

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Etching

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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 for etching the surface of a metal object, and is more particularly concerned with an improved method and bath for etching photoengraving plates.

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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, or one of their alloys is firstly coated with a light-sensitive coating or "enamel," applied to the generally flat or cylindrical metal surface. This coated surface is then exposed to light through a negative having an image thereon so as to produce a corresponding image on the coating. The exposed coated surface is then "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. In prior art techniques, as the etching proceeds, the acid tends to etch laterally and thereby undercut the resist, causing a weakening or a distorting of the image. While art techniques have proposed to prevent or reduce the amount of undercutting by repeatedly "powdering" the plate, and partially etching between each powdering application, this has been a time-consuming and difficult operation.

It is a principal object of the present invention to provide an improved method for etching metal and particularly photoengraving plates. Another object of the present invention is the provision of etching baths for carrying out the improved process for etching. Still a further object of the present invention is to

provide etching baths containing particular sulphated fats, oils and/or waxes. Another object of the present invention is the provision of such etching baths containing particular amounts of the above materials.

The invention provides a method of etching the surface of an acid-soluble metal consisting of magnesium, zinc, magnesium-base or zinc-base alloys said surface having portions thereof masked with an acid resistant coating, which method comprises repeatedly impinging upon the surface of the object, so as to contact both the masked and unmasked portions thereof, an aqueous mixture which contains (1) from 1 to 25 per cent of HNO_3 , (2) from 1 to 12 per cent a water-immiscible organic liquid substantially unreactive with the nitric acid in the aqueous mixture, and (3) between 0.4 and 2.0 per cent of a water-soluble, anionic, surface-active half ester of sulphuric acid containing at least one hydrophobic group of from 10 to 26 carbon atoms in an uninterrupted chain, and said ester containing at least 8 per cent sulphation as herein defined. The ester is usually derived from the sulphuric acid treatment of naturally-occurring fats, oils and waxes.

Suitable metals which may be etched by the process and bath of the present invention are magnesium, magnesium base alloys containing at least 85 per cent magnesium, and zinc and zinc base alloys containing at least 90 per cent zinc. To prepare a photoengraving plate, the surface of the metal is first coated uniformly with a light-sensitive material, exposed to light through a negative, developed, and, if necessary, heated to increase the acid resistance of the resist. When the plate to be etched has been so treated, it is then ready for use in the method of the present invention.

Aqueous nitric acid for the bath of the present invention is employed in an amount by weight of the total bath to provide between 1 and 25 per cent HNO_3 , concentrations in the range of from 3 to 20 per cent HNO_3 , being most generally useful, while a concentration of from 4 to 12.5 per cent is pre-

ferred. The aqueous nitric acid is mixed with a water-immiscible organic material which is liquid at those temperatures employed for etching. This organic liquid should also be substantially unreactive with the aqueous nitric acid solution. Suitable organic materials which may be used in the method and bath of the present invention include, for example, the various petroleum fractions boiling in the range of 70° to 390°C., such as gasolene, benzene, kerosene, coal oil, and lubricating oils. Other organic liquids which may be employed include turpentine, perchloroethylene, the diethylbenzenes, tetramethylbenzenes, isopropylbenzene, and carbon tetrachloride. The amount of organic liquid employed will vary with the type of metal surface to be processed, but will fall within the range of 1 to 12 per cent by weight of the total bath and preferably is from 5 to 8 per cent.

A third component of the bath is a sulphated organic surface-active agent. This component can further be described as being a half ester of sulphuric acid, which is water-soluble and anionic, and which contains at least 8 per cent sulphation, preferably at least 14 per cent. Percentage of sulphation, as used herein, is intended to mean the average amount of sulphate (SO_4) contained in the molecule divided by the practical amount of sulphation possible multiplied by one hundred. The hydrophobic portion of the surface-active agent must contain at least one aliphatic organic group containing at least 10 carbon atoms and not more than 26 carbon atoms, and preferably from 14 to 26 carbon atoms. Suitable sulphated materials which may be used in the bath of the present invention include, for example, sulphated tall oil, sulphated castor oil, sulphated sperm oil, sulphated tallow, sulphated propylolate, alkylaryl polyether sulphates, sulphated amides, sulphated alcohols and the monoglyceride ester of coconut oil sulphate. These materials are generally available commercially under various trade names. It has been found that the amount of half ester employed is critical, the effective range of concentration being between 0.4 and 2.0 per cent by weight of a total etching bath. For example, Monosulph (Nopco Chemical Company—a sulphated castor oil having 45 per cent sulphation) has an optimum effective concentration of 1.16 per cent.

In practising the present invention it has been found to be desirable to impinge the bath against the surface to be etched, as by splashing. In theory, at least, the etching bath of the present invention forms a partially acid-resistant film on the resist-free metal surfaces, and when the bath is impinged against the surface to be etched in a direction normal to that surface, the film is broken. On the other hand, when the bath hits the sides of the relief the film is generally not broken because of insufficient striking force and etching of the sides

(or undercutting) is substantially reduced. 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.

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 divided by one-half of the loss in width of metal immediately beneath the resist. Etch factors of 10 and higher are readily obtained by the method of the present invention and etch factors as high as 100 are not unusual.

Following is a description by way of example of methods of carrying the present invention into effect.

EXAMPLE 1

A magnesium photoengraving sheet having a nominal composition of 3 per cent aluminium, 1.0 per cent zinc, and minor alloying elements, the balance being magnesium, and impurities was photoprinted and developed in the conventional manner to prepare an acid resistant coating in the form of an image. A machine of the type described in Patent Specification No. 725,110, was provided and approximately 3 litres of water at a temperature of about 60°F. placed therein. Thereafter, technical nitric acid of 42° Baume was added to make a final concentration of HNO_3 in the bath of 10 per cent. Next, sufficient Monosulph (Nopco Chemical Company—a 45 per cent sulphated castor oil) to make a 1.22 per cent final solution mixed with sufficient diethylbenzene to get a final concentration of 7 per cent was added to the bath, and the volume adjusted with water to 5700 millilitres. The solution was mixed by running the paddles for two minutes. A photoengraving sheet, as above described, having the image thereon was descummed with an aqueous solution containing 12 ounces of potassium hydroxide and 4 ounces of potassium permanganate per gallon of solution. This plate was then placed in the plate holder of the machine, and the lid closed.

After the temperature of the bath had been brought to 72°F. by the heat exchanger, the paddles were started and adjusted to 500 R.P.M. and the etching continued for 8 minutes. There was thus obtained an average etch depth of .014 to .015 inch with a smooth etched surface and a sharply delineated relief. The etch factor was 50.

EXAMPLE 2

In a manner similar to that of the above Example 1, except that zinc photoengraving plate having a nominal composition of 0.7 per cent aluminium, and minor alloying elements, balance zinc, was substituted for the magnesium plate, the amount of Monosulph was reduced to 1.04 per cent, the paddle speed was

were substituted for the above Monosulph and 10 the etching procedure repeated. The following table summarizes these results:

EXAMPLE 3
In a manner similar to that of the foregoing Example 1, other half esters of sulphuric acid

5 was 50.

600 R. V. M. and the time was 94 minutes. There was thus obtained an average etch depth of 0.19 inch having a smooth etched surface and a sharply delineated relief. The etch factor

TABLE

Trade Name	Sulphated	Manufacturer	Etch Factor Range	Concentration Per Cent Range Tested	Per Cent Optimum Concentration
Turkey Red Oil	Castor Oil	Nopco Chem. Co.	2.6 to 100+	0.1 to 1.8	1.0
Cordon 800/75	Castor Oil	Finetex Inc.	4.5 to 25	0.36 to 1.04	0.90
Cordon 900	Sperm Oil	Finetex Inc.	2.5 to 15	0.18 to 1.17	1.0
Cordon LB870	Tall Oils	Finetex Inc.	6.2 to 15	0.36 to 0.81	0.7
Drutone D	Coconut and Olive Oils	E. F. Drew & Co.	6 to 8	0.25 to 1.17	1.1
Estol—T75	Tallow	E. F. Drew & Co.	3 to 14	0.25 to 1.17	1.1

In the above table, the Turkey Red Oil contained approximately 22 per cent sulphation, while the others contained between 10 and 20 per cent sulphation, depending on the amount of reaction products remaining with the desired material after purification by the supplier.

Each of the baths was relatively stable and each bath gave a very favourable etch when conditions were adjusted.

WHAT WE CLAIM IS:—

1. A method of etching the surface of an acid-soluble metal consisting of magnesium, zinc, magnesium-base or zinc-base alloys said surface having portions thereof masked with an acid resistant coating, which method comprises repeatedly impinging upon the surface of the object, so as to contact both the masked and unmasked portions thereof, an aqueous mixture which contains (1) from 1 to 25 per cent of HNO_3 , (2) from 1 to 12 per cent of a water-immiscible organic liquid substantially unreactive with the nitric acid in the aqueous mixture, and (3) between 0.4 and 2.0 per cent of a water-soluble, anionic, surface-active half ester of sulphuric acid containing at least one hydrophobic group of from 10 to 26 carbon atoms in an uninterrupted chain, and said ester containing at least 8 per cent sulphation as hereinbefore defined.

2. A method as claimed in claim 1 wherein the half ester of sulphuric acid is a sulphated naturally-occurring oil.

3. A method as claimed in claim 2 wherein the sulphated oil is castor oil containing substantially 45 per cent sulphation.

4. The method of etching the surface of a magnesium plate having a portion of its surface masked with an acid-resistant coating, which includes: repeatedly impinging upon the surface of the plate so as to contact both the masked and unmasked portions thereof an aqueous mixture which contains (1) 4 to 12.5 per cent nitric acid, (2) 5 to 8 per cent diethylbenzene, and (3) 1.16 per cent sulphated castor oil having 45 per cent sulphation as hereinbefore defined.

5. An etching bath comprising an aqueous mixture of 1 to 25 per cent HNO_3 , from 1 to

12 per cent of a water-immiscible organic liquid substantially unreactive with the nitric acid in the mixture, and between 0.4 and 2.0 per cent of a water-soluble, anionic, surface-active, half ester of sulphuric acid containing at least one hydrophobic group of from 10 to 26 carbon atoms in an uninterrupted chain, said ester containing at least 8 per cent sulphation as hereinbefore defined.

6. An etching bath comprising a mixture of 1 to 25 per cent nitric acid, from 1 to 12 per cent of a water-immiscible organic liquid substantially unreactive with the nitric acid in the mixture and between 0.4 and 2.0 per cent of a water-soluble, anionic, surface-active, sulphated, naturally-occurring oil containing a hydrophobic group of 10 to 26 carbon atoms in a chain, said oil containing at least 8 per cent sulphation as hereinbefore defined.

7. A bath as claimed in claim 6 wherein the sulphated oil is castor oil containing about 45 per cent sulphation.

8. A bath as claimed in any one of the preceding claims wherein the organic liquid is diethylbenzene.

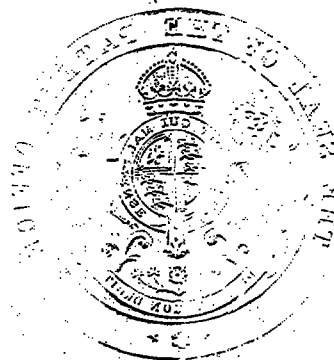
9. An etching bath comprising a mixture of 4 to 12.5 per cent nitric acid, 7 per cent diethylbenzene, and 1.16 per cent sulphated castor oil having 45 per cent sulphation as hereinbefore defined.

10. An etching bath comprising from 1 to 25 per cent of nitric acid, from 1 to 12 per cent of a water-immiscible organic liquid and between 0.4 and 2 per cent of a compound selected from the group consisting of sulphated fats, oils and waxes, containing a hydrophobic group of 10 to 26 carbon atoms in a chain, said compound containing at least 8 per cent sulphation, as hereinbefore defined.

11. A method of etching the surface of a metal substantially as described in any one of the specific examples hereinbefore set forth.

12. Etched metal objects when etched by the method claimed in any one of claims 1 to 4 or claim 11.

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Chartered Patent Agents.



Monotype Ltd

In the above table, the Turkey Red Oil contained approximately 22 per cent sulphation, while the others contained between 10 and 20 per cent sulphation, depending on the amount of reaction products remaining with the desired material after purification by the supplier.

Each of the baths was relatively stable and each bath gave a very favourable etch when conditions were adjusted.

WHAT WE CLAIM IS:—

1. A method of etching the surface of an acid-soluble metal consisting of magnesium, zinc, magnesium-base or zinc-base alloys said surface having portions thereof masked with an acid resistant coating, which method comprises repeatedly impinging upon the surface of the object, so as to contact both the masked and unmasked portions thereof, an aqueous mixture which contains (1) from 1 to 25 per cent of HNO_3 , (2) from 1 to 12 per cent of a water-immiscible organic liquid substantially unreactive with the nitric acid in the aqueous mixture, and (3) between 0.4 and 2.0 per cent of a water-soluble, anionic, surface-active half ester of sulphuric acid containing at least one hydrophobic group of from 10 to 26 carbon atoms in an uninterrupted chain, and said ester containing at least 8 per cent sulphation as hereinbefore defined.

2. A method as claimed in claim 1 wherein the half ester of sulphuric acid is a sulphated naturally-occurring oil.

3. A method as claimed in claim 2 wherein the sulphated oil is castor oil containing substantially 45 per cent sulphation.

4. The method of etching the surface of a magnesium plate having a portion of its surface masked with an acid-resistant coating, which includes: repeatedly impinging upon the surface of the plate so as to contact both the masked and unmasked portions thereof an aqueous mixture which contains (1) 4 to 12.5 per cent nitric acid, (2) 5 to 8 per cent diethylbenzene, and (3) 1.16 per cent sulphated castor oil having 45 per cent sulphation as hereinbefore defined.

5. An etching bath comprising an aqueous mixture of 1 to 25 per cent HNO_3 , from 1 to

12 per cent of a water-immiscible organic liquid substantially unreactive with the nitric acid in the mixture, and between 0.4 and 2.0 per cent of a water-soluble, anionic, surface-active, half ester of sulphuric acid containing at least one hydrophobic group of from 10 to 26 carbon atoms in an uninterrupted chain, said ester containing at least 8 per cent sulphation as hereinbefore defined.

6. An etching bath comprising a mixture of 1 to 25 per cent nitric acid, from 1 to 12 per cent of a water-immiscible organic liquid substantially unreactive with the nitric acid in the mixture and between 0.4 and 2.0 per cent of a water-soluble, anionic, surface-active, sulphated, naturally-occurring oil containing a hydrophobic group of 10 to 26 carbon atoms in a chain, said oil containing at least 8 per cent sulphation as hereinbefore defined.

7. A bath as claimed in claim 6 wherein the sulphated oil is castor oil containing about 45 per cent sulphation.

8. A bath as claimed in any one of the preceding claims wherein the organic liquid is diethylbenzene.

9. An etching bath comprising a mixture of 4 to 12.5 per cent nitric acid, 7 per cent diethylbenzene, and 1.16 per cent sulphated castor oil having 45 per cent sulphation as hereinbefore defined.

10. An etching bath comprising from 1 to 25 per cent of nitric acid, from 1 to 12 per cent of a water-immiscible organic liquid and between 0.4 and 2 per cent of a compound selected from the group consisting of sulphated fats, oils and waxes, containing a hydrophobic group of 10 to 26 carbon atoms in a chain, said compound containing at least 8 per cent sulphation, as hereinbefore defined.

11. A method of etching the surface of a metal substantially as described in any one of the specific examples hereinbefore set forth.

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