

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Etching Process and Improved Etching Bath

5 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:—

10 This invention relates to an improved etching bath and methods for etching photo-engraving plates, name plates, metal patterns and the like. More particularly, it is concerned with an additive for improving and controlling etching bath characteristics.

15 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 no more require the protection of the resist 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 which adjuvants are generally added to the aqueous acid making up the etching bath. These methods have been described, for instance, in Patent Specifications Nos. 703,814, 709,315 and 818,744. One undesirable characteristic of some etching baths is their tendency to permit localized defilming on relief side walls. This results in a chipped surface which, in aggravated situations, causes poor printing plates. Another problem stems from the inability of some baths to quickly form a protective film in the initial stage of etching that will protect the resist from lateral etching directly beneath it and as the etching action of the acid penetrates

to greater depths, there is a problem of preventing lateral etching of relief side walls with the formation of proper relief shoulders. Another problem of great importance is the etching bath's capacity to produce proper depths of etch in all areas of a combination plate, e.g., line and halftone images on the same plate. Often the combined effect of the foregoing problem factors in the unimproved baths is readily apparent to even the casual observer due to the rough appearance of the plate.

A change in bath formulation either with respect to the filming agent, the water-immiscible organic fluid or the amount of the acid to improve one of these bath characteristics will usually have an adverse effect on some other characteristic. For example, a bath formulation that increases the depth of penetration obtainable will generally have an adverse effect by permitting greater lateral etching to occur. Similarly, when the film permanency on the relief side wall is enhanced, there is a tendency to diminish depths of etch in halftone areas and other small non-image areas.

These problems can be readily overcome and control of these factors is now possible if one employs the process and bath of the present invention. The novel process of the invention comprises etching, by the powderless etching technique, with the employment of an aqueous bath containing as major constituents a dilute strong acid, a water-immiscible organic fluid, and a filming agent whereby one or more carboxylic acids or their salts are added in small proportions, as a film-controlling agent, to the bath and/or to the ingredients used to make up the bath. The additive of this invention is designated as a film-controlling agent since it affords both a means for improving etching bath characteristics and a means for adjusting the bath's filming tendency.

[Price 4s. 6d.]



Generally, one will employ as the film-controlling agent a mono- and/or a dicarboxylic acid. Preferred are those which are composed of carbon, hydrogen and oxygen atoms only and which have from 4 to 22 carbon atoms.

One of the great advantages of the invention is to be found in the fact that it is now possible to control the performance characteristics of the etching bath and/or the physical structure and the quality and usefulness of the etched articles, such as printing plates, by varying the amount and/or kind of the carboxylic acid which is present in or which is added to the etching bath. Depending upon the desired effect and modification of the process or characteristics of the etching bath, one will employ a monocarboxylic or a dicarboxylic acid. Generally, the dicarboxylic acids may be used with advantage as the film-controlling agent in combination line and halftone etchings.

It was found that monocarboxylic acids tend to stabilize the films, particularly at the relief side walls. This apparently has the effect that the film adheres better and more permanently to these particular portions or areas of the etched relief without interfering with the etching process in the areas remote from these places. Dicarboxylic acids, on the other hand, were found to generally improve penetration of the etching bath through the film, primarily in the halftone areas, without substantially increasing lateral etching. Thus the action of the monocarboxylic acids and that of the dicarboxylic acids in the bath of the type used in the process of the invention is very specific and, in some respects, in diametrically opposite directions as to the effect achieved in the process.

It is important to note that neither of the acids acts directly as the filming agent. The acids are generally used in amounts which are much below those required of a filming agent, regardless of whether used alone or in combination with another filming agent and particularly with sulfated oils, such as sulfated castor oil. The beneficial effects as film-controlling agents can be realized only if the acids are used in addition to a suitable filming agent in relatively small proportions compared to the filming agent, which proportions are carefully adjusted to achieve and control the desired degree of modification of the etching bath characteristics. It is desirable that the filming agent is one that is not directly derived by chemical modification from the carboxylic acids used as the film-controlling agent.

Filming agents which can be used with particular benefit in conjunction with the film-controlling agent of the present invention can be found among the group of certain ionic hydrophobic-hydrophilic organic filming

agents which group comprises such compounds as petroleum sulfonates, alkyl and/or aryl substituted diaryloxide sulfonates, alkyl and/or aryl substituted halogenated diaryloxide sulfonates, alkylaryl sulfonates, esters of sulfo-succinic acid and/or organic sulfonates, the hydrophobic portion of which is made up of two organic radicals which are connected over an amide, ester, or ether bridge and wherein at least one of the organic radicals contains 12 or more carbon atoms in an uninterrupted series of carbon to carbon bonds. As has been taught, certain sulfated oils and particularly sulfated castor oil require nearly a 1:1 ratio of the acid for satisfactory performance. In these cases, the acid apparently acts as a filming agent rather than as a film-controlling agent as is taught by the present invention.

The etching process of the present invention and the novel bath containing controlling amounts of the film-controlling agents permit the production of proper depth of etch in all kinds of image areas of combination plates. Furthermore, it is now possible to protect the plates against lateral etching and chipping of relief side walls. Such articles as name plates, metal patterns, templates, and the like can now be produced in excellent quality by the powderless etching technique.

In the following detailed description of the invention, the compositions of the bath and amounts of ingredients contained therein are expressed in terms of grams per liter of bath. Nitric acid is taken to mean 100 per cent nitric acid unless otherwise specified.

The acid additive is generally nitric acid although mixtures of nitric acid and small quantities of sulfuric, hydrochloric or acetic acids may be beneficial in some instances. 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 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 filming agent employed. Substantially stable is defined as the nonoccurrence 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, dicapryladipate, and the like. 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 per cent aromatics, has a flash point of 60° C. and a distillation temperature range at 760 mm. Hg.; initial boiling point of 171.1° C., 50 per cent distilled at 230° C. and dry point at 277.8° C. Another commercial aromatic solvent employed is a mixture of approximately 90 per cent alkylbenzenes, 2 per cent naphthalene and 8 per cent naphthenes. It has a flash point of 65.6° C. and a distillation temperature range at 760 mm. Hg.; initial boiling point of 150.6° C., 50 per cent distilled at 192.2° C. and dry point at 46.1° 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.

A third bath additive is a filming agent which may be a single compound or a blend of compounds. The filming agent employed in this invention may be further described as an ionic hydrophobic-hydrophilic, organic compound or mixture of such compounds which tends to form a film on the surface of the metal to be etched. It is believed that a polar part of a filming agent molecule attaches to the metal surface and the hydrophobic segment on this molecule having an affinity for the molecules of the water-immiscible organic fluid attracts such molecules to it thereby perfecting an acid-resistant film. Such filming agents as are operable within this invention must have selective filming properties, i.e., they must contribute to the forming of a stable acid-resistant film on relief side walls while permitting etching in adjacent resist free areas under the conditions of bath application. Such filming agents must also be totally soluble in the bath and partially soluble (at least 0.01 per cent of the solute) in each of the bath phases. Examples of filming agents suitable for use in this invention include petroleum sulfonic acids and their salts as disclosed in Patent Specification No. 709,315, sulfonated esters of succinic acid of Patent Specification No. 703,814, sulfated fats, oils, and waxes of Patent Specification No. 818,744, substituted halogenated diaryloxide

sulfonates of copending Application No. 19494/60 (Serial No. 928,164), and sulfonated esters, amides and ethers of copending Application No. 19496/60 (Serial No. 928,166).

The amounts of the filming agent employed can range from 0.2 to 20 grams per liter of bath but a preferred range is from 1 to 15 grams per liter of bath. A desired range is from 2 to 10 grams per liter of bath.

The fourth bath additive, the film-controlling agent, may be a single compound or a blend of such compounds. This agent is generally an organic compound consisting of only hydrogen, carbon and oxygen having 5 to 22 carbon atoms, up to 3 carbon to carbon double bonds which refers to aromatic unsaturation as well as that in aliphatic chains, and 1 to 2 carboxyl groups. The film-controlling additive is limited in that it must be soluble in the bath at bath temperatures, and although it may be aryl, cycloaliphatic or aliphatic or a combination such as alkylaryl, it is essential that there be at least one carboxyl group present. By their use, it is possible to regulate the depths of etch obtainable in such areas as halftones where proper depths of etch are difficult to obtain. Likewise, some agents also have a beneficial stabilizing effect on the protective film in open line areas of the plate thereby minimizing lateral etching and chipped or rough surfaces. Another example of the beneficial effect of such agents is evident in areas where there are isolated small images such as leader dots. The etching action of the bath without the proper additive will often etch away the entire dot but with such an additive present, the small isolated dots are not etched away. Also, when a bath as formulated has a tendency to form films that are too heavy to be operable or the bath has developed a heavy filming tendency during use, it may be modulated by the use of this agent to improve bath etching characteristics.

The amounts of the film-controlling agent usually employed may vary in a wide range, depending upon the bath composition and the effect derived and usually is in the ranges from 0.05 to 3 grams per liter of bath. A preferred range is from 0.08 to 2.5 grams per liter of bath. The most desired range is from 0.10 to 2.0 grams per liter of bath.

The remainder of the bath is water but it should be understood that other materials may also be present within the bath, since as a practical matter it is not possible to employ the aforementioned bath components in a pure state.

In the practice of the present invention, it has been found desirable to impinge the bath upon the surface to be etched as by spraying or by splashing. The bath selectively forms an acid-resistant film on the plate

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under the conditions of its application thereby allowing etching in resist-free areas normal to the surface of the metal plate while at the same time protecting the resist and the relief side walls from lateral etching.

In formulating the etching bath, as a general rule, as the concentration of the nitric acid is increased within the aforementioned limits, it is necessary to also increase the proportion of filming agent employed. 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 the process of this invention 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 70 per cent of the base component. The average bath temperature may be within a range from 4.4° C. to 48.9° C. but a preferred range is from 15.6° C. to 32.2° C.

A preferred embodiment of this invention comprises nitric acid in an amount from 80 to 120 grams per liter of bath, preferably 103 grams per liter of bath, diethylbenzene in an amount from 20 to 80 grams per liter of bath, preferably 40 grams per liter of bath and sodium monochloro dodecyl diphenyloxide monosulfonate of at least 80 per cent of the para isomer and not more than 20 per cent of the ortho isomer in an amount from 2-1/2 to 6 grams per liter of bath, preferably 3 to 5 grams per liter of bath. The fourth component is adipic acid in an amount from 0.3 to 2.0 grams per liter of bath, preferably 1.5 grams per liter of bath. The remainder of the mixture is water.

To carry out the etching process, one may with advantage employ an etching machine of the type disclosed in Patent Specification No. 725,110. In this "Dow Etch" machine, rotated elongated paddles intermittently splash the etching bath against the image-bearing surface of the object being etched. The splashing action of the paddles also serves to keep the bath in a homogeneous state.

A bath employing the film-controlling agent of this invention may be improved by as much as 50 per cent in depths of etch obtainable in various image areas of the plate, particularly in the small image areas such as halftones. Etch factors may be increased by as much as 100 per cent. "Etch factor" as used in this specification is defined as the ratio of the depths of etch adjacent to a line of resist divided by one-half of the loss in width of metal immediately beneath the resist. Obviously, it is desirable to have as high etch factors as possible for faithful reproduction of the image in relief

but as the etch factor formula indicates, the factor can be sensitive to changes in depth and therefore it should be considered as only a rough approximation of plate quality. In a similar manner, excessive nonuniform depths of etch in a particular kind of image area of the plate may be eliminated by the film-controlling agent of this invention.

EXAMPLE 1

A powderless etching bath of 6 liters was prepared by mixing together in a miniature "Dow Etch" machine 708 grams of nitric acid, 30 grams of sodium monochlorododecyl diphenyloxide monosulfonate, 360 grams of aromatic solvent which contains 84 per cent aromatics, has a flash point of 60° C. and a distillation temperature range at 760 mm. Hg: initial boiling point of 171.1° C., 50 per cent distilled at 230° C. and dry point at 277.8° C. and sufficient water to bring the volume up to 6 liters. The bath temperature was adjusted to 24° C. A photoengraving plate of a magnesium base alloy containing 3 per cent aluminum, 1 per cent zinc 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 and the etching action was allowed to continue for 6 minutes. In open line areas of the plate, the depth of etch was 0.43 mm. and in 65 line screen halftone areas of the same plate, the depth of etch was 0.115 mm. For a second run, 10 grams of adipic acid was added to the foregoing bath. Another plate similar to the foregoing plate was prepared and etched for 6 minutes. Depths of etch of 0.38 mm. in open line areas and 0.165 mm. in 65 screen halftone areas were achieved. A third run was made on another similar plate with the adipic acid bath where-in etching was allowed to continue for 10 minutes. Open line areas had a depth of etch of 0.63 mm. and 65 screen halftone areas had a depth of etch of 0.165 mm. Lateral etching was at a minimum and the result was good printing plate.

EXAMPLE 2

In a manner similar to that of the foregoing example, a powderless etching bath of 6 liters was prepared by mixing together 708 grams of nitric acid, 90 grams of di-2-ethylhexylmaleate, 90 grams of diisodecyl phthalate, 90 grams of diethylbenzene and 18.5 grams of sodium-dioctyl sulfosuccinate. The remainder of the bath was water. The bath temperature was adjusted to approximately 27° C. and a photoengraving plate similar to that of Example 1 having a resist thereon was descummed and etched for 6 minutes. In 65 line screen halftone areas there was severe pitting with depths of etch up to 0.25



mm. The smaller leader dots were etched away. The depth of etch in line areas was 0.43 mm.

- 5 For a second run 1.2 grams of sodium benzoate was added to the same bath and a duplicate plate etched under the above conditions for 6 minutes. In this instance, 65 lines screen halftone areas indicated very little pitting and very few halftone dots were etched away. Thus, the second plate was much improved.

EXAMPLE 3

- 15 In a manner similar to that of Example 1, an etching bath was prepared by mixing together 708 grams of nitric acid, 30 grams of dodecylbenzene, 60 grams of diethylphthalate, 90 grams of the aromatic solvent mixture used in Example 1 and 13 grams of sodium monochlorododecyl diphenyloxide monosulfonate. The remainder of the bath was water. The bath temperature was adjusted to 22.2° C. and a photoengraving plate similar to that employed in Example 1 was etched for 6 minutes. The depth of etch in open line areas was about 0.38 mm. Also, there was evidence of slight lateral etching a general roughness and shallowness in small type areas.

- 20 For a second run, 1 gram of maleic acid was added to the same bath and another plate identical to that above was etched under the same conditions for 6 minutes. The depth of etch in open line areas was again 0.38 mm. with slight lateral etching, but comparatively, the second plate was smooth and adequate penetration in small type areas had been achieved.

EXAMPLE 4

- 40 In a manner similar to that of Example 1, an etching bath of 6 liters was prepared by mixing together 708 grams of nitric acid, 360 grams of a mixture of approximately 90 per cent alkylbenzenes, 2 per cent naphthalene and 8 per cent naphthenes having a flash point of 65.6° C. and a distillation temperature range at 760 mm. Hg: initial boiling point of 150.6° C., 50 per cent distilled at 192.2° C. and dry point at 46.1° C. and 32 grams of sodium monochlorododecyl diphenyloxide monosulfonate. The remainder of the bath was water. The bath temperature was brought to 24° C. and a photoengraving plate similar to that of Example 1 was etched for 6 minutes, obtaining thereby depths of etch of 0.495 mm. in open line areas and 0.125 mm. in halftone areas. However, small isolated images were severely attacked.

- 55 For a second run, 6 grams of succinic acid were added to the same bath and an identical plate etched under the same conditions for 6 minutes, obtaining thereby a depth of etch in open line areas of 0.44 mm. and

0.18 mm. in halftone areas, but in this instance small images remained intact and, as indicated, more depth was obtained in the halftone areas.

EXAMPLE 5

In a manner similar to that of the foregoing examples, a 6 liter etching bath was prepared from 708 grams of nitric acid, 360 grams of the solvent mixture used in Example 4, and 20 grams of sodium monochlorododecyl diphenyloxide monosulfonate. The remainder of the bath was water. The bath temperature was brought to 24° C. and a photoengraving plate similar to that of Example 1 was etched for 6 minutes. Depths of etch in open line areas of approximately 0.48 mm. and in 65 line screen halftone areas of about 0.125 mm. However, isolated small images such as leader dots were etched away.

For a second run, 6 grams of pimelic acid were added to the same bath and an identical plate etched under the same conditions for 6 minutes. Depths of etch in open line areas were again approximately 0.48 mm. and depths of etch in 65 line screen halftone areas were about 0.14 mm. with very little loss in the small isolated images.

EXAMPLE 6

In a manner similar to that of the foregoing examples, a 6 liter etching bath was prepared from 588 grams of nitric acid, 150 grams of dimethylphthalate and 30 grams of a mahogany soap having an average molecular weight from 400 to 410. The remainder of the bath was water. The bath temperature was adjusted to 24° C. and a plate similar to that of Example 1 was etched for 6 minutes. Depth of etch in open line areas was about 0.43 mm. and the depth of etch in 65 line screen halftone areas was about 0.09 mm. In this instance, halftone depths were insufficient.

A second run was made after adding 10 grams of adipic acid to the same bath. An identical plate was etched for 6 minutes. The depth of etch in open line areas was about 0.28 mm. and the depth of etch in 65 line screen halftone areas was about 0.14 mm.

EXAMPLE 7

In a manner similar to that of the foregoing examples, a 6 liter etching bath was prepared from 708 grams of nitric acid, 90 grams of diethylbenzene, 50 grams of castor oil, and 20 grams of sodium monochlorododecyl diphenyloxide monosulfonate. The remainder of the bath was water. The bath temperature was adjusted to 24° C., and a plate similar to that of Example 1 was etched for 8 minutes. Depth of etch in open line areas was about 0.51 mm. and depths of

etch in 65 line screen halftone areas range from 0.18 to 0.28 mm. Direct measurements of lateral etching indicated a side etch per side of image of 0.03 mm.

- 5 For a second run, 1.5 grams of stearic acid was added to the same bath and an identical plate was etched for 8 minutes. Depths of etch in open line areas were again about 0.51 mm. and depths of etch in 10 line screen halftone areas were about 0.165 mm. The etching in the halftone areas was uniform and direct measurements of lateral etching indicating a side etch of 0.02 mm. In this example, the excessive depths of etch 15 in halftone areas were beneficially decreased by the addition of a film-controlling agent.

EXAMPLE 8

- In a manner similar to that of the foregoing examples, a 6 liter etching bath was 20 prepared from 703 grams of nitric acid, 76 grams of the solvent mixture used in Example 4, 46 grams of sulfated castor oil which contains nominally 48 per cent active organic material and 52 per cent water and 25 inorganic impurities. The remainder of the bath was water. The bath temperature was adjusted to 22.2° C. and a zinc base alloy photoengraving plate having a nominal composition of less than 1 per cent aluminum 30 and less than 1 per cent magnesium with a balance of zinc and trace impurities was descummed. This plate was etched for 6 minutes. The depth of etch in open line areas was about 0.28 mm. and there was substantial lateral etching with accompanying 35 image loss.

- For a second run, 2 grams of stearic acid were added to the foregoing bath and a duplicate plate etched in an identical manner. 40 The depths of etch in open line areas again were about 0.28 mm. but there was a significant decrease in the amount of side etch.

- For a third run, 5 more grams of stearic acid were added to the foregoing bath and 45 again a duplicate plate etched in the same manner. The depths of etch in open line areas were 0.28 mm. and the extent of lateral etching was vastly reduced. Etch factors were about 40 or more.

EXAMPLE 9

- In a manner similar to that of the foregoing examples, a 134 liter etching bath was prepared in a commercial size "Dow Etch" 50 machine from 12,435 kg. of nitric acid, 5,360 kg. of the solvent mixture used in Example 4, 738 grams of sodium monochloro- 55 dodecyl diphenyloxide monosulfonate, and 200 grams of adipic acid. The remainder of the bath was water. Bath temperature was adjusted to 22.2° C. and a template approximately 23×15.3×0.163 cm. of a magnesium 60 base alloy having 3 per cent aluminum, 1 per cent zinc and trace amounts of impurities,

with a resist covering all of the plate but the periphery of the shape to be produced, was placed in the machine and etched for 28 minutes.

The metal was etched through resulting in the production of an accurate metal template having side walls substantially perpendicular to the surface of the template. 70

In like manner to that of the foregoing examples, improved results are achieved with a powderless etching bath in which the following film-controlling agents are substituted 75 for the specific film-controlling agents shown in the foregoing examples: suberic, azelaic, sebacic, caprylic, capric, lauric, myristic, palmitic, arachidic, behenic, palmitoleic, oleic, ricinoleic, linolic, cetoleic, and the like acids. Also in the like manner to that of 80 the foregoing specific examples, other filming agents may be employed achieving similar improved results. Examples of such other filming agents are sulfated fats, oils and 85 waxes, halogenated diaryloxide sulfonates, alkyl benzene sulfonates, alkyl naphthalene sulfonates, sulfonated esters, amides and ethers and the like.

WHAT WE CLAIM IS:—

1. Process of etching by the powderless etching technique with the employment of an aqueous bath containing as major constituents a dilute strong acid, a water-immiscible organic fluid, and a filming agent, 90 wherein a small quantity of one or more carboxylic acids or their salts is added as a film-controlling agent to the bath and/or to the ingredients used to make up the bath. 95

2. Process in accordance with Claim 1, wherein the film-controlling agent is monocarboxylic acid which is composed of carbon, hydrogen, and oxygen atoms only and which has from 4 to 22 carbon atoms. 100

3. Process in accordance with Claim 1, wherein the film-controlling agent is a dicarboxylic acid which is composed of carbon, hydrogen, and oxygen atoms only and which has from 4 to 22 carbon atoms. 105

4. Process in accordance with Claim 1, wherein the film controlling agent is a combination of one or more mono- and dicarboxylic acids composed of carbon, hydrogen, and oxygen atoms and having from 4 to 22 carbon atoms. 110

5. Process in accordance with Claims 1 to 4, wherein the performance characteristics of the etching bath and/or the quality and usefulness of the etched articles, such as printing plates, are controlled by varying the amount or kind of the carboxylic acid present in or added to the bath. 115

6. Process in accordance with any one of Claims 1 to 5, wherein the dicarboxylic acid is employed as a film-controlling agent in etching combination line and halftone printing plates. 120 125



etch in 65 line screen halftone areas range from 0.18 to 0.28 mm. Direct measurements of lateral etching indicated a side etch per side of image of 0.03 mm.

- 5 For a second run, 1.5 grams of stearic acid was added to the same bath and an identical plate was etched for 8 minutes. Depths of etch in open line areas were again about 0.51 mm. and depths of etch in 65 line screen halftone areas were about 0.165 mm. The etching in the halftone areas was uniform and direct measurements of lateral etching indicating a side etch of 0.02 mm. In this example, the excessive depths of etch in halftone areas were beneficially decreased by the addition of a film-controlling agent.

EXAMPLE 8

- 20 In a manner similar to that of the foregoing examples, a 6 liter etching bath was prepared from 703 grams of nitric acid, 76 grams of the solvent mixture used in Example 4, 46 grams of sulfated castor oil which contains nominally 48 per cent active organic material and 52 per cent water and inorganic impurities. The remainder of the bath was water. The bath temperature was adjusted to 22.2° C. and a zinc base alloy photoengraving plate having a nominal composition of less than 1 per cent aluminum and less than 1 per cent magnesium with a balance of zinc and trace impurities was descummed. This plate was etched for 6 minutes. The depth of etch in open line areas was about 0.28 mm. and there was substantial lateral etching with accompanying image loss.

- 35 For a second run, 2 grams of stearic acid were added to the foregoing bath and a duplicate plate etched in an identical manner. The depths of etch in open line areas again were about 0.28 mm. but there was a significant decrease in the amount of side etch.

- 40 For a third run, 5 more grams of stearic acid were added to the foregoing bath and again a duplicate plate etched in the same manner. The depths of etch in open line areas were 0.28 mm. and the extent of lateral etching was vastly reduced. Etch factors were about 40 or more.

EXAMPLE 9

- 50 In a manner similar to that of the foregoing examples, a 134 liter etching bath was prepared in a commercial size "Dow Etch" machine from 12,435 kg. of nitric acid, 55 5,360 kg. of the solvent mixture used in Example 4, 738 grams of sodium monochlorododecyl diphenyloxide monosulfonate, and 200 grams of adipic acid. The remainder of the bath was water. Bath temperature was adjusted to 22.2° C. and a template approximately 23×15.3×0.163 cm. of a magnesium base alloy having 3 per cent aluminum, 1 per cent zinc and trace amounts of impurities,

with a resist covering all of the plate but the periphery of the shape to be produced, was placed in the machine and etched for 28 minutes.

The metal was etched through resulting in the production of an accurate metal template having side walls substantially perpendicular to the surface of the template.

In like manner to that of the foregoing examples, improved results are achieved with a powderless etching bath in which the following film-controlling agents are substituted for the specific film-controlling agents shown in the foregoing examples: suberic, azelaic, sebacic, caprylic, capric, lauric, myristic, palmitic, arachidic, behenic, palmitoleic, oleic, ricinoleic, linolic, cetoleic, and the like acids. Also in the like manner to that of the foregoing specific examples, other filming agents may be employed achieving similar improved results. Examples of such other filming agents are sulfated fats, oils and waxes, halogenated diaryloxide sulfonates, alkyl benzene sulfonates, alkyl naphthalene sulfonates, sulfonated esters, amides and ethers and the like.

WHAT WE CLAIM IS:—

1. Process of etching by the powderless etching technique with the employment of an aqueous bath containing as major constituents a dilute strong acid, a water-immiscible organic fluid, and a filming agent, wherein a small quantity of one or more carboxylic acids or their salts is added as a film-controlling agent to the bath and/or to the ingredients used to make up the bath.

2. Process in accordance with Claim 1, wherein the film-controlling agent is monocarboxylic acid which is composed of carbon, hydrogen, and oxygen atoms only and which has from 4 to 22 carbon atoms.

3. Process in accordance with Claim 1, wherein the film-controlling agent is a dicarboxylic acid which is composed of carbon, hydrogen, and oxygen atoms only and which has from 4 to 22 carbon atoms.

4. Process in accordance with Claim 1, wherein the film controlling agent is a combination of one or more mono- and dicarboxylic acids composed of carbon, hydrogen, and oxygen atoms and having from 4 to 22 carbon atoms.

5. Process in accordance with Claims 1 to 4, wherein the performance characteristics of the etching bath and/or the quality and usefulness of the etched articles, such as printing plates, are controlled by varying the amount or kind of the carboxylic acid present in or added to the bath.

6. Process in accordance with any one of Claims 1 to 5, wherein the dicarboxylic acid is employed as a film-controlling agent in etching combination line and halftone printing plates.



7. Process in accordance with any one of any combination of Claims 1 to 6, wherein the filming agent is one which is not directly derived by chemical modification from the carboxylic acid used as the film-controlling agent. 65
8. Process in accordance with any one of Claims 1 to 7, wherein the filming agent is an ionic hydrophobic-hydrophilic organic filming agent. 70
9. Process in accordance with Claim 8, wherein the filming agent is a petroleum sulfonate, an alkyl and/or aryl substituted diaryloxide sulfonate, an alkyl and/or aryl substituted halogenated diaryloxide sulfonate, an alkylaryl sulfonate, an ester of sulfosuccinic acid, an organic sulfonate the hydrophobic portion of which is made up of 2 organic radicals which are connected over an amide, ester, or ether bridge and wherein at least one of the organic radicals contains 12 or more carbon atoms in an uninterrupted series of carbon to carbon bonds. 75
10. Process in accordance with any one of Claims 1 to 9, wherein the filming agent is employed in a proportion of from 0.2 to 20 grams per one liter of the bath. 80
11. Process in accordance with any one of Claims 1 to 10, wherein the film-controlling agent is added to the bath in a proportion of from 0.05 to 3.0 grams per liter of bath. 85
12. Process in accordance with any one of Claims 1 to 10, wherein the film-controlling agent is present in the bath in a proportion of from 0.05 to 3.0 grams per liter of bath. 90
13. Process in accordance with any one of Claims 1 to 12, wherein the bath contains, as the strong acid, nitric acid. 95
14. Process in accordance with Claim 13, wherein the nitric acid is present in a proportion of from 30 to 200 grams per one liter of the bath. 100
15. Process in accordance with any one of Claims 1 to 14, wherein the water-immiscible organic fluid is present in a proportion of from 3 to 100 grams per one liter of bath. 105
16. Process in accordance with any one of Claims 1 to 15, wherein the filming agent is an alkylated halogenated diaryloxide sulfonate, and the film-controlling agent is succinic acid or adipic acid. 110
17. Process in accordance with Claim 16, wherein the alkylated halogenated diaryloxide sulfonate comprises a substantial proportion of an alkylated monochlorodiphenyloxide monosulfonate. 115
18. Process in accordance with any one of Claims 1 to 17, wherein the carboxylic acid is admixed to the filming agent and/or the water-immiscible organic fluid before they are added to the bath. 120
19. Process of etching by the powderless etching bath technique using an aqueous bath containing a dilute strong acid, a water-immiscible organic fluid, a filming agent, and one or more carboxylic acids or their salts as a film-controlling agent, substantially as described hereinbefore. 65
20. Process of etching by the powderless etching bath technique using an aqueous bath containing a dilute strong acid, a water-immiscible organic fluid, a filming agent, and one or more carboxylic acids or their salts as a film-controlling agent, substantially as described with respect to the specific examples. 70
21. Etched articles and particularly printing plates whenever prepared by a process as claimed in the preceding Claims 1 to 20. 80
22. An improved etching bath, comprising a dilute aqueous strong acid, a water-immiscible organic fluid, a filming agent, and a controlled proportion of a mono- and/or dicarboxylic acid as a film-controlling agent. 85
23. An improved etching bath in accordance with Claim 22, wherein the film-controlling agent is present in a proportion in the range from 0.05 to 3.0 grams per liter of bath. 90
24. An improved etching bath in accordance with Claims 22 or 23, wherein the film-controlling agent is a monocarboxylic acid which is composed of carbon, hydrogen and oxygen atoms only and which acid has from 4 to 22 carbon atoms. 95
25. An improved etching bath in accordance with Claims 22 or 23, wherein the film-controlling agent is a dicarboxylic acid which is composed of carbon, hydrogen and oxygen atoms only, and which acid has from 4 to 22 carbon atoms. 100
26. An improved etching bath in accordance with any one of Claims 22 to 25, wherein the filming agent is one which is not directly derived by chemical modification from the carboxylic acid used as the film-controlling agent. 105
27. An improved etching bath in accordance with any one of Claims 22 to 26, which bath contains from 30 to 200 grams nitric acid, 3 to 100 grams of the water immiscible organic fluid, from 0.2 to 20 grams of the filming agent, and 0.05 to 3.0 grams of the film-controlling agent per liter of the aqueous bath. 115
28. Improved etching bath comprising a dilute aqueous strong acid, a water-immiscible organic fluid, a filming agent, and a mono- and/or dicarboxylic acid as a film-controlling agent, substantially as described hereinbefore. 120
29. Improved etching bath comprising a dilute aqueous strong acid, a water-immis-



cible organic fluid, a filming agent, and a mono- and/or dicarboxylic acid as a film-controlling agent, substantially as described with reference to the specific examples.

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