponding to the following formula:



Wherein M in the sulfonic group is hydrogen, an alkali metal, an alkaline earth metal, ammonium, or a substituted ammonium radical, the presence of other chloro isomers not exceeding about 20 percent, said filming agent comprising at least about 70 percent monosulfonate, there being up to about 30 percent disulfonate, the alkyl group herein designated as dodecyl containing an average of 12 carbon atoms, but ranging from about 9 to about 15 carbon atoms, there being a preponderance of C_{12} material.

The filming agents thus delineated are further characterized in that they must be soluble in the etching bath with partial solubility in each of the bath phases, viz., the aqueous and organic phases.

The amounts of the filming agent employed can range from about 5 to about 12.5 gms. per liter of bath, a preferred range being from about 5.75 to 7.5 gms. per liter of bath. A particularly desirable amount is about 6.25 gms. per liter of bath. Conveniently, the filming agent is added to the bath as a 50 percent solution in an aromatic naphtha solvent such as Solvesso 150 (defined hereinafter).

(C) Solvent mixture

The solvent component of the powderless etching bath of the present novel method comprises an aromatic naphtha and an alkyl benzene mixture. The aromatic naphtha component is a hydrocarbon liquid characterized by a boiling range at 760 mm. of Hg starting at about 325° F., 50 percent distilled at 450° F., and dry point at 540° F. It is a mixture of aromatics from C_8 to C_{12} plus some naphthalenes and contains 80 percent aromatics with the remainder being aliphatics, having a Kauri Butanol range of from about 100 to about 110.

A particular aromatic naphtha found suitable for use in the invention is a commercial aromatic solvent sold under the tradename of Penola H.A.N. (Heavy Aromatic Naphtha), which contains 84 percent aromatics, has a flash point of 140° F. and a distillation temperature range at 760 mm. Hg: initial boiling point of 340° F., 50 percent distilled at 446° F., and dry point at 532° F.

The alkyl benzene component is a branched chain hydrocarbon liquid with a distillation range at 760 mm. Hg: 5 percent recovery from about 525 to 545° F. and 95 percent recovery from about 550 to 575° F., and a Kauri Butanol value range of from about 40 to about 50. An alkyl benzene found particularly desirable for use in the invention consists of dodecyl benzene having a boiling range at 760 mm. of Hg: 5 percent recovery at about 533° F. and 95 percent recovery at 563° F. Such material is commercially available, as "Chevron Alkylate 21," from the Chevron Chemical Co., Oronite Division.

The amount of the aromatic naphtha liquid to be used ranges from about 9 to about 46 gms. of liquid per liter of bath, a preferred amount being about 28 gms. per liter of bath. The alkyl benzene liquid is used in an amount of from about 9 gms. to about 18 gms. of liquid per liter of bath, preferably about 13 gms. per liter of bath.

The remainder or balance of the bath, other than the optional additional ingredients described hereinafter, is water but it should be understood that other materials may also be present in the bath. One reason for the presense of such other materials is that as a practical matter it is difficult if not impossible to employ the aforementioned bath components in a pure state since they are not readily obtained pure. Another reason for the presence of other materials is that they may enhance the bath performance in some particular respect, or, as a convenience and facility in making additions. For example, the solid filming agent (sodium ar-monochloro-ar′-dodecyldiphenyl oxide sulfonate) is conveniently added to the bath as a 50 percent solids solution thereof in an aromatic solvent such as Solvesso 150 (SC–150). Solvesso 150 is a trademark for a commercial aromatic solvent which is a mixture of approximately 90 percent alkyl benzenes, 2 percent naphthalene, 8 percent naphthenes, a flash point of 150° F., initial boiling point (at 760 mm. of Hg) of 330° F., 50 percent distilled at 378° F., and dry point at 415° F.

(D) Optional additional ingredients as film controlling agents

As optional additional ingredients, the film-controlling agents which may be used in the powderless etching bath of the invention may be a single aliphatic dicarboxylic acid or a blend of such compounds which individually consist of only hydrogen, carbon and oxygen and have 4 to 10 carbon atoms. These compounds, by viture of the results achieved when they are employed in etching baths individually or in blends, are called film-controlling agents. By their use in the above-described etching baths, it is possible to increase the depths of etch at lower etch rates, e.g., at 0.004″/min., obtainable in small areas of penetration in combination photoengraving plates such as halftone areas where proper or adequate depths of etch are usually difficult to obtain by bath modulation, without, at the same time, adversely weakening the protection achieved in open line areas of the same plate. At higher etch rates, e.g., at 0.005″/min., benefits from the film-controlling agent component are minimal.

Another film-controlling agent which may optionally be employed to enhance the etching action of the bath comprises one or more inorganic sulfates soluble in aqueous dilute nitric acid solution. These inorganic sulfates include, for example, sulfuric acid, sodium sulfate, sodium acid sulfate, magnesium sulfate, aluminum sulfate, and ammonium sulfate. In general, most any inorganic sulfate may be used, except heavy metal sulfates.

Amounts of the dicarboxylic acid film-controlling agent employed are surprisingly small for the results to be accomplished. The amount employed can range from about 0 to about 1.5 gm. per liter of bath but a preferred range is from 0.4 to 0.6 gram per liter of bath. With respect to the inorganic sulfate compounds, sufficient amount of the material should be added such that the sulfate ($SO_4^{=}$) content of the solute ranges from about 0.1 to about 0.4 gram per liter of bath solution, the preferred range being from about 0.2 to about 0.3 gram per liter of bath.

In general, in formulating the foregoing powderless etching bath in a powderless etching machine of a given capacity, e.g., in liters, the machine is normally first filled about half full with tap water, whereupon, the nitric acid is added. Thereafter, the filming agent and film-controlling agent are added, either singly or together, the filming agent being preferably added as aforesaid as a 50 percent solution with SC–150 organic liquid. The machine is then filled to the proper level with water for the particular machine. The bath is then brought to the desired temperature. Obtaining a homogeneous mixture of the bath so-formulated is important and is achieved by operating the machine for a few minutes before etching any plates.

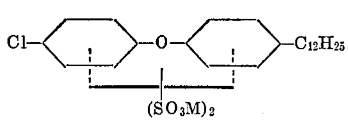
While etching machines of various designs may be used, it is preferred to employ an etching machine of the type disclosed in U.S. Patent 2,669,048, issued Feb. 16, 1954. In powderless etching a plate employing the above bath and machine, the plate to be etched is mounted with the surface to be etched in the machine facing the bath. The machine is then actuated to impinge the bath against the plate for a time sufficient to obtain the depth of etch desired, while controlling the temperature within a range of from about 65° to about 80° F., preferably from about 72° to about 78° F. In general the machine paddle speed, or force of impingement in nonpaddle machines, during etching is held sufficient to obtain the maximum etch rate, as may be predetermined, without detrimental affect on plate quality such as, e.g., by loss of halftone dots, chipping of the image, and undercutting. The paddle speed of a paddle type machine may vary, e.g., from 400 to about 700 r.p.m., depending upon the particular design of the machine. Etching machines of the type disclosed in the aforesaid patent may be operated for example from about 550 to 625 r.p.m. in accordance with the present invention to get the maximum etch rate. In any event the paddle speed or force of impingement of the particular powderless etching machine must be adjusted by a few simple test runs to determine the maximum r.p.m.'s or force of impingement at which a maximum etch rate is obtained as well as consistent satisfactory quality plates suitable for the printing purpose intended for such plates.

Extender composition

The extender composition of the present invention consists essentially of a three component organic liquid mixture of a petroleum sulfonate, sodium ar-monochloro-ar-dodecyldiphenyl oxide disulfonate, and an aromatic solvent, and is added to the foregoing powderless etching bath as a liquid in an amount of each component within the range herein specified for each. The extended components are most conveniently added after each plate is etched by the bath.

The petroleum sulfonate component of the extender is a petroleum sulfonate having a molecular weight of from about 350 to about 450. Petroleum sulfonates containing mineral oil may also be employed and are included in the meaning of the term petroleum sulfonates as used herein. For example, "Twitchell Oil" (tradename available from Emery Industry, Inc.) designated No. 7231, may be employed. This material is approximately a 30 percent solution of petroleum sulfonate in mineral oil. The petroleum sulfonate undiluted with mineral oil is employed by addition to the bath in an amount of from about .058 to about .104 gram per gm. of dissolved base metal, and preferably about .083 gram per gm. of dissolved base metal.

The sodium ar-monochloro-ar'-dodecyldiphenyl oxide disulfonate component of the extender corresponds to the following formula:



wherein M in the sulfonic group is hydrogen, an alkali metal, an alkaline earth metal, ammonium, or a substituted ammonium radical, the presence of other chloro isomers not exceeding about 20 percent, and said sodium ar-monochloro-ar'-dodecyldiphenyl oxide disulfonate being essentially a disulfonate, and preferably at least about 90 percent disulfonate, the dodecyl alkyl group containing an average of 12 carbon atoms, but ranging from about 9 to about 15 carbon atoms, there being a preponderance of C_{12} material.

This disulfonate material as an extender component is employed in an amount of by addition to the bath of from about 0.04 to about 0.07 gram of disulfonate material per gram of dissolved base metal in said bath, and preferably about 0.055 gram per gram of dissolved base metal.

Conveniently, the disulfonate component of the extender is added as, e.g., a 25 percent solids solution in water.

The aromatic solvent component of the extender is a material characterized as a high Kauri Butanol, low viscosity, solvent, immiscible with water, having a KB value of from about 100 to about 130. In addition, the solvent is substantially unreactive with the acid component of the powderless etching bath to which it may be added and contains substantially no terminal functional groups but rather a preponderance of carbon and hydrogen atoms. A particular high boiling aromatic naphtha solvent known under the tradename of Panasol AN-1 (Amoco Chemicals Corp.) found to be quite suitable, is a low volatile aromatic naphtha of wide boiling range, having a KB value of about 108 and contains typically 99 percent of said high boiling aromatics.

The aromatic naphtha liquid component of the extender is employed in an amount of from about 0.715 to about 1.195 gram per gram of dissolved base metal in the bath, and preferably from about 0.9 to about 1.0 gram per gram of dissolved metal.

The following examples serve further to illustrate the present invention and are not to be construed as limiting the invention thereto.

Example I

A powderless etching bath of 130 liters volume was prepared in a Chemco powderless etching machine Model 510 B by mixing together 15,600 ml. of 42° Bé. nitric acid (170 grams per liter of bath), 1625 ml. of a 50 percent solution of sodium ar-monochloro-ar'-dodecyldiphenyl oxide sulfonate (filming agent) in Solvesso 150 (13 grams per liter of bath), 52 grams of adipic acid (0.4 gram/liter of bath), 3900 ml. of Penola H.A.N. aromatic solvent (28 grams per liter of bath), and 1950 ml. of dodecyl benzene (12.9 grams per liter of bath) and sufficient water to bring the volume up to 130 liters. The bath temperature was adjusted and a number of photoengraving grade sheets of magnesium base alloy containing about 3 percent by weight aluminum and 1 percent of zinc, and having an etch resist PVC image thereon, were etched in said bath until the bath was depleted. After the first and each successive plate was etched and weighted for loss of metal, an extender solution was added to the bath at a rate of about 2 ml. of extender per gram of dissolved magnesium. Along with the extender, nitric acid additions (about 5 ml. per gram of dissolved magnesium) were made to the bath after each plate etched.

The extender components were employed in the preferred amounts stated hereinbefore when conveniently added in 2 ml. portions per gram of dissolved base metal in the powderless etching bath.

The following Table I presents the results of this etching sequence showing, in tabulated forms, additions of acid, extender solution, total etch time for each plate in minutes, the bath temperature, paddle speed, plate size, depth of etch in inches, metal lost, in grams, by each plate, etch rate, and an evaluation of plate quality by means of a visual qualitative inspection.

The term "shoulder angle" or "shoulder profile," used herein as an indication of plate quality, is the angle, expressed in degrees, that the shoulder slope, formed by etching, makes with a line perpendicular to the plane of the printing plate commencing at the top edge of a relief image. The shoulder angle is determined by measuring the horizontal shoulder projection from the perpendicular line of the plane of the printing plate at the top edge of the relief image (shoulder width) and the depth of etch. Then the shoulder width is divided by the depth of etch which gives the tangent of the shoulder angle. The angle is then determined from the tangent.

TABLE I.—(EXAMPLE I)

Sample Number	Bath Additions	Etch Time in Mins.	Bath Temp. ° F.	Paddle Speed, r.p.m.	Plate Size	Erch Depth [1]	Metal Loss [2]	Etch Rate [3]	Results
(1)		9	73	570	18″ x 24″	.035	194	3.88	Very good engraving.
(2)	970 ml. of HNO_3+388 ml. of Extender	9½	73	570	18″ x 24″	.036	196	3.8	Do.
(3)	980 ml. of HNO_3+392 ml. of Extender	10	74	570	18″ x 24″	.036	194	3.6	Do.
(4)	970 ml. of HNO_3+388 ml. of Extender	10	74	570	18″ x 24″	.035	191	3.5	Do.
(5)	955 ml. of HNO_3+382 ml. of Extender	10½	75	570	18″ x 24″	.035	192	3.33	Do.
(6)	960 ml. of HNO_3+384 ml. of Extender	11	75	570	18″ x 24″	.035	193	3.18	Do.
(7)	965 ml. of HNO_3+386 ml. of Extender	11½	76	570	18″ x 24″	.037	202	3.2	Good engraving.
(8)	1,020 ml. of HNO_3+404 ml. of Extender	12	77	570	18″ x 24″	.035	200	2.91	Very good engraving.
(9)	1,000 ml. of HNO_3+400 ml. of Extender	12	77	570	18″ x 24″	.034	195	2.83	Good engraving.
		Bath Depleted					1,757		

[1] Etch depth is the depth of etching in the open areas measured in inches.
[2] Metal loss is grams of magnesium dissolved per plate.
[3] Etch rate is mils of metal dissolved per minute.
Average etch rate=3.36 mils/minute.

(A) *Comparative example* (not illustrative of invention).—A conventional powderless etching bath was prepared in accordance with U.S. Patent 3,152,083 by mixing together in a 130 liter capacity Chemco Powderless Etching Machine Model 510 B 13,000 ml. of 42° Bé. nitric acid (142 grams per liter of bath), 850 ml. of a 50 percent solution of sodium ar-monochloro-ar′-dodecyldiphenyl oxide sulfonate in Solvesso 150, 195 grams of adipic acid (1.5 grams per liter of bath), 5850 ml. of Solvesso 150 aromatic solvent (40 grams per liter of bath), and sufficient water to bring the volume up to 130 liters. The bath temperature was adjusted and a number of magnesium photoengraving grade metal sheets having an etch resist image coating thereon were etched in said bath until the bath was depleted. After each plate was etched and weighed, replenishment amounts of nitric acid were added. After the 3rd, 4th and 5th plates a conventional bath additive known as Dowetch Extender (not in accordance with the present invention) was added to the bath according to the conventional practice.

The following Table II presents the results and conditions of this comparative etching sequence as additions of acid and of extender, total etch time per plate in minutes, bath temperature, paddle speed, plate size, depth of etch in inches, metal lost in grams by each plate, etch rate, and an evaluation of plate quality by means of visual qualitative inspection, and determination of the shoulder angle of the relief.

TABLE II.—(COMPARATIVE EXAMPLE)

Sample Number	Bath Additions	Etch Time in Mins.	Bath Temp.	Paddle Speed, r.p.m.	Plate Size	Etch Depth	Metal Loss	Etch Rate [1]	Results
1		10	65	420	9″ x 12″	.022	27	2.2	Very good engraving.
2	135 ml. of HNO_3	10	65	440	9″ x 12″	.024	28	2.4	Do.
3	140 ml. of HNO_3	15	65	430	18″ x 24″	.034	190	2.27	Good engraving. Slight chipping on hot line end.
4	950 ml. of HNO_3+290 ml. of Extender.	16	65	425	18″ x 24″	.034	187	2.12	Very good engraving.
5	935 ml. of HNO_3+ 290 ml. of Extender.	16½	65	425	18″ x 24″	.034	189	2.05	Do.
6	945 ml. of HNO_3+ 290 ml. of Extender.	17	65	425	18″ x 24″	.0335	186	1.97	Do.
7	930 ml. of HNO_3	18	65	425	18″ x 24″	.033	189	1.83	Do.
8	945 ml. of HNO_3	19	65	425	18″ x 24″	.034	186	1.78	Do.
9	930 ml. of HNO_3	20	65	425	18″ x 24″	.032	190	1.6	Do.
		Bath Depleted					1,372		

[1] Average etch rate=2.02 mils per minute.

The novelty, usefulness, and unobviousness of the present invention are clearly revealed in a detailed comparison of Example I and the comparative example.

The outstanding increase in average etch rate of the Example I of 3.36 mils per minute, as compared to the average of 2.02 mils in the comparative example employing a conventional bath, is readily apparent. This represents an average increase of about 66.3 percent in etch rate. In both Example I and the comparative example the etching conditions were maximized to obtain the highest etch rate without sacrificing quality in the etched plate. common practice in the industry is also to etch under conditions to obtain the highest etch rate and the desired degree of quality on the etched product. A typical etch rate for conventional powderless etching baths is 1.5 to 2 mils per minute. The time savings attending the high etch rate of Example I when compared to the comparative example is also readily apparent. The total time to etch 9 plates in each bath is 95½ minutes for the Example I bath as compared to 141.5 minutes for the bath of the comparative example—over 30 percent less time. Such time savings are beneficial in meeting production deadlines.

The bath capacity in dissolved metal, i.e., ability to dissolve more magnesium per bath is greatly increased by the present invention as is further manifest from Example I in relation to the comparative example by comparing the columns headed "plate size," "etch depth," and "metal loss." The total capacity of the bath in Example I in dissolving metal before being depleted is 1757 grams, whereas, in the comparative example the capacity is 1372 grams—approxiamtely a 28 percent greater capacity in the Example I bath.

Both in the comparative example and in Example I, the plate quality was substantially at the same high level. The Example I bath, however, gave a greater capacity in dissolving metal and at a much faster rate.

Example II

The procedure of Example I was followed except that only one 9″ x 12″ test plate was etched and the proportions of ingredients in the etching bath were as follows:

20,550 ml. of 42° Bé. nitric acid (213 gm./l.)
3,425 ml. of filming agent (25 gm./l.)
4,100 ml. of Penola H.A.N. (28 gm./l.)
2,050 ml. of dodecyl benzene (12.9 gm./l.)

Water—balance to make up 137 liters, employing a powderless etching machine in acordance with U.S. Patent 2,669,048.

The powderless etching machine was operated at 600 r.p.m. paddle speed with a bath temperature of 75° F. An etch rate of 5 thousandths of an inch per minute was obtained and the quality of etch was good. No extender of any kind was added.

(B) *Comparative example* (not illustrative of present invention).—A 9 x 12 inch photoengraving grade magnesium base metal plate having an image pattern thereon was etched in a powderless etching bath having the same formulation as the bath in the comparative Example A above except that the paddle speed of the machine was run at 650 r.p.m. to give an etch rate of 3.45 mils. The resultant engraving was completely unusable because of severe image loss.

Example III

This example compares the desirable shoulder profile obtained in accordance with the present invention as obtained in Example I above with the less favorable shoulder profile obtained in etched plates made employing conventional powderless bath and methods such as, e.g., in comparative Example A.

Sample No. 3 of Table I above and Sample No. 5 of Table II above were employed as direct comparisons for purposes of this example in that the machines employed were the same as well as the image, the amount of dissolved metal in the bath, and the like. The shoulder angle of the selected plates was measured in five different type areas, as described below, to show the more desirable shoulder angle obtained by means of the invention:

Image Area	Example I Plate	"A" comparative Plate
1. Line in open area	41°	52°
2. Line in confined area	39°	45°
3. Small type	35°	37°
4. Large type	33°	42°
5. Large reverse type	29°	38°

Shoulder angles were determined as hereinbefore described. It can be seen that the shoulder angles of the Example I plate are significantly smaller than those of the plate from comparative Example A. In general, smaller shoulder angles are desired. Shoulder angles in the order of those obtained in said Example I plate are normally unobtainable in conventional powderless etching baths and methods.

The present invention concerns a novel and unobvious method of powderless etching with an outstanding average increase in etch rate wherein a consistent high quality of etch product is obtained and an increased capacity in said powderless etching bath to dissolve metal. The method comprises an unobvious combination of etching bath ingredients, conditions of operation, and process steps which together provide a peculiar and specific method not heretofore disclosed. In addition, if conventional powderless etching baths and methods were modified to, inter alia, increase the amount of nitric acid therein, and increase the bath temperature and paddle speed to obtain etch rates comparable to the present invention, poor if not unusable quality etched products would result, giving rise in effect, to little or no useful bath capacity. Moreover, with the bath composition used in the present invention, if, for example, the paddle speed and bath temperature were lowered to conventional levels, poor if not unusable quality engravings would result. The present invention, therefore, lies in a critical combination of ingredients and amounts, conditions of etching, and process steps.

The present invention may be modified and changed without departing from the spirit or scope thereof, and it is understood that the present invention is only limited as defined in the appended claims.

I claim:

1. A method of etching comprising: in an etching machine, impinging a powderless etching bath at a temperature within the range of from about 65° to about 85° F. against an etchable magnesium base metal plate having an acid resistant coated image pattern thereon, said powderless etching bath comprising (A) from about 10 to about 15 volume percent of nitric acid, (B) from

about 5.0 to about 12.5 grams per liter of bath of an ionic sulfonated ar-monochloro-ar'-dodecyldiphenyl oxide consisting of at least about 70 percent by weight of the monosulfonate and the balance the disulfonate, (C) a liquid organic mixture consisting essentially of (1) an aromatic naphtha characterized by a mixture of aromatics from C_8 to C_{12} in a concentration of at least about 80 percent, and a Kauri Butanol value range of from about 100 to 110, and (2) an alkyl benzene branched chain hydrocarbon liquid characterized by a boiling range at 5 percent recovery of about 525 to about 545° F. and 95 percent recovery at about 550 to 575° F. and a Kauri Butanol value range of from about 40 to about 50, said aromatic naphtha being employed in an amount of from about 9 to about 46 grams per liter of bath, said aliphatic substituted benzene being employed in an amount of from about 9 to about 18 grams per liter of bath, and (D) the balance of the bath being water; as etching proceeds upon successive plates, using said bath, adding to and maintaining in the bath, per gram of dissolved base metal therein, from about 0.058 to about 0.104 gram of a petroleum sulfonate, from about 0.04 to about 0.07 gram of sodium ar-monochloro-ar'-dodecyldiphenyl oxide disulfonate, and from about 0.715 to about 1.195 grams of an aromatic naphtha solvent, said aromatic naphtha solvent being characterized by a Kauri Butanol value of from about 100 to about 130, by being substantially unreactive with the acid component of the etching bath and by containing substantially no terminal functional groups but rather a preponderance of carbon and hydrogen atoms.

2. The method of claim **1**, wherein the powderless etching bath includes as an optional additional component from about 0 to about 15 grams per liter of bath of an organic dicarboxylic acid consisting of only hydrogen, carbon and oxygen and having 4 to 10, inclusive, carbons.

3. The method of claim **1**, wherein the powderless etching bath includes as an optional additional component an inorganic sulfate-containing compound soluble in aqueous dilute nitric acid solution in an amount sufficient such that the sulfate content of the bath ranges from about 0.1 to about 0.4 gram per liter of bath.

4. The method as in claim **1** in which etching is carried out at a rate in the range of about 2.8 to 4 mils depth per minute.

5. In a method of powderless etching an etchable magnesium base metal plate in an etching machine in which a powderless etching bath, while at a temperature of about 65 to 85° F., is repeatedly impinged against said etchable plate, the bath comprising (A) from about 10 to about 15 volume percent of nitric acid, (B) from about 5.0 to about 12.5 grams per liter of bath of an ionic sulfonated ar-monochloro-ar'-dodecyldiphenyl oxide consisting of at least about 70 percent by weight of the monosulfonate and the balance the disulfonate, (C) from about 18 to 64 grams of organic hydrocarbon solvent per liter of bath, and (D) the balance water, and as etching proceeds with the etching of successive plates in said bath, replenishing the nitric acid consumed and adding, to the bath, increments of an extender mixture of a petroleum sulfonate and of sodium ar-monochloro-ar'-dodecyldiphenyl oxide disulfonate dissolved in an aqueous glycol ether, the improvement which comprises:

utilizing as the organic hydrocarbon solvent a liquid organic mixture consisting essentially of (1) an aromatic naphtha characterized by a mixture of aromatics from C_8 to C_{12} in a concentration of at least about 80 percent, and a Kauri Butanol value range of from about 100 to 110, and (2) an alkyl benzene branched chain hydrocarbon liquid characterized by a boiling range at 5 percent recovery of about 525 to about 545° F. and 95 percent recovery at about 550 to 575° F. and a Kauri Butanol value range of from about 40 to about 50, said aromatic naphtha being employed in an amount of from about 9 to about 46 grams per liter of bath, said aliphatic substituted benzene being employed in an amount of from about 9 to about 18 grams per liter of bath;

and maintaining in the bath, per gram of metal plate dissolved in the bath, as etching proceeds on successive plates, from about 0.058 to about 0.104 gram of petroleum sulfonate, from about 0.04 to about 0.07 gram of sodium ar-monochloro-ar'-dodecyldiphenyl oxide dilsulfonate, and from about 0.715 to about 1.195 grams of an aromatic naphtha solvent, said aromatic naphtha solvent being characterized by a Kauri Butanol value of from about 100 to about 130, by being substantially unreactive with the acid component of the etching bath, and by containing substantially no terminal functional groups but rather a preponderance of carbon and hydrogen atoms.

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