RESERVE COPY

1,143,059

PATENT SPECIFICATION

NO DRAWINGS

1,143,059

Inventor: JAMES ALLEN BROWN

Date of Application and filing Complete Specification: 19 Sept., 1967.

No. 42646/67.

Application made in United States of America (No. 580,622) on 20 Sept., 1966

Complete Specification Published: 19 Feb., 1969.

© Crown Copyright 1969.

Index at acceptance:—B6 JA6A

Int. Cl.:—C 23 f 1/00

COMPLETE SPECIFICATION

Powderless 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:—

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

Prior to about 1953, most engraving of magnesium and zinc was done, primarily in the photoengraving art, by a so-called powder process which had been used without significant improvements for a period of years. With the advent of the powderless etching process the old powder technique of etching in photoengraving has been essentially 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 up to about 0.004 inch (0.1 mm.) per minute may occasionally be obtained in a high quality plate, such high etch rates are essentially not reproducible by design under production conditions with consistent high quality results. Conventionally, however, high quality powderless etched plates are obtained over a series of plates from an etching bath with an average etch rate of from about .0015 inch to 0.0020 inch (0.04—0.05 mm.). High etch rates from any conventional powderless etching bath can be obtained, for example, by 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 commercially and unusable.

The above defects and deficiencies have been overcome by the present invention which is a method of etching magnesium characterized by impinging a powderless etching bath at a temperature of from 65° to 85°F. (18.3°—29.4°C.) against an etchable magnesium base metal plate having an acid resistant coated image pattern thereon, said powderless etching bath consisting of (A) from 10 to 15 volume percent of nitric acid, (B) from 5.0 to 12.5 grams per liter of bath of sulfonated monochlorododecyldiphenyl oxide, (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 80 percent, and a Kauri Butanol value range of from 100 to 110, and (2) an alkyl benzene branched chain hydrocarbon liquid characterized by a boiling range at 5 percent recovery of 525 to 545°F. (274°—285°C.) and 95 percent recovery at 550 to 575°F. (288°—302°C.) and a Kauri Butanol value range of from 40 to 50, said aromatic naphtha being employed in an amount of from 9 to 46 grams per liter of bath, said alkyl benzene branched chain hydrocarbon liquid in an amount of from 9 to 18 grams per liter of bath, the balance of the bath being water; admixing with said bath after etching the first and each successive plate from 0.058 to 0.104 grams of a petroleum sulfonate per gram of dissolved base metal in the bath, from 0.04 to 0.07 grams of sodium monochlorododecyldiphenyl oxide disulfonate per gram of dissolved base metal in the bath, and from 0.715 to 1.195 grams of an aromatic naphtha solvent per gram of dissolved base metal in the bath, said solvent being characterized by a Kauri Butanol value of from 100 to 130, being substantially unreactive with the acid component of the etching bath and containing substantially no terminal functional groups.

The powderless etching bath composition

[*Price 4s. 6d.*]

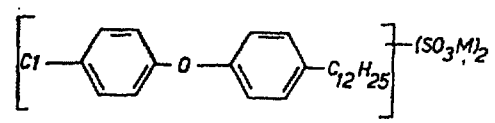
employed in the present novel method consists essentially of the components and amounts described below.

(A) NITRIC ACID.

Operable amounts of nitric acid range from 10 to 15 percent by volume (142 to 213 grams per liter) (based on 42° Bé Nitric Acid, technical grade), and preferably 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 monochlorododecyldiphenyl 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 20 percent, said filming agent comprising at least 70 percent monosulfonate, there being up to 30 percent disulfonate, the dodecylalkyl group containing an average of 12 carbon atoms, but ranging from 9 to 15 carbon atoms, there being a preponderance of C_{12} material.

The filming agents 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 5 to 12.5 gm. per liter of bath, a preferred range being from 5.75 to 7.5 gms. per liter of bath. A particularly desirable amount is 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 alkylbenzene mixture. The aromatic naphtha component is a hydrocarbon liquid characterized by a boiling range at 760 mm. starting at about 325°F. (163°C.), 50 percent distilled at 450°F. (232°C.), and dry point at 540°F. (282°C.). 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 100 to 110.

A particular aromatic naphtha found suitable for use in the invention is a commercial aromatic solvent under the tradename of Penola H.A.N. (*H*eavy *A*romatic *N*aphtha), which contains 84 percent aromatics, has a flash point of 140°F. (60°C.) of a distillation temperature range at 760 mm.; initial boiling point of 340°F. (171°C.), 50 percent distilled at 446°F. (230°C.), and dry point at 532°F. (278°C.).

The alkylbenzene component is a branched chain hydrocarbon liquid with a distillation range at 760 mm of 5 percent recovery from 525 to 545°F. (274°—285°C.) and 95 percent recovery from 550 to 575°F., (288°—302°C.), and a Kauri Butanol value range of from 40 to 50. An alkylbenzene found particularly desirable for use in the invention consists of dodecyl benzene having a boiling range at 760 mm of 5 percent recovery of about 533°F. (278°C.) and 95 percent recovery at 563°F. (295°C.). Such material is commercially available as "Chevron Alkylate 21" by the Chevron Chemical Co., Oronite Division.

The amount of the aromatic naphtha liquid to be used ranges from 9 to 46 gms. of liquid per liter of bath, a preferred amount being about 28 gms. per liter of bath. The alkylbenzene liquid is used in an amount of from 9 gms. to 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 presence 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. 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 monochlorododecyldiphenyl 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 commercial aromatic solvent tradename which is a mixture of 90 percent alkylbenzenes, 2 percent naphthalene, 8 percent naphthenes, a flashpoint of 150°F. (65.6°C.), initial boiling point (at 760 mm.) of 330°F. (166°C.), 50 percent distilled at 378°F. (192°C.), and dry point at 415°F. ~~(123°C.)~~ (213°C.).

(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 virtue of the results achieved when they are employed in etching baths individu-

ally 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. (0.1 mm./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. (0.12 mm./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 can range from 0 to 1.5 gm. per liter of bath but a preferred range is from 0.4 to 0.6 grams 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 0.1 to 0.4 grams per liter of bath solution, the preferred range being from 0.2 to 0.3 grams per liter of bath.

In general, in formulating the foregoing powderless etching bath in a powderless etching machine of a given capacity, the machine is normally first filled about half full with tap water, and then 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 and the bath is then brought to the desired temperature. The machine should be operated for a few minutes before etching any plates to make certain that the bath is homogeneous.

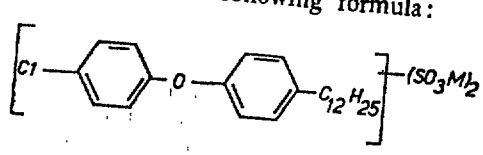
While etching machines of various designs can be used, it is preferable to employ one of the type disclosed in United States Patent 2,669,048, issued February 16, 1954. When employing the above bath and machine, the plate is mounted with the surface to be etched facing the bath. The machine is then actuated 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 65° to 80°F. (18.3°—26.7°C.), preferably from 72 to 78°F. (~~22.2~~—25.6°C.). In general, the paddle speed, or in non-paddle machines the force of impingement, of the machine during etching is held sufficient to obtain the maximum etch rate. The paddle speed may vary from 400 to 700 r.p.m., depending on the particular design of the machine. Etching machines of the type disclosed in U.S. Patent 2,669,048, for example, can be operated at from about 550 to 625 r.p.m. in accordance with the present invention to obtain the maximum etch rate.

Extender Composition.

The extender composition of the present invention consists essentially of a three component organic liquid mixture of a petroleum sulfonate, sodium monochlorododecyldiphenyl 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 extender 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 350 to 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 .058 to .104 grams per gm. of dissolved base metal, and preferably about .083 grams per gm. of dissolved base metal.

The sodium monochlorordodecyldiphenyl 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 20 percent, said sodium salt being essentially a disulfonate, preferably at least 90 percent disulfonate, the dodecylalkyl group containing an average of 12 carbon atoms, but ranging from 9 to 15 carbon atoms, there being a preponderance of C_{12} material. This disulfonate material, as an extender component, is employed in an amount of from 0.04 to 0.07 grams of disulfonate material per gram of dissolved base metal in said bath, and preferably 0.055 grams per gram of dissolved base metal.

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

The aromatic naphtha 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 100 to 130. In addition, these solvents are substantially unreactive with the acid component of the powderless etching bath to which it may be added, and contain 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 108 and contains typically 99 percent of said high boiling aromatics.

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

The following examples illustrate the present invention.

EXAMPLE I.

A powderless etching bath of 130 liters in an Chemco powderless Etching Machine Model 510 B was prepared 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 monochlorododecyldiphenyl oxide sulfonate (filming agent) in Solvesso 150 (13 grams per liter of bath), 52 grams of adipic acid (0.4 grams/liter of bath), 3900 ml. of Penola H.A.N. aromatic solvent (28 grams per liter of bath), and 1950 ml. of dodecylbenzene (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 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 weighed for loss of metal, an extender solution was added to the bath at a rate of 2 ml. of extender per gram of dissolved magnesium. Along with the extender, nitric acid additions (5 ml. per gram of dissolved magnesium) were made to the bath after each plate etched.

The extender components were added to the bath in the preferred amounts stated hereinbefore, as a solution 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 by additions of acid, an extender solution, total etch time for each plate in minutes, the bath temperature, depth of etch in inches (mm.), metal lost in grams by each plate, etch rate, and an evaluation of plate quality by means of a visual qualitative inspection. In each run, a paddle speed of 570 r.p.m. and a plate size of 18" × 24" (45.7×61 cm.) were employed.

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)

Etch Time	Bath Temp.	Etch Depth*	Metal	Etch Rate***

TABLE I (EXAMPLE I)

Sample No.	Bath Additions	Etch Time in Mins.	Bath Temp. °F. °C.	Etch Depth* (mm.)	Metal Loss**	Etch Rate*** (mm./min.)	Results
(1)		9	73 (22.8°)	.035" (0.89)	194	3.88 (0.099)	Very good engraving
(2)	970 ml. of HNO_3 + 388 ml. of Extender	9—1/2	73 (,,)	.036" (0.91)	196	3.8 (0.096)	Very good engraving
(3)	980 ml. of HNO_3 + 392 ml. of Extender	10	74 (23.3°)	.036" (0.91)	194	3.6 (0.091)	Very good engraving
(4)	970 ml. of HNO_3 + 388 ml. of Extender	10	74 (,,)	.035" (0.89)	191	3.5 (0.089)	Very good engraving
(5)	955 ml. of HNO_3 + 382 ml. of Extender	10—1/2	75 (23.9°)	.035" (0.89)	192	3.33 (0.085)	Very good engraving
(6)	960 ml. of HNO_3 + 384 ml. of Extender	11	75 (,,)	.035" (0.89)	193	3.18 (0.081)	Very good engraving
(7)	965 ml. of HNO_3 + 386 ml. of Extender	11—1/2	76 (24.4°)	.037" ~~(0/94)~~	202	3.2 (0.082)	Good engraving
(8)	1020 ml. of HNO_3 + 404 ml. of Extender	12	77 (25°)	.035" (0.89)	200	2.91 (0.074)	Very good engraving
(9)	1000 ml. of HNO_3 + 400 ml. of Extender	12	77 (,,)	.034" (0.86)	195	2.83 (0.072)	Good engraving
			Bath Depleted		1757		

* Etch depth is the depth of etching in the open areas measured in inches (mm.)

** Metal loss is grams of magnesium dissolved per plate.

*** Etch rate is mils of metal dissolved per minute (mm./min.)

Average Etch Rate = 3.36 mils/minute (0.085 mm./min.).

1,143,059

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 both), 850 ml. of a 50 percent solution of sodium monochlorododecyldiphenyl 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 ~~compaartive~~ comparative etching sequence by additions of acid and of extender, total etch time per plate in minutes, paddle speed, plate size, depth of etch in inches (mm.), 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. In each run, the bath temperature was maintained at 65°F. (18.3°C.) and at the end of the ninth run the bath was depleted.

TABLE II (COMPARATIVE EXAMPLE)

TABLE II (COMPARATIVE EXAMPLE)

Sample No.	Bath Additions	Etch Time in Mins.	Paddle Speed, rpm	Plate Size In. (cm.)	Etch Depth In. (mm.)	Metal Loss, g./plate	Etch* Rate (mm./min.)	Results
1		10	420	9″ × 12″ (22.8 × 30.4)	.022″ (0.56)	27	2.2 (0.056)	Very good engraving
2	135 ml. of HNO_3	10	440	9″ × 12″ (22.8 × 30.4)	.024″ (0.61)	28	2.4 (0.061)	Very good engraving
3	140 ml. of HNO_3	15	430	18″ × 24″ (45.7 × 61.0)	.034″ (0.86)	190	2.27 (0.057)	Good engraving Slight chipping on hot line end
4	950 ml. of HNO_3 + 290 ml. of Extender	16	425	18″ × 24″ (45.7 × 61.0)	.034″ (0.86)	187	2.12 (0.054)	Very good engraving
5	935 ml. of HNO_3 + 290 ml. of Extender	16—1/2	425	18″ × 24″ (45.7 × 61.0)	.034″ (0.86)	189	2.05 (0.052)	Very good engraving
6	945 ml. of HNO_3 + 290 ml. of Extender	17	425	18″ × 24″ (45.7 × 61.0)	.0335″ (0.85)	186	1.97 (0.050)	Very good engraving
7	930 ml. of HNO_3	18	425	18″ × 24″ (45.7 × 61.0)	.033″ (0.84)	189	1.83 (0.047)	Very good engraving
8	945 ml. of HNO_3	19	425	18″ × 24″ (45.7 × 61.0)	.034″ (0.86)	186	1.78 (0.045)	Very good engraving
9	930 ml. of HNO_3	20	425	18″ × 24″ (45.7 × 61.0)	.032″ (0.81)	190	1.6 (0.041)	Very good engraving
						1372		

* Average etch rate = 2.02 mils per minute (0.051 mm./min.)

The novelty, usefulness, and unobviousness of the present invention are clearly revealed in a detail comparison of Example I and the Comparative Example.

The outstanding increase in average etch rate of the Example I of ~~3.13~~ mils (0.085 mm.) per minute as compared to the average of 2.02 mils (0.051 mm.) 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 ~~Compaartive~~ 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 (0.038—0.051 mm.) 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, or 32 percent less time required. 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 ~~Compaartive~~ Example by comparing "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, a 28 percent greater capacity in the Example I bath.

Both in the Comparative Example and in Example I, the plate quality was essentially 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" × 12" (22.8 × 30.4 cm.) 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 dodecylbenzene (12.9 gm/l)
Water—balance to make up 137 liters,

employing a powderless etching machine in accordance 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. (23.9°C.). An etch rate of 5 thousandths of an inch (0.127 mm.) per minute was obtained and the quality of etch was good. No extender of any kind was added.

WHAT WE CLAIM IS:—

1. A method of etching magnesium comprising impinging a powderless etching bath at a temperature of from 65° to 85°F. (18.3°—29.4°C.) against an etchable magnesium base metal plate having an acid resistant coated image pattern thereon, said powderless etching bath comprising (A) from 10 to 15 volume percent of nitric acid, (B) from 5.0 to 12.5 grams per liter of bath of sulfonated monochlorododecyldiphenyl oxide, (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 80 percent, and a Kauri Butanol value range of from 100 to 110, and (2) an alkyl benzene branched chain hydrocarbon liquid characterized by a boiling range at 5 percent recovery of 525 to 545°F. (274°—285°C.) and 95 percent recovery at 550 to 575°F. (288°—302°C.) and a Kauri Butanol value range of from 40 to 50, said aromatic naphtha being employed in an amount of from 9 to 46 grams per liter of bath, said alkyl benzene branched chain hydrocarbon liquid in an amount of from 9 to 18 grams per liter of bath, the balance of the bath being water; admixing with said bath after etching the first and each successive plate from 0.058 to 0.104 grams of a petroleum sulfonate per gram of dissolved base metal in the bath, from 0.04 to 0.07 grams of sodium monochlorododecyldiphenyl oxide disulfonate per gram of dissolved base metal in the bath, and from 0.715 to 1.195 grams of an aromatic naphtha solvent per gram of dissolved base metal in the bath, said solvent being characterized by a Kauri Butanol value of from 100 to 130, being substantially unreactive with the acid component of the etching bath and containing substantially no terminal functional groups.

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

3. The method as claimed in 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 0.1 to 0.4 grams per liter of bath.

The novelty, usefulness, and unobviousness of the present invention are clearly revealed in a detail comparison of Example I and the Comparative Example.

The outstanding increase in average etch rate of the Example I of ~~3.13~~ mils (0.085 mm.) per minute as compared to the average of 2.02 mils (0.051 mm.) 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 ~~Compaartive~~ 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 (0.038—0.051 mm.) 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, or 32 percent less time required. 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 ~~Compaartive~~ Example by comparing "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, a 28 percent greater capacity in the Example I bath.

Both in the Comparative Example and in Example I, the plate quality was essentially 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" × 12" (22.8 × 30.4 cm.) 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 dodecylbenzene (12.9 gm/l)
Water—balance to make up 137 liters,

employing a powderless etching machine in accordance 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. (23.9°C.). An etch rate of 5 thousandths of an inch (0.127 mm.) per minute was obtained and the quality of etch was good. No extender of any kind was added.

WHAT WE CLAIM IS:—

1. A method of etching magnesium comprising impinging a powderless etching bath at a temperature of from 65° to 85°F. (18.3°—29.4°C.) against an etchable magnesium base metal plate having an acid resistant coated image pattern thereon, said powderless etching bath comprising (A) from 10 to 15 volume percent of nitric acid, (B) from 5.0 to 12.5 grams per liter of bath of sulfonated monochlorododecyldiphenyl oxide, (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 80 percent, and a Kauri Butanol value range of from 100 to 110, and (2) an alkyl benzene branched chain hydrocarbon liquid characterized by a boiling range at 5 percent recovery of 525 to 545°F. (274°—285°C.) and 95 percent recovery at 550 to 575°F. (288°—302°C.) and a Kauri Butanol value range of from 40 to 50, said aromatic naphtha being employed in an amount of from 9 to 46 grams per liter of bath, said alkyl benzene branched chain hydrocarbon liquid in an amount of from 9 to 18 grams per liter of bath, the balance of the bath being water; admixing with said bath after etching the first and each successive plate from 0.058 to 0.104 grams of a petroleum sulfonate per gram of dissolved base metal in the bath, from 0.04 to 0.07 grams of sodium monochlorododecyldiphenyl oxide disulfonate per gram of dissolved base metal in the bath, and from 0.715 to 1.195 grams of an aromatic naphtha solvent per gram of dissolved base metal in the bath, said solvent being characterized by a Kauri Butanol value of from 100 to 130, being substantially unreactive with the acid component of the etching bath and containing substantially no terminal functional groups.

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

3. The method as claimed in 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 0.1 to 0.4 grams per liter of bath.

* C L M S *

4. Method for etching magnesium base metal plate as hereinbefore described in the Examples.

5. Magnesium base metal plate whenever etched by any of the methods of Claims 1 to 4.

BOULT, WADE & TENNANT,
111 and 112, Hatton Garden, London, E.C.1,
Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

YR.

