

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Etching

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 a method of etching metal and to a bath therefor, and more particularly to an improved method of etching photoengraving plates.

In the conventional method of making a metal printing surface, such as a photoengraving, a plate of an acid-soluble metal such as magnesium, zinc and their alloys is coated with a light-sensitive coating or "enamel" which is applied to the metal surface which is usually flat or cylindrical. The coated surface is exposed to light through a negative having an image thereon so as to produce a corresponding image in the coating. The exposed coated surface is "developed" forming an acid resistant coating in the form of the image produced by the exposure. This acid resistant coating is further hardened by heating and the image-bearing surface of the plate is then subjected to etching by an acid. As the etching proceeds, the acid tends to etch laterally and undercut the resist and thus distort the image. The standard method of preventing or reducing this undercutting is to "powder" the plate which is a time consuming and difficult operation.

It is an object of the present invention to provide an improved method for etching metal and particularly printing plates. Another object of the invention is to provide etching baths for carrying out the improved processes of etching. The accompanying drawing comprises graphs showing the relationship between etch factor and the concentration of examples of constituents of the improved etching bath under stated conditions.

It has been discovered that by adding certain alkylarylsulphonates or the corresponding alkyl aryl sulphonic acids to a nitric acid etching bath in carefully controlled amounts and by splashing this bath in a predetermined manner against the metal object to be etched, enhanced etching of the metal may be obtained.

The bath employed in carrying out the present invention comprises a mixture of: (1) an aqueous solution containing nitric acid and from 0.1 to 2.0 per cent by weight of an alkylarylsulphonate, or a chemically equivalent amount of the corresponding acid, the sulphonate or sulphonic acid consisting of one of the alkylbenzene sulphonates or sulphonic acids wherein the alkyl portion contains from 8 to 18 carbon atoms or one of the alkyl-naphthalene sulphonates or sulphonic acids wherein the alkyl portion contains from 3 to 18 carbon atoms. The alkylarylsulphonates or sulphonic acids employed have the general formula $RA-SO_3X$ in which R is an alkyl radical having from 3 to 18 carbon atoms inclusive, A is benzene or naphthalene, and X is H or a salt forming anion, e.g. an alkali metal or alkaline earth metal. (2) A water-immiscible organic liquid substantially unreactive with the aqueous nitric acid solution.

Typical of the alkylarylsulphonates that may be employed are decylbenzene sodium sulphonate, dodecylbenzene sodium sulphonate, tetradecylbenzene sodium sulphonate, propylnaphthalene sodium sulphonate, amyl-naphthalene sodium sulphonate, diamyl-naphthalene sodium sulphonate, dodecyl-naphthalene sodium sulphonate. It has been found that the amount of alkylarylsulphonate or sulphonic acid employed is critical and it is essential that this compound be present within the range of 0.1 to 2.0 per cent by weight of the total etching bath. Below 0.1 per cent by weight of alkylarylsulphonate or sulphonic acid undercutting of the image occurs rapidly and an extremely low etch factor is obtained. Decylbenzene sulpho-

propionic ester (Surfax 1288) is effective in concentrations of 0.18 to 0.35 per cent. As used in this specification the term "etch factor" is defined as the ratio of the depth of the etch adjacent to a line of resist to one-half of the loss in width of metal at the top of the surface of the relief beneath the line of resist. The upper limit is not sharply critical and as much as 2 per cent of the alkylaryl-sulphonate or sulphonic acid may be employed, although it is preferred not to use above 0.5 per cent. In using these larger amounts, undercutting of the resist area is prevented, but blanking off, i.e. inhibition of etching adjacent image areas, occurs. In this respect, however, the etching baths, as defined herein, are not nearly as sensitive as other etching baths.

Nitric acid (expressed as HNO_3) is employed in amounts varying from 3 to 20 per cent by weight of the total bath and is usually added as 42° Baumé acid. While the amount of nitric acid may vary widely depending upon the particular conditions encountered in any specific photoengraving plate, it is preferred to maintain the concentration of the nitric acid between 5 and 12 per cent.

The water-immiscible organic liquid which is employed is one which is either liquid at ordinary temperatures or liquifies below the temperature at which the etching bath is normally used and is substantially unreactive with the aqueous nitric acid solution. Illustrative of substances suitable for the purpose are the various petroleum fractions boiling in the range of 70° to 390°C., such as gasoline, benzene, kerosene, coal oil and lubricating oils. These liquids are mixtures of various hydrocarbons, mostly saturated, of the paraffin series having from 6 to 18 carbon atoms. Other organic liquids which may be employed are turpentine, perchloroethylene and diethylbenzene. The amount of organic liquid employed will vary with the type of metal surface to be processed, but will fall within the range of from 1 to 14 per cent by weight of the total bath. The preferred range is from 4 to 10 per cent.

In practicing the present invention it has been found to be essential that the bath be splashed or thrown against the surface to be etched in an intermittent action which permits the etching solution to drain to some extent from the surface between each contact. In theory at least the etching bath comprising the present invention forms a film on the image surface of the object being etched, and as the bath is projected against that surface the film is broken in those areas devoid of resist and which are normal to the direction of travel of the thrown bath composition. It is believed that continuous application of the bath, for example, by means of a spray, to the surface to be etched, breaks this film along the sides of the relief or etched areas, because such pro-

cedures produce undercutting of the resist. The extent of such undercutting precludes employment of spraying commercially on a practicable basis. In practicing the present invention in which splashing is used to impinge sheets of the bath on the work, in contrast to spraying, it is preferred to employ an etching machine of the type disclosed in Specification No. 725,110. In this machine elongated paddles dipping into the bath composition intermittently throw, by splashing, the etching bath composition in sheets upwardly against the image bearing side of the object being etched, e.g. a plate. Because of the spacing of the paddle surfaces, the etching bath composition that is splashed or thrown against the plate, has an opportunity to drain therefrom to some extent before the following paddle throws more etching solution against the plate. As noted above, this intermittent splashing action with draining of the etching solution between each contact between the bath composition and the plate is essential in the production of a commercially practicable etching.

In order to illustrate the present invention in more detail, the following description by way of example is set forth.

EXAMPLE 1.

An etching solution was prepared in an etching machine of the type set forth in Specification No. 725,110, above referred to, having an etching tank with an operating capacity of 5.7 litres, by adding approximately three litres of water to the machine with the circulating pump in operation. Nitric acid of 42° Baumé Technical Grade was then added. The alkylaryl sulphonate, diluted with water, was added and followed by the addition of a commercial diethylbenzene (consisting of a mixture of the three isomeric forms of diethylbenzene). A further amount of water was added to bring up the bath volume to a total of 5.7 litres. The bath was thoroughly mixed by running the paddles of the machine for 2 minutes and the temperature of the bath was held at 72°F. The bath so made had the following composition:

nitric acid 42° Bé	600 ml	
diethylbenzene	400 ml	
dodecyl-naphthalene sodium		115
sulphonate	6 grams	
octyl alcohol (a defoamer)	3 ml	
water to make 5.7 litres		

Magnesium photoengraving sheet previously photo printed with an image of printed matter in sans serif 10 point type was descummed by swabbing with a scumming out solution consisting of 12 ounces of potassium hydroxide and 4 ounces of potassium permanganate per gallon of descumming solution. The magnesium sheet employed was of 0.064 inch gauge and test plates, one and one-half inch by 4 inch dimension, were cut from it. The composition of the sheet was 3 per cent aluminium, 1.0 per cent zinc, 0.10 per cent

manganese, 0.03 per cent calcium and the balance essentially magnesium except for minor amounts of impurities. One of the test plates was then placed in the plate holder of the machine, the lid closed, and the paddles and plate holder set in motion. The paddles speed was 700 r.p.m. for one minute and then reduced to 600 r.p.m. for five minutes, producing a velocity of impingement of bath composition on the plate of about 640 and 550 feet per minute respectively. The plate was removed from the machine, rinsed with water to remove all traces of the etching bath, and dried in a current of air. Examination of the so etched plate revealed that the average etch factor was 40 and the open areas outside the printed letters were etched to an average depth of 0.0155 inch.

EXAMPLE 2.

In the same manner as in Example 1, an etching bath was made up having the following composition:

nitric acid (42° Baumé)	600 ml
diethylbenzene	400 ml
calcium dodecylbenzene sulphonate	15 gms
water to make	5.7 litres

One of the test plates of Example 1 was splash etched in a similar manner to that of Example 1 for a total time of 8 minutes at a paddle speed of 550 r.p.m. (producing a velocity of impingement of about 500 feet per minute) then removed, rinsed, and air dried. The plate was found to be etched in the open areas to an average depth of 0.020 inch and to have an average etch factor of 35.

EXAMPLE 3.

The same procedure and bath as set forth

in Example 2 was used except that a zinc test plate was substituted for the magnesium plate. The zinc plate had a nominal composition of 0.50 per cent aluminium, the balance being zinc substantially free from cadmium and lead impurities. The plate was splash etched for a total time of 10 minutes at 600 r.p.m. paddle speed at a bath temperature of 72°F. after being so etched the zinc plate was removed, rinsed and air dried. In the open areas away from the letters ~~and~~ the plate was found to be etched to an average depth of 0.018 inch and to have an average etch factor of 67.

EXAMPLE 4.

A magnesium test plate of Example 1, was splash etched with the following bath:

nitric acid 42° Baumé	600 ml
diethylbenzene	400 ml
dodecylbenzene sodium sulphonate	8 gms
water to make	5.7 litres

The splash etch was continued for a total time of 11 minutes at 600 r.p.m. paddle speed and a bath temperature of 72°F. The so etched plate was removed, rinsed and air dried. In the open areas the plate was found to be etched to an average depth of 0.019 inch and to have an average etch factor of 50.

EXAMPLE 5.

A number of different alkylarylsulphonates falling within the scope of the present invention was tested as in Example 1. The amount of the sulphonate used was adjusted to obtain the most favourable etch factor. The alkylarylsulphonates tested and the average etch factors obtained are set forth in the table:

Alkylarylsulphonate	per cent by wt. in bath	average etch factor
amyl-naphthalene sodium sulphonate	0.33	27
propyl-naphthalene sodium sulphonate	0.24	29
dodecyl-naphthalene sodium sulphonate	0.15	40
dodecylbenzene sodium sulphonate	0.22	40
diamyl-naphthalene sodium sulphonate	0.17	30

EXAMPLE 6

The effect of the concentration of a number of alkylarylsulphonates upon the etch factor was determined using the plates and procedure of Example 1, the etching baths being compounded all alike except that each contained a different amount of an alkylarylsulphonate. The sulphonates so tested were dodecyl-naphthalene sodium sulphonate, decylbenzene sulphopropionic ester, and propyl-naphthalene sodium sulphonate. The etch factors obtained in these tests are set forth in the single figure which comprises a graph showing the concentration of the sulphonate as related to the etch factor. It is at once evident from this graph that alkylarylsul-

phonates in the amounts of 0.05 per cent by weight have but little effect in increasing the etch factor of the etching baths. Above about 0.10 per cent by weight, however, the alkylarylsulphonates produce a pronounced increase in etch factor of the bath and appear to exert a maximum effect between about 0.15 per cent and 0.3 per cent by weight.

While certain procedures have been set forth above for employing the present invention, it will be apparent to those skilled in the art that variations therefrom may be made without departing from the scope of the invention. For example, in compounding the etching bath the alkylarylsulphonate may be dissolved in either or both the water-immis-



cible organic liquid or the nitric acid solution. In place of the sodium salts the corresponding alkyl aryl sulphonic acids if available may be used. The sodium salts are preferred since it is known that they will not interfere in any way with the action of the bath. The photoengraving plate may be composed of magnesium, magnesium base alloys containing at least 90 per cent magnesium, zinc, and zinc base alloys containing at least 90 per cent zinc.

It is apparent to those skilled in the art from the above detailed description that the method of etching described herein, and the bath for use in such method, produce enhanced results in the etching of printing plates and other similar metal articles. One of the unexpected results obtained by practising the present invention is the elimination of blanking off, that is failure to etch to adequate depths in small non-printing areas. Another is that the use of gelatin and similar materials in the bath heretofore considered necessary is obviated. Furthermore, the bath employed in the present invention is quite insensitive to minor changes in concentrations, other than the alkylarylsulphonate content, and may be used to etch a wide variety of magnesium alloys, especially those which contain no aluminium and which are not readily etchable by known procedures in which powdering is eliminated.

WHAT WE CLAIM IS:—

1. The method of etching a photoengraving plate consisting of magnesium, magnesium base alloys containing at least 90 per cent magnesium, zinc or zinc base alloys containing at least 90 per cent zinc, which method comprises paddling an etching bath comprising a mixture of (1) an aqueous solution containing nitric acid and from 0.1 to 2.0 per cent by weight of an alkylaryl sulphonate, or a chemically equivalent amount of the corresponding acid, the sulphonate or sulphonic acid consisting of an alkylbenzene sulphonate or sulphonic acid wherein the alkyl portion contains from 8 to 18 carbon atoms or an alkylnaphthalene sulphonate or sulphonic acid wherein the alkyl portion contains from 3 to 18 carbon atoms and (2) a water-immiscible organic liquid substantially unreactive with the aqueous nitric acid solution, said paddling being sufficiently vigorous to throw the bath against said plate in intermittent sheets and continuing this paddling action until the plate has been etched to a satis-

factory depth.

2. The method of etching a photoengraving plate according to claim 1, wherein the aqueous solution contains from 5 to 20 per cent by weight of nitric acid and from 0.1 to 0.5 per cent by weight of the alkylaryl-sulphonate or sulphonic acid and the water-immiscible organic liquid is present in an amount of from 1 to 14 per cent by weight of the aqueous nitric acid solution.

3. The method as claimed in claim 1 or claim 2 wherein the alkylaryl sulphonate is dodecylbenzene sulphonate and the water-immiscible organic liquid is diethylbenzene.

4. The method of etching substantially as described in any one of the specific examples hereinbefore set forth.

5. An etching bath comprising a mixture of (1) an aqueous solution containing nitric acid and from 0.1 to 2.0 per cent by weight of an alkylaryl sulphonate, or a chemically equivalent amount of the corresponding acid, the sulphonate or sulphonic acid consisting of an alkylbenzene sulphonate or sulphonic acid wherein the alkyl portion contains from 8 to 18 carbon atoms or an alkylnaphthalene sulphonate or sulphonic acid wherein the alkyl portion contains from 3 to 18 carbon atoms, and (2) a water-immiscible organic liquid substantially unreactive with the aqueous nitric acid solution.

6. An etching bath according to claim 5 wherein the aqueous solution contains from 5 to 20 per cent by weight of nitric acid and from 0.1 to 0.5 per cent by weight of the alkylarylsulphonate or sulphonic acid and the water-immiscible organic liquid is present in an amount of from 1 to 14 per cent by weight of said aqueous nitric acid solution.

7. An etching bath according to claim 6 wherein the aqueous solution contains from 0.18 to 0.35 per cent of decylbenzene sulphopropionic ester.

8. An etching bath according to claim 7 in which the water-immiscible liquid is a diethylbenzene.

9. An etching bath substantially as described with reference to any one of the specific examples hereinbefore set forth.

10. A photoengraving plate when etched by the method of any one of claims 1 to 4 or by use of the etching bath claimed in any one of claims 5 to 9.

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cible organic liquid or the nitric acid solution. In place of the sodium salts the corresponding alkyl aryl sulphonic acids if available may be used. The sodium salts are preferred since it is known that they will not interfere in any way with the action of the bath. The photoengraving plate may be composed of magnesium, magnesium base alloys containing at least 90 per cent magnesium, zinc, and zinc base alloys containing at least 90 per cent zinc.

It is apparent to those skilled in the art from the above detailed description that the method of etching described herein, and the bath for use in such method, produce enhanced results in the etching of printing plates and other similar metal articles. One of the unexpected results obtained by practising the present invention is the elimination of blanking off, that is failure to etch to adequate depths in small non-printing areas. Another is that the use of gelatin and similar materials in the bath heretofore considered necessary is obviated. Furthermore, the bath employed in the present invention is quite insensitive to minor changes in concentrations, other than the alkylarylsulphonate content, and may be used to etch a wide variety of magnesium alloys, especially those which contain no aluminium and which are not readily etchable by known procedures in which powdering is eliminated.

WHAT WE CLAIM IS:—

1. The method of etching a photoengraving plate consisting of magnesium, magnesium base alloys containing at least 90 per cent magnesium, zinc or zinc base alloys containing at least 90 per cent zinc, which method comprises paddling an etching bath comprising a mixture of (1) an aqueous solution containing nitric acid and from 0.1 to 2.0 per cent by weight of an alkylaryl sulphonate, or a chemically equivalent amount of the corresponding acid, the sulphonate or sulphonic acid consisting of an alkylbenzene sulphonate or sulphonic acid wherein the alkyl portion contains from 8 to 18 carbon atoms or an alkylnaphthalene sulphonate or sulphonic acid wherein the alkyl portion contains from 3 to 18 carbon atoms and (2) a water-immiscible organic liquid substantially unreactive with the aqueous nitric acid solution, said paddling being sufficiently vigorous to throw the bath against said plate in intermittent sheets and containing this paddling action until the plate has been etched to a satis-

factory depth.

2. The method of etching a photoengraving plate according to claim 1, wherein the aqueous solution contains from 5 to 20 per cent by weight of nitric acid and from 0.1 to 0.5 per cent by weight of the alkylaryl-sulphonate or sulphonic acid and the water-immiscible organic liquid is present in an amount of from 1 to 14 per cent by weight of the aqueous nitric acid solution.

3. The method as claimed in claim 1 or claim 2 wherein the alkylaryl sulphonate is dodecylbenzene sulphonate and the water-immiscible organic liquid is diethylbenzene.

4. The method of etching substantially as described in any one of the specific examples hereinbefore set forth.

5. An etching bath comprising a mixture of (1) an aqueous solution containing nitric acid and from 0.1 to 2.0 per cent by weight of an alkylaryl sulphonate, or a chemically equivalent amount of the corresponding acid, the sulphonate or sulphonic acid consisting of an alkylbenzene sulphonate or sulphonic acid wherein the alkyl portion contains from 8 to 18 carbon atoms or an alkylnaphthalene sulphonate or sulphonic acid wherein the alkyl portion contains from 3 to 18 carbon atoms, and (2) a water-immiscible organic liquid substantially unreactive with the aqueous nitric acid solution.

6. An etching bath according to claim 5 wherein the aqueous solution contains from 5 to 20 per cent by weight of nitric acid and from 0.1 to 0.5 per cent by weight of the alkylarylsulphonate or sulphonic acid and the water-immiscible organic liquid is present in an amount of from 1 to 14 per cent by weight of said aqueous nitric acid solution.

7. An etching bath according to claim 6 wherein the aqueous solution contains from 0.18 to 0.35 per cent of decylbenzene sulphonylpropionic ester.

8. An etching bath according to claim 7 in which the water-immiscible liquid is a diethylbenzene.

9. An etching bath substantially as described with reference to any one of the specific examples hereinbefore set forth.

10. A photoengraving plate when etched by the method of any one of claims 1 to 4 or by use of the etching bath claimed in any one of claims 5 to 9.

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