

928,164



PATENT SPECIFICATION

NO DRAWINGS

928,164

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International Classification:—B44b.

COMPLETE SPECIFICATION

Etching process and improved Etching Bath

We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to an improved etching bath and methods for etching photoengraving plates, name plates, patterns and the like. More particularly it is concerned with the utilization of novel filming agents in the so-called powderless etching technique and in the baths used in these methods.

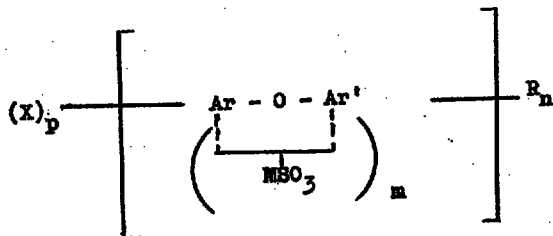
Recently, novel methods of etching have been devised and perfected which permit etching of intricate patterns and reliefs in acid-soluble metals, such as magnesium, zinc or one of their alloys. These new methods, which are generally referred to as the "powderless etching technique", do not require the protection of the resists and/or relief side walls, e.g., by repeated separate powdering or similar steps. The powderless etching technique generally employs so-called filming agents in combination with an organic, water-immiscible fluid serving the function of protecting certain areas from undesired acid attack. As is readily apparent, various agents proposed for this purpose serve this function to a different degree. Furthermore, various types of etching patterns such as line etchings, half-tone etchings, combinations of line and half-tone etchings, template etching and so forth, require different properties and performance of the bath and filming agent contained therein. The filming agents and other adjuvants are often added to the aqueous acid making up the etching bath, though they may be incorporated in any other desired manner. Methods used in powderless etching technique have been described, for instance, in Specifications Nos. 703,814, 709,315 and 818,744.

A particularly challenging problem in the powderless etching art has been the difficulty in obtaining proper depths in different parts of the plate being etched, e.g., line and half-tone images on combination plates. Desirable depths of etch vary somewhat but depths of 0.50 mm in open line areas and 0.13 mm in 65 line screen half-tone areas are generally satisfactory. Another problem, chemical stability, has two aspects, namely, depletion and deterioration. In the event of depletion as when nitric acid is used up in etching the metal, more of the chemical can be added to reactivate the bath. This can be repeated a number of times until the presence of excessive nitrate salts has such a depreciating effect that the bath must be discarded. A more serious problem is posed by chemical deterioration as a function of time, which occurs due to the reactivity of bath components, particularly the filming agent with dilute nitric acid. Bath formulations with such a defect have short periods of effectiveness during which peak results can be obtained in consecutive applications.

The present invention overcomes these problems by the provision of a new type of filming agent and of an improved process of etching by the powderless etching technique with the employment of an aqueous bath which contains as major constituents a dilute strong acid, a water-immiscible organic fluid and a filming agent. The filming agents employed in this process are substituted halogenated diaryloxide

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sulfonic acids or the salts thereof, wherein the substituents on the diaryloxide radical are hydrophobic groups containing from 1 to 30 carbon atoms. The preferred filming agents of the present invention fall under the general formula

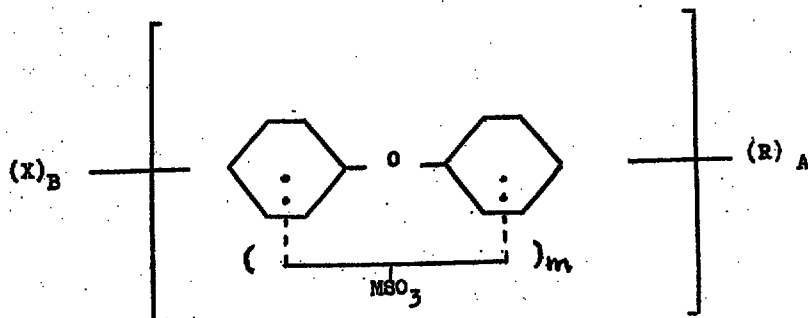


wherein the bracketed radical represents a diaryloxide radical in which Ar and Ar' are phenyl or naphthyl, R is a hydrophobic substituent having up to 30 carbon atoms, n is an integer from 1 to 8 with the limitation that the total number of carbon atoms of the entire compound does not exceed 50, X is a halogen and m and p are integers from 1 to 3, and M is a hydrogen displaceable ion.

The hydrophobic-hydrophilic filming agent may be employed as a single compound or, more conveniently, as a blend of compounds falling under the above-described general formula.

Generally the filming agent should be selected in such manner that it is soluble in the particular etching bath used. It should also be at least partially soluble in each the aqueous and the organic phases. It is often of advantage to add the substituted halogenated diaryloxide sulfonic acid to the bath in the form of the alkali or alkaline earth metal, or ammonium or substituted ammonium salt. The compounds wherein the halogen is chlorine and/or bromine are generally preferred.

The filming agents of the present invention which are generally preferred are substituted halogenated diphenyloxide sulfonic acids or sulfonates which have the general formula



wherein R is an alkyl radical containing from 1 to 30 carbon atoms, A is an integer from 1 to 8 with the limitation that the total number of carbon atoms of all alkyl substituents is no less than 4 and no more than 30, X is a halogen, B is an integer from 1 to 2 and M is a hydrogen-displaceable ion.

It is to be understood by the foregoing language that there is always at least one alkyl substituent and when more than one, the alkyl substituents may contain the same or different numbers of carbon atoms. The preferred form of the foregoing compound contains one sulfonic radical but more than one sulfonic radical may be present in a compound so long as such a compound is a minor proportion of the filming agent. Whatever constitutes M is unimportant so long as it is hydrogen or a salt-forming ion capable of being displaced by hydrogen in the dilute aqueous nitric acid of the bath. Suitable materials for M in addition to hydrogen are the alkali metals, alkaline earth metals (defined as including magnesium), ammonium and substituted ammonium radicals. The means of diagraming the sulfonic acid groups indicates immateriality as to which ring group they are attached.

Excellent results are obtained if one employs as the filming agent a composition or mixture of compounds which consists at least in part of an alkylated chlorodiphenyloxide monosulfonic acid or monosulfonate which has one alkyl substituent of from 9 to 30 carbon atoms, and preferably from 8 to 18 carbon atoms, and advantageously, an average of 12 carbon atoms.

The process and bath of the present invention permit the production of superior quality metal photoengraving plates having the proper depth of etch in different kinds of image areas on the same plate. The baths containing the improved filming agent of the present invention, furthermore, are distinguished by being chemically stable and less subject to hydrolysis or deterioration found in some of the older baths used for this purpose.

Since the baths are usually made up to a stated volume, the units employed to designate amounts, as a matter of convenience, are on the basis of grams per liter of bath. The quantities of nitric acid are given on the basis of 100 percent nitric acid, unless otherwise specified.

The acid additive is generally nitric acid although the inclusion of small amounts of sulfuric acid, hydrochloric acid, acetic acid and the like with nitric acid has been found to be beneficial in some baths. Operable amounts of nitric acid range from 30 to 200 grams per liter of bath but a preferred range is from 50 to 150 grams per liter of bath. A desired range is from 60 to 140 grams per liter of bath.

A second additive is an organic, water-immiscible fluid which may be a single compound or blend of such compounds. Required properties of this additive are that it be substantially stable in the presence of dilute nitric acid, at bath temperatures, and that it have some solvency for the substituted diaryloxide sulfonate. Substantially stable is defined as the non-occurrence of deterioration, within a reasonable time period due to the presence of dilute nitric acid which significantly alters the function of the organic water-immiscible component within the bath in an unfavorable manner. Also it is essential that this additive is a liquid at bath temperatures. Suitable organic materials which can be used individually or in combination are hydrocarbon aromatics, aliphatics and naphthenics boiling from 90° to 390°C., as for example, ligroin, kerosene, gas oils, diethylbenzenes, tetramethylbenzenes, diisopropylbenzenes, and dodecylbenzenes. Other examples of water-immiscible fluids include turpentine, monochloroethylbenzene, ethylbutyl ketone, isophorone, methylhexyl ketone, d-limonene, diisodecyl phthalate and hexylacetate. Generally, it may be said that water-immiscible esters, ketones, terpenes, ethers (aliphatic, naphthenic and aromatic hydrocarbons are operable). Certain commercial solvents also serve very effectively as this component of the bath. An example is a commercial aromatic solvent which contains 84 percent aromatics, has a flash point of 60.0°C., an aniline point of minus 18.9°C. and a distillation temperature range at 760 mm. Hg: initial boiling point of 171.1°C., 50 percent distilled at 230.0°C. and dry point at 277.8°C. Another commercial aromatic solvent which may be employed with advantage is a mixture of approximately 90 percent alkyl benzenes, 2 percent naphthalene and 8 percent naphthenes. It has a flash point of 65.6°C., an aniline point of minus 27.8°C. and a distillation temperature range at 760 mm. Hg: initial boiling point of 150.6°C., 50 percent distilled at 192.2°C. and dry point at 212.3°C. The amounts of the water-immiscible organic fluid employed may range from 3 to 150 grams per liter of bath but a preferred range is from 5 to 100 grams per liter of bath. A desired range is 10 to 60 grams per liter of bath.

The bracketed radical of the filming agent or blend of filming agents provided by the present invention which are hereinbefore shown in the general formula as containing an ether linkage and 1 to 3 sulfonic acid radicals in any ring position is strongly hydrophilic. An ideal balance between the hydrophilic and hydrophobic properties of the entire molecule is achieved by the substituent on the aryl rings of one or more hydrophobic hydrocarbons and one or more halogens. The hydrophobic hydrocarbon substituents may be connected to the diaryloxide by means of ether, amide, ester or carbon to carbon linkages. Likewise, within the substituent hydrophobic group itself there may be similar chemical linkages so long as it is essentially hydrophobic. However, the hydrophobic aryl ring substituents and more importantly the entire molecule itself should, for best operability, retain its hydrophobic-hydrophilic balance for at least several hours in the presence of dilute nitric acid as employed in this invention. Furthermore, as has been stated, the filming agent should be totally soluble in the bath and present to some extent in both bath phases, i.e., the aqueous nitric acid solution and the organic water-immiscible fluid.

It is believed that in forming a film the polar part of the filming molecule attaches to the metal surface while the hydrophobic non-polar segment of the molecule,

substitut

having an affinity for the organic water-immiscible fluid or, as it is sometimes called, the solvent, draws such atoms to it, thereby perfecting a substantially acid-resistant film. By virtue of the objects to be accomplished, the bath of this invention must have selective filming tendencies under the conditions present as the etching process is carried out, i.e., acid-resistant films must be formed and retained upon the side walls of the relief but adjacent resist-free areas must be susceptible to the etching action of the nitric acid in a direction normal to the surface of the plate being etched.

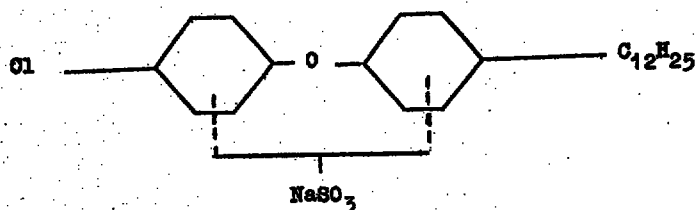
Some substituted diaryloxy sulfonic acids and their salts which can be produced in a halogenated form as employed in the present invention are described in United States Patent Specification No. 2,081,876. Other chlorinated alkylated diaryloxides useful in the present invention are described in copending Application No. 39992/59 (Serial No. 912,340). Others may be by-products of the methods disclosed therein. Amounts of the filming agent to be employed in accordance with the present invention may range from 0.5 to 20 grams per liter of bath but a preferred range is from 0.9 to 8 grams per liter of bath. Desirably, 1.6 to 5.0 grams per liter are employed.

Water constitutes the remaining essential component of the bath. It is to be noted, however, that in some baths there may be other materials present, particularly by-products from the production of the foregoing components. Alternatively, other materials which enhance a particular effect may be employed.

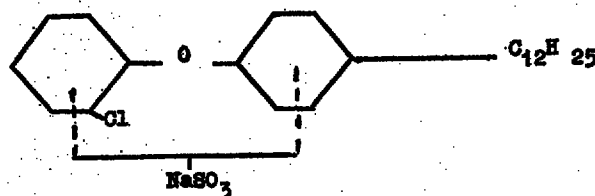
In the practice of the present invention, it has been found to be desirable to impinge the bath upon the surface to be etched as by spraying or by splashing. In the formulation of the etching bath, it has been found to be a general rule that as the concentration of the nitric acid is increased within the aforementioned limitations, it is necessary to also increase the proportion of filming agent employed. However, due to bath depletion as the etching process is carried out, it is better to designate amounts of components in terms of their initial concentrations.

Suitable metals which may be etched by this process include zinc, zinc base alloys, magnesium and magnesium base alloys all of which are substantially homogeneous metals suitable for photoengraving. A zinc or magnesium base alloy is defined as having at least 70 percent of the base component. The average bath temperature may be within a range from less than 4° to about 50°C. or more but a preferred range is from 15.6° to 32.2°C.

A preferred embodiment of this invention comprises nitric acid in an amount from about 90 to 120 grams per liter of bath, diethylbenzene (a mixture of the isomers) in an amount from about 20 to 70 grams per liter of bath and sodium monochlorododecyl diphenyloxy sulfonate of at least 80 percent of the para isomer



and not more than 20 percent of the ortho isomer



in an amount from 3 to 7 grams per liter of bath, preferably 4 to 6 grams per liter of bath. The remainder of the mixture is water.

To carry out the etching process, it is preferred to employ an etching machine of the type disclosed in Patent Specification No. 725,110. In this "Dow Etch" machine, rotating elongated paddles intermittently splash the etching bath upwardly

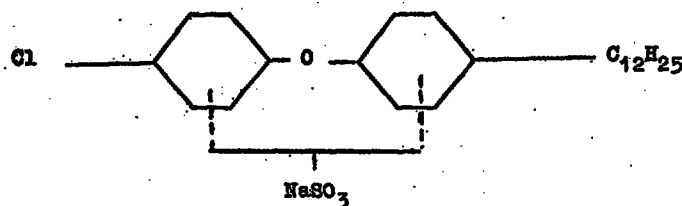


serves

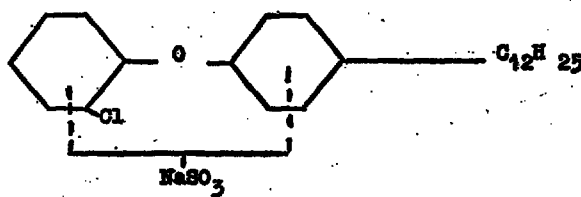
against the image-bearing surface of the object being etched. The splashing action of the paddles also serve to keep the bath in a homogeneous state. A bath of this invention applied in the described manner for about 10 minutes will usually produce depths of etch from approximately 0.63 mm. to 0.89 mm. in line areas of the plate while producing proper depths in various other parts of the plate. Also, etch factors in line image areas from 30—50 are readily obtainable. Etch factor as used in this specification is defined as the ratio of the depths of the etch adjacent to a line of resist divided by one-half of the loss in width of metal immediately beneath the resist. It is obviously desirable to have as high etch factors as possible for faithful reproduction of the image in relief, however, it should be noted that the etch factor can be sensitive to changes in depth. Thus, it should be considered as only one rough approximation of etching bath quality. The foregoing bath also has very good chemical stability as a function of time since it is capable of producing uniform and good results on consecutive plates over periods of many hours.

EXAMPLE 1.

A powderless etching bath of 6.0 liters was prepared in a miniature "Dow Etch" machine by adding 1008 grams of 42° Baume nitric acid, 150 grams of diethylbenzene (a mixture of the isomers), and 30 grams of sodium monochloro-dodecyl diphenyloxide monosulfonate containing at least 80 percent of the para isomer



and not more than 20 percent of the ortho isomer



The remainder of the bath was water. Addition of the filming agent monochloro-dodecyl diphenyloxide monosulfonate was conveniently accomplished by first dissolving or dispersing it in a small amount of water and then adding the resulting solution to the bath. Bath temperature was adjusted to about room temperature, approximately 22.2°C. A plate approximately 12.7 x 12.7 x 0.16 cm. of a magnesium base alloy containing approximately 3 percent Al, 1 percent Zn and trace amounts of impurities, having a polyvinyl alcohol resist thereon was descummed by brushing the surface with dilute nitric acid until the surface was bright.

The plate was then placed in the machine, the paddles turned on and etching allowed to continue for 6 minutes. The depth of etch in line areas was about 0.46 mm. and in 65 line screen halftone areas the depth was about 0.127 mm. The etch factor in the line area was approximately 25.

EXAMPLES 2—20.

In a similar manner to that of the foregoing example, other tests were made as reported in the following tabulated data.

Pertinent definitions of symbols found in Table I are:

Alloys:

- "A" = A Mg base alloy rolled sheet containing 3 percent Al and 1 percent Zn and trace amounts of impurities having been given no solution heat treatment after final rolling.
- "B" = The same alloy composition as "A" that has been solution heat treated for approximately one hour at 316°C.
- "C" = A Zn base alloy rolled sheet containing less than 1 percent Mg and less than 1 percent Al.
- "D" = A Mg base alloy rolled sheet containing 2.6 percent Zn.
- "E" = A Mg base alloy rolled sheet containing 1 percent Zn and 0.2 percent Mn.

Organic immiscible fluids:

- "Penola H.A.N." = A commercial aromatic solvent containing 84 percent aromatics, having a KB of 97, an aniline point of minus 18.9°C., a flash point of 60.0°C. and a distillation temperature range at 760 mm. Hg: initial boiling point of 171.1°C., 50 percent distilled at 230.0°C. and a dry point at 277.8°C. ("Penola" is a registered Trade Mark).
- "Solvesso 150" = A commercial aromatic solvent containing aromatics (alkyl benzenes) 90 percent, naphthalene 2 percent, naphthenes 8 percent, having a KB of 87, an aniline point of minus 27.8°C., a flash point of 65.6°C. and a distillation range at 760 mm. Hg: initial boiling point of 150.6°C. 50 percent distilled at 192.2°C. and a dry point of 212.3°C.

Filming agents:

- "W" = Sodium monochloro dodecyl diphenyloxide monosulfonate
- "X" = Sodium monochloro nonyl diphenyloxide ~~monosulfate~~
- "Y" = Sodium monochloro pentadecyl diphenyloxide monosulfonate

Wherever a concentration range is omitted, the concentration employed is that given under the optimum column. The nitric acid concentration stated are initial concentrations and in some instances optimum results were achieved after several plates had been etched; therefore, the actual nitric acid concentration at the time of optimum results may be less than the initial nitric acid concentration. Also all baths except for Examples numbered 19 and 20 were made up to a volume of 6.0 liters and employed in a miniature "Dow Etch" machine as in Example 1. The excepted baths 19 and 20 were made up to a volume of 134 liters and employed in a commercial size "Dow Etch" machine. Also, larger plates were used, e.g., 46 x 61 x 0.16 cm., but in other respects such examples were run in a similar manner to that of the foregoing smaller baths. Concentrations of bath additives are expressed as grams per liter of bath.



monosulfonate

concentrations

TABLE I

Com- pound	Filming Agent		Organic Immiscible Liquid	Gm./L. of Bath		Initial HNO ₃	Plate Alloy	Etch Conditions		Etch Results					
	Range	Opt.		Compound	Range			Opt.	Gm./L. of Bath as 42°Be as HNO ₃		Time Min.	Temp. of Bath °C.	Line Area Depth (mm)	Halfstone 65 Screen Depth (mm)	Etch Factor (in line area)
2 W	—	3.3	Monochloro-ethylbenzene	—	15	168	118	A	8.0	23.9	0.53	0.127	25+		
3 "	—	5.0	Isophorone	—	10	168	118	A	8.0	23.9	0.51	0.165	20+		
4 "	3.3—4.2	4.2	Dodecylbenzene	10—50	50	140	98	A	12.0	23.9	0.66	0.115	40+		
5 "	—	4.2	Diethylbenzene	—	50	140	98	A	12.0	23.9	0.71	0.115	40+		
6 "	—	2.6	Penola H.A.N. + Diisodecyl phthalate	—	20	168	118	A	12.0	23.9	0.76	0.127	40+		
7 "	1.7—2.5	2.5	Dicapryl adipate	10—20	20	140	98	A	6.0	23.9	0.36	0.127	25+		
8 "	—	5.8	Solvesso 150	10—30	30	140	98	A	6.0	23.9	0.41	0.127	20+		
9 "	5—6.7	6.7	Methylhexyl-ketone	—	15	168	118	A	8.0	23.9	0.51	0.178	20		
10 "	—	4.1	d-Limonene	10—50	50	168	118	A	8.0	22.2	0.56	0.101	20		
11 "	—	3.3	Solvesso 150	—	10	168	118	D	8.0	23.9	0.61	—	40+		
12 "	—	1.7	Dodecylbenzene	—	30	168	118	B	6.0	23.9	0.46	0.127	25+		
13 "	0.8—0.9	0.9	Penola H.A.N. + Diisodecyl-phthalate + Dodecylbenzene	—	10	168	118	E	11.0	22.2	0.64	0.140	50+		
				—	5	168	118								
				—	2.5										

TABLE I (Continued)

TABLE I

Filming Agent	Organic Immiscible Liquid	Initial HNO ₃	Plate Alloy	Etch Conditions		Etch Results	
Com-pound	Gm./L. of Bath		Gm./L. of Bath as 42°Be as HNO ₃	Time Min.	Temp. of Bath °C.	Line Area	Half-tone
	Range	Opt.				Depth (mm)	65 Screen Depth (mm)
14 "	—	1.1	Penola H.A.N.	10			
			+ Diisodecyl-phthalate	—	5	168	118
				6.0	22.8	0.46	0.191
15 "	4.1—5.0	5.0	Solvesso 150	30	22.2	0.28	0.114
16 X	—	3.3	Diethylbenzene	80	22.2	0.51	0.114
17 Y	1.6—3.7	3.7	Diethylbenzene	40	22.2	0.69	0.127
18 W	—	3.3	Diethylbenzene	40	22.2	0.36	—
19 "	—	3.5	Solvesso 150	40	23.9	0.84	0.076
20 "	—	2.3	Solvesso 150	22.4	23.9	0.81	0.152
			+ Diisodecyl-phthalate	16	8.0	0.81	0.152
				8.0	23.9	0.81	0.152
				10.0	22.2	0.69	0.127
				7.0	22.2	0.51	0.114
				7.0	22.2	0.28	0.114
				6.0	22.8	0.46	0.191
				5.0	22.2	0.36	—
				11.0	23.9	0.84	0.076
				8.0	23.9	0.81	0.152
				10.0	22.2	0.69	0.127
				7.0	22.2	0.51	0.114
				7.0	22.2	0.28	0.114
				6.0	22.8	0.46	0.191
				5.0	22.2	0.36	—
				11.0	23.9	0.84	0.076
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				10.0	22.2	0.69	0.127
				7.0	22.2	0.51	0.114
				7.0	22.2	0.28	0.114
				6.0	22.8	0.46	0.191
				5.0	22.2	0.36	—
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				8.0	23.9	0.81	0.152
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				6.0	22.8	0.46	0.191
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				7.0	22.2	0.51	0.114
				7.0	22.2	0.28	0.114
				6.0	22.8	0.46	0.191
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				7.0	22.2	0.28	0.114
				6.0	22.8	0.46	0.191
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				7.0	22.2	0.28	0.114
				6.0	22.8	0.46	0.191
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				11.0	23.9	0.84	0.076
				8.0	23.9	0.81	0.152
				10.0	22.2	0.69	0.127
				7.0	22.2	0.51	0.114
				7.0	22.2	0.28	0.114
				6.0	22.8	0.46	0.191
				5.0	22.2	0.36	—
				11.0	23.9	0.84	0.076
				8.0	23.9	0.81	0.152
				10.0	22.2	0.69	0.127
				7.0	22.2	0.51	0.114
				7.0	22.2	0.28	0.114
				6.0	22.8	0.46	0.191
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				7.0	22.2	0.51	0.114
				7.0	22.2	0.28	0.114
				6.0	22.8	0.46	0.191
				5.0	22.2	0.36	—
				11.0	23.9	0.84	0.076
				8.0	23.9	0.81	0.152
				10.0	22.2	0.69	0.127
				7.0	22.2	0.51	0.114
				7.0	22.2	0.28	0.114
				6.0	22.8	0.46	0.191
				5.0	22.2	0.36	—
				11.0	23.9	0.84	0.076
				8.0	23.9	0.81	0.152
				10.0	22.2	0.69	0.127
				7.0	22.2	0.51	0.114
				7.0	22.2	0.28	0.114
				6.0	22.8	0.46	0.191
				5.0	22.2	0.36	—
				11.0	23.9	0.84	0.076
				8.0	23.9	0.81	0.152
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				7.0	22.2	0.51	0.114
				7.0	22.2	0.28	0.114
				6.0	22.8	0.46	0.191
				5.0	22.2	0.36	—
				11.0	23.9	0.84	0.076
				8.0	23.9	0.81	0.152
				10.0	22.2	0.69	0.127
				7.0	22.2	0.51	0.114
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				6.0	22.8	0.46	0.191
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				5.0	22.2	0.36	—
				11.0	23.9	0.84	0.076
				8.0	23.9	0.81	0.152
				10.0	22.2	0.69	0.127
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				6.0	22.8	0.46	0.191
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				11.0	23.9	0.84	0.076
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				6.0	22.8	0.46	0.191
				5.0	22.2	0.36	—
				11.0	23.9	0.84	0.076
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				5.0	22.2	0.36	—
				11.0	23.9	0.84	0.076
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				5.0	22.2	0.36	—
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				7.0	22.2	0.51	0.114
				7.0	22.2	0.28	0.114
				6.0	22.8	0.46	0.191
				5.0			

EXAMPLE 21.

In a manner similar to that of Example 1, a powderless etching bath of 6 liters was prepared from 708 grams of 42° Baume nitric acid, 150 grams of diisodecylphthalate, 252 grams of Solvesso 150, 5 grams of a polyethylene glycol having an average molecular weight of 2050 (polyethylene glycol being used to obtain better emulsification of the bath) and 28 grams of sodium monochlorododecyl diphenyloxide sulfonate.

A total of nine photoengraving plates similar to that described in Example 1 were etched. After the ninth plate, the acid was replenished by adding 144 grams of nitric acid and the next plate was etched for 10 minutes at a bath temperature of 23.9°C. The resulting good quality plate had depths of etch of 0.79 mm. in line areas and 0.127 mm. in 65 line screen halftone areas with a minimum of lateral etching in all areas.

This bath was then allowed to stand overnight and the next morning, some 16 hours later, a duplicate plate was etched under the same conditions without further additions to the bath. This plate had depths of etch of 0.76 mm. in line areas and 0.127 mm. in 65 line screen halftone areas and was nearly qualitatively identical to the plate etched on the previous day.

In a like manner to that of the foregoing examples, comparable results are achieved with a powderless etching bath in which the following substituted halogenated diaryloxide sulfonic acids or their salts are substituted for the specific film forming agents shown in the foregoing examples such as the sulfonic acid isomers of chloropentyl dinaphthyl oxide, chlorohexyl dinaphthyl oxide, chloroheptyl dinaphthyl oxide, chlorooctyl dinaphthyl oxide, chlorononyl naphthyl - phenyl oxide, chlorodecyl naphthyl - phenyl oxide, chloroundecyl naphthyl - phenyl oxide, chlorododecyl diphenyl oxide, chlorotridecyl diphenyl oxide, chlorotetradecyl diphenyl oxide, chloropentadecyl diphenyl oxide, chlorohexadecyl diphenyl oxide, chloroheptadecyl diphenyl oxide, chlorooctadecyl diphenyl oxide, chlorononadecyl diphenyl oxide, chloroeicosyl diphenyl oxide, chloroheneicosyl diphenyl oxide, chloropentyloxy dinaphthyl oxide, chlorohexyloxy dinaphthyl oxide, chloroheptyloxy dinaphthyl oxide, chlorooctyloxy dinaphthyl oxide, chlorononyloxy naphthyl - phenyl oxide, chlorodecyloxy naphthyl - phenyl oxide, chloroundecyloxy naphthyl - phenyl oxide, chlorododecyloxy diphenyl oxide, chlorotridecyloxy diphenyl oxide, chlorotetradecyloxy diphenyl oxide, chloropentadecyloxy diphenyl oxide, chlorohexadecyloxy diphenyl oxide, chloroheptadecyloxy diphenyl oxide, chlorooctadecyloxy diphenyl oxide, chlorononadecyloxy diphenyl oxide, chloroeicosyloxy diphenyl oxide, chloroheneicosyloxy diphenyl oxide, chlorovaleramido dinaphthyl oxide, chlorohexanamido dinaphthyl oxide, chlorooctanamido dinaphthyl oxide, chloroheptanamido dinaphthyl oxide, chlorononanamido naphthyl - phenyl oxide, chlorodecanamido naphthyl - phenyl oxide, chloroundecanamido diphenyl oxide, chlorotetradecanamido diphenyl oxide, chloropentadecanamido diphenyl oxide, chlorohexadecanamido diphenyl oxide, chloroheptadecanamido diphenyl oxide, chlorooctadecanamido diphenyl oxide, chlorononadecanamido diphenyl oxide, chloroeicosanamido diphenyl oxide, chloroheneicosanamido diphenyl oxide, chlorovaleryloxy dinaphthyl oxide, chlorohexanoyloxy dinaphthyl oxide, chloroheptanoyloxy naphthyl - phenyl oxide, chlorodecanoyloxy naphthyl - phenyl oxide, chloroundecanoyloxy naphthyl - phenyl oxide, chlorododecanoyloxy diphenyl oxide, chlorotridecanoyloxy diphenyl oxide, chlorotetradecanoyloxy diphenyl oxide, chloropentadecanoyloxy diphenyl oxide, chlorohexadecanoyloxy diphenyl oxide, chloroheptadecanoyloxy diphenyl oxide, chlorooctadecanoyloxy diphenyl oxide, chlorononadecanoyloxy diphenyl oxide, chloroeicosanoyloxy diphenyl oxide, chloroheneicosanoyloxy diphenyl oxide and the like.

Others are the sulfonic acids or salts thereof of the isomers of iododiisopropyl dinaphthyl oxide, fluorotributyl dinaphthyl oxide, chlorodipentadecyl dinaphthyl oxide, dichlorotridecyl dinaphthyl oxide, trichlorodiethyl dinaphthyl oxide, bromooctamethyl dinaphthyl oxide, dibromotetramethyl dinaphthyl oxide, bromotetraethyl naphthyl - phenyl oxide, diiodotriheptyl naphthyl - phenyl oxide, trichlorotetramethyl naphthyl - phenyl oxide, difluorododecyl naphthyl - phenyl oxide, diiododioctyl naphthyl - phenyl oxide, fluorodiheptyldecyl naphthyl - phenyl oxide, fluorotetraethyl diphenyl oxide, difluorodioctyl diphenyl oxide, trifluorodiethyl diphenyl oxide, chlorodinonadecyl diphenyl oxide, dichloroeicosyl diphenyl oxide, trichlorodibutyl diphenyl oxide, bromooctamethyl diphenyl oxide, dibromotetraethyl diphenyl oxide, tribromodibutyl diphenyl oxide, iodohehexadecyl diphenyl oxide, diiododidecyl diphenyl oxide, triiodotetraheptyl diphenyl oxide, iodoctyloxy dinaphthyl oxide, diiodopentyloxy dinaphthyl oxide, di-

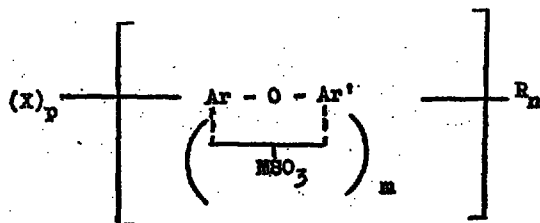
iodovaleramido dinaphthyl oxide, triiodoheptanoyloxy dinaphthyl oxide, bromononamido naphthyl - phenyl oxide, bromodecanoyloxy naphthyl - phenyl oxide, dibromotri-dodecanoyloxy naphthyl - phenyl oxide, dichlorodidecyloxy naphthyl - phenyl oxide, dichlorotetrahexyloxy dinaphthyl oxide, iodoctadecyloxy naphthyl - phenyl oxide, difluorotetrahexanamido naphthyl - phenyl oxide, diiodononadecanamido naphthyl-phenyl oxide, fluorodiheptadecanamido diphenyl oxide, difluorotridecyloxy diphenyl oxide, chloroeicosyloxy diphenyl oxide, dichlorodidecyloxy diphenyl oxide, dichloro-tetradecylanoyloxy diphenyl oxide, trichlorooctadecanoyloxy diphenyl oxide and the like.

In a similar manner to that of the foregoing examples, comparable results may be achieved when the foregoing etching baths are employing to produce such objects as metal name plates, metal patterns and metal templates.

WHAT WE CLAIM IS:—

1. A process of etching by the powderless etching technique with the employment of an aqueous bath which contains as major constituents a dilute strong acid, a water-immiscible organic fluid and a filming agent, characterized in that the filming agent employed is a substituted halogenated diaryloxy sulfonic acid or a salt thereof wherein the substituents on the diaryloxy radical are hydrophobic groups containing from 1 to 30 carbon atoms.

2. Process in accordance with Claim 1, characterized in that the filming agent has the general formula



wherein the bracketed radical represents a diaryloxy radical in which Ar and Ar' are phenyl or naphthyl, R is a hydrophobic substituent having up to 30 carbon atoms, n is an integer from 1 to 8 with the limitation that the total number of carbon atoms of the entire compound does not exceed 50, X is a halogen, and m and p are integers from 1 to 3, and M is a hydrogen-displaceable ion.

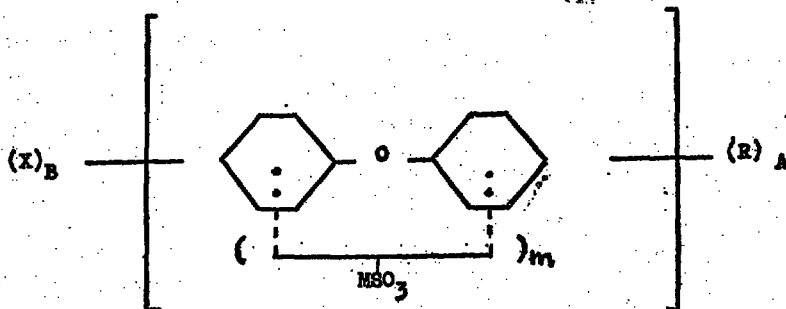
3. Process in accordance with Claims 1 or 2, characterized in that the etching bath contains from 30 to 200 grams of nitric acid, from 3 to 150 grams of the water-immiscible organic fluid, and from 0.5 to 20 grams, of the filming agent per liter of the aqueous bath.

4. Process in accordance with any one of Claims 1 to 3, characterized in that the filming agent is soluble in the etching bath and at least partially soluble in the aqueous and in the organic bath phase.

5. Process in accordance with any one of Claims 1 to 4, characterized in that the halogen is chlorine and/or bromine.

6. Process in accordance with any one of Claims 1 to 5, characterized in that the substituted halogenated diaryloxy sulfonic acid is in the form of the alkali or alkaline earth metal, or ammonium or substituted ammonium salt.

7. Process in accordance with any one of Claims 1 to 6, characterized in that the filming agent is a substituted halogenated diphenyloxy sulfonic acid or sulfonate which has the general formula



employed



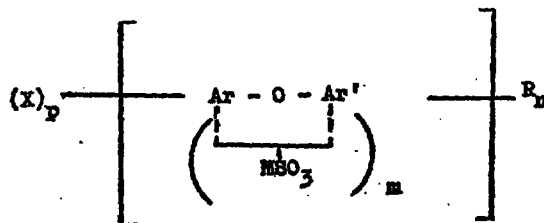
iodoaleramido dinaphthyl oxide, triiodoheptanoyloxy dinaphthyl oxide, bromononamido naphthyl - phenyl oxide, bromodecanoyloxy naphthyl - phenyl oxide, dibromotridodecanoyloxy naphthyl - phenyl oxide, dichlorodidecyloxy naphthyl - phenyl oxide, dichlorotetrahexyloxy dinaphthyl oxide, iodoctadecyloxy naphthyl - phenyl oxide, difluorotetrahexanamido naphthyl - phenyl oxide, diiodononadecanamido naphthyl-phenyl oxide, fluorodiheptadecanamido diphenyl oxide, difluorotridecyloxy diphenyl oxide, chloroeicosyloxy diphenyl oxide, dichlorodidecyloxy diphenyl oxide, dichlorotetradecylanoyloxy diphenyl oxide, trichlorooctadecanoyloxy diphenyl oxide and the like.

In a similar manner to that of the foregoing examples, comparable results may be achieved when the foregoing etching baths are employing to produce such objects as metal name plates, metal patterns and metal templates.

WHAT WE CLAIM IS:—

1. A process of etching by the powderless etching technique with the employment of an aqueous bath which contains as major constituents a dilute strong acid, a water-immiscible organic fluid and a filming agent, characterized in that the filming agent employed is a substituted halogenated diaryloxy sulfonic acid or a salt thereof wherein the substituents on the diaryloxy radical are hydrophobic groups containing from 1 to 30 carbon atoms.

2. Process in accordance with Claim 1, characterized in that the filming agent has the general formula



wherein the bracketed radical represents a diaryloxy radical in which Ar and Ar' are phenyl or naphthyl, R is a hydrophobic substituent having up to 30 carbon atoms, n is an integer from 1 to 8 with the limitation that the total number of carbon atoms of the entire compound does not exceed 50, X is a halogen, and m and p are integers from 1 to 3, and M is a hydrogen-displaceable ion.

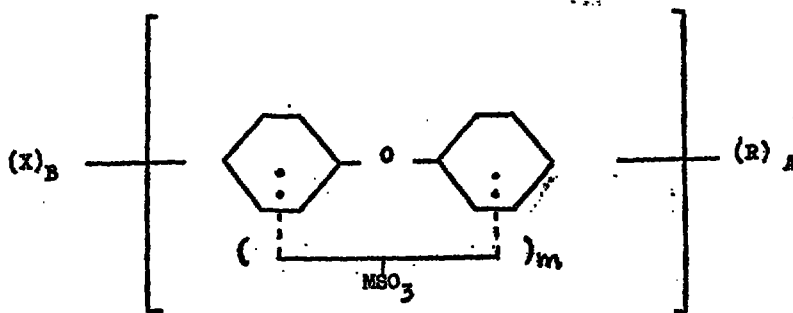
3. Process in accordance with Claims 1 or 2, characterized in that the etching bath contains from 30 to 200 grams of nitric acid, from 3 to 150 grams of the water-immiscible organic fluid, and from 0.5 to 20 grams, of the filming agent per liter of the aqueous bath.

4. Process in accordance with any one of Claims 1 to 3, characterized in that the filming agent is soluble in the etching bath and at least partially soluble in the aqueous and in the organic bath phase.

5. Process in accordance with any one of Claims 1 to 4, characterized in that the halogen is chlorine and/or bromine.

6. Process in accordance with any one of Claims 1 to 5, characterized in that the substituted halogenated diaryloxy sulfonic acid is in the form of the alkali or alkaline earth metal, or ammonium or substituted ammonium salt.

7. Process in accordance with any one of Claims 1 to 6, characterized in that the filming agent is a substituted halogenated diphenyloxy sulfonic acid or sulfonate which has the general formula



wherein R is an alkyl radical containing from 1 to 30 carbon atoms, A is an integer from 1 to 8 with the limitation that the total number of carbon atoms of all alkyl substituents is no less than 4 and no more than 30, X is a halogen, B is an integer from 1 to 2, m is an integer from 1 to 3, and M is a hydrogen-displaceable ion.

8. Process in accordance with any one of Claims 1 to 7, characterized in that the filming agent is a composition which consists at least in part of an alkylated monochlorodiphenyloxide monosulfonic acid or monosulfonate which has one alkyl substituent of from 9 to 30 carbon atoms, and preferably from 8 to 18 carbon atoms, and advantageously an average of 12 carbon atoms.

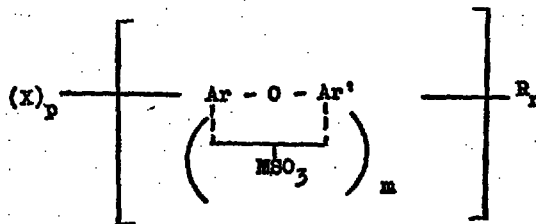
9. Process in accordance with Claim 8, characterized in that the monochloroalkyl-diphenyloxide monosulfonic acid or monosulfonate is employed in the form of a mixture of the para-isomer and ortho-isomer which contains, preferably, at least 80 percent of the para-isomer and no more than 20 percent of the ortho-isomer.

10. Process in accordance with Claims 8 or 9, characterized in that the filming agent comprises, in addition, a monochloroalkyldiphenyloxide disulfonic acid or disulfonate wherein the alkyl group contains, preferably, from 8 to 18 carbon atoms.

11. Process in accordance with any one of Claims 8 to 10, characterized in that from 2 to 10 percent of the isomers of the monochloroalkyldiphenyloxide disulfonic acid or disulfonate are employed.

12. An etching bath comprising (A) acid; (B) a water-immiscible organic fluid substantially stable in the presence of dilute acid, (C) a substituted halogenated diaryloxide sulfonic acid wherein the substituents on the diaryloxide radical are hydrophobic groups containing from 1 to 30 carbon atoms, and (D) water.

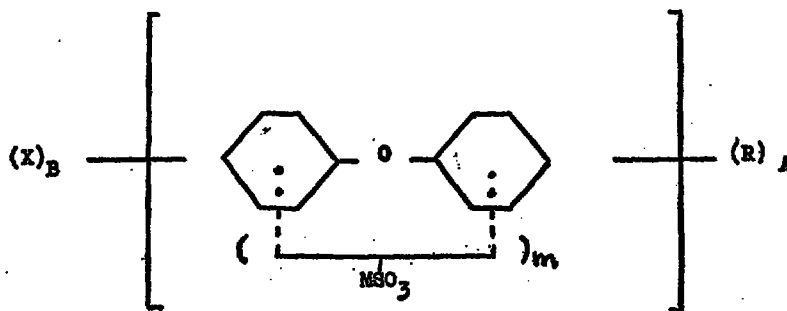
13. An etching bath in accordance with Claim 12, wherein the filming agent is a hydrophobic - hydrophilic compound of the general formula



wherein the bracketed radical represents a diaryloxide radical in which Ar and Ar' are phenyl or naphthyl and to which molecule is appended from 1 to 3 sulfonic groups, R is a hydrophobic substituent having up to 30 carbon atoms, n is an integer from 1 to 8 with the limitation that the total number of carbon atoms of the entire compound does not exceed 50, X is a halogen, and m and p are integers from 1 to 3, and M is a hydrogen displaceable ion.

14. An etching bath in accordance with Claims 12 or 13, which contains from 30 to 200 grams of nitric acid, from 3 to 150 grams of the water-immiscible organic fluid, and from 0.5 to 20 grams, and preferably from 0.9 to 8 grams of the filming agent per liter of the aqueous bath.

15. An etching bath in accordance with any one of Claims 12 to 14, wherein the filming agent is a substituted halogenated diphenyloxide sulfonic acid which has the general formula



wherein R is an alkyl radical containing from 1 to 30 carbon atoms, A is an integer from 1 to 8 with the limitation that the total number of carbon atoms of all alkyl substituents is no less than 4 and no more than 30, X is a halogen, B is an integer from 1 to 2, m is an integer from 1 to 3 and M is a hydrogen-displaceable ion.

16. An etching bath in accordance with any one of Claims 12 to 15, wherein the filming agent is a composition which consists at least in part of an alkylated chlorodiphenyloxide monosulfonic acid or monosulfonate, respectively, which has one alkyl substituent of from 9 to 30 carbon atoms, and preferably from 8 to 18 carbon atoms, and advantageously, an average of 12 carbon atoms.

17. An etching bath in accordance with any one of claims 12 to 16, wherein the filming agent contains the monochloroalkyldiphenyloxide monosulfonic acid or monosulfonate as a mixture of the para-isomer and ortho-isomer, which mixture comprises, preferably, at least 80 per cent of the para-isomer and preferably no more than 20 per cent of the ortho-isomer.

18. An etching bath in accordance with claims 16 or 17, which contains, in addition, a monochloroalkyldiphenyloxide disulfonic acid or disulfonate wherein the alkyl group contains preferably from 8 to 18 carbon atoms.

19. A process for etching by the powderless etching technique employing an aqueous bath which contains as major constituents, water, a dilute strong acid, a water-immiscible organic fluid and as a filming agent, a substituted halogenated diaryloxide sulfonic acid or a salt thereof substantially as described hereinbefore.

20. A process for etching by the powderless etching technique employing an aqueous bath which contains as major constituents water, a dilute strong acid, a water-immiscible organic fluid and as a filming agent, a substituted halogenated diaryloxide sulfonic acid or a salt thereof, substantially as described with particular reference to the preceding examples.

21. An etching bath containing as the major constituents, water, a dilute strong acid, a water-immiscible organic fluid and as a filming agent, a substituted halogenated diaryloxide sulfonic acid or a salt thereof, substantially as described hereinbefore.

22. An etching bath containing as the major constituents water, a dilute strong acid, a water-immiscible organic fluid and as a filming agent, a substituted halogenated diaryloxide sulfonic acid or a salt thereof substantially as described with particular reference to the preceding examples.

23. Etched articles whenever produced by a process as claimed in any of the preceding claims 1 to 12, 19 or 20.

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Agents for the Applicants.

Gb

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