

PATENT SPECIFICATION

808,893



Date of Application and filing Complete Specification July 29, 1957.

No. 24008/57.

Application made in United States of America on July 31, 1956.

Complete Specification Published Feb. 11, 1959.

Index at acceptance:—Class 100(2), LA6A.

International Classification.—B44h.

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. It more particularly concerns an improved method of producing a relief in the surface of an object easily soluble in acid, as in making a printing plate by etching with an acid solution.

A new etching process was introduced into the art, and one which is particularly adapted to photoengraving, upon the issuance of British Patents Nos. 704,824; 705,004; 703,815; 703,814 and 709,315. In this new etching procedure, the bath composition is so controlled and the bath itself is impinged upon the photoengraving plate in such a manner that lateral etching and/or undercutting of the image areas is reduced or, in some cases, eliminated. A major advantage of this procedure lay in the fact that the time consuming powdering techniques were substantially eliminated.

In the commercial use of the above-mentioned patents, it was found that the bath composition must be varied to obtain optimum results depending upon the type of image that is to be etched. In line areas, where the image to be etched comprises printed matter or images containing only solid lines, it has been generally found that the image must be etched to a depth of at least 0.020 inches. In such cases undercutting is a problem and when employing the process disclosed and claimed in Specification No. 703,814, the amount of water-immiscible organic liquid employed must be maintained at a relatively high level. When treating photoengraving plates containing half-tone areas, which comprise images made up of a plurality of very small dots which

produce the effect of shading due to variation in the size of the dots on different portions on the plate, it is necessary to etch only from 0.0025 inch up to 0.007 inch, depending upon the screen ruling employed, and the amount of water-immiscible organic liquid used in these baths may be reduced to a minimum. Line areas and half-tone areas, by themselves, present no great problem in the use of the new process so described, but it has been found to be very difficult to etch plates known in the trade as combination plates, which contain both half-tone areas and line areas. This problem is due to the fact that the depth to which line areas are generally etched is many times greater (by a factor of 3 to 10) than the depth to which half-tone areas are normally etched. While these combination plates represent a highly specific problem in the photoengraving art, they are still representative of an important phase of this art because of the large number of such plates used in newspapers.

It is an object of this invention to provide an improved method and bath for etching acid-soluble metal objects, particularly developed photoengraving plates which bear a resist image. Another object of this invention is to provide an improved method and bath for etching developed photoengraving plates containing both half-tone and line areas.

It has been discovered that the etching action of etching baths, such as defined in the above-cited patents and in each case including a water-immiscible organic liquid may be greatly enhanced by adding thereto a sulphur-containing compound as herein defined, soluble in aqueous dilute nitric acid solution.

According to the invention there is provided an etching bath comprising a mixture of an aqueous solution containing nitric acid, a wetting agent comprising succinic acid esters, petroleum sulphonates, saturated aliphatic acids or esters of polyhydric alcohols and aliphatic acids and from 0.02 to 0.3 grams per litre of bath solution of a sulphur-containing

[Price 3s. 6d.]



compound selected from the group consisting of sulphuric acid, inorganic sulphates, organic sulphates or organic sulphonates wherein the organic portion of the molecule consists of alkyl radicals containing not more than 8 carbon atoms, naphthenic radicals, phenyl radicals, or alkyl phenyl radicals wherein the alkyl portion comprises one or more alkyl groups and contains a maximum of 6 carbon atoms and a water immiscible organic liquid substantially unreactive with the aqueous nitric acid solution. The inorganic sulphates include sodium sulphate, sodium acid sulphate, magnesium sulphate, aluminium sulphate and ammonium sulphate. The organic sulphates comprise diethyl sulphate, dimethyl sulphate, and ethyl hydrogen sulphate. Illustrative of the organic sulphonates are *n*-butyl sodium sulphonate, benzene sulphonic acid, sodium xylene sulphonate, and sodium toluene sulphonate. It will be apparent to those skilled in the art that compounds which, in a nitric acid solution, produce the sulphates or sulphonates above defined may also be employed. For reasons of economy and performance, either sulphuric acid or sodium sulphate are preferably employed.

The sulphur-containing compound must be present in solution in the bath in amounts such that the sulphur content of the solute ranges from 0.02 to 0.3 grams per litre of bath solution. This range defines critical limits for sulphuric acid and sodium sulphate, but it will be apparent to those skilled in the art that certain variations in this range will occur depending upon the particular sulphur-containing compound employed. Also, the sulphur content of the solute may be in part made up from sulphur derived from adventitious elements, so that the amount of sulphur-containing compound added may vary, for example, with the sulphate content of the water employed. In order to derive the enhanced etching action required to produce satisfactory combination plates, sufficient sulphur-containing compound must be added so that the sulphur content in the solute ranges from 0.03 to 0.18 grams per litre of bath solution, and the preferred range is from 0.04 to 0.095 grams per litre. The present invention is all the more remarkable when it is considered just how small a percentage of the sulphur-containing compound is required to produce the desired results. The addition of an equivalent amount of nitric acid produces no perceptible distinction in the characteristics of the bath.

Although the ability of the sulphur-containing compound to enhance etching action is exhibited to varying degrees when added to each of the baths defined in British Patents Nos. 704,824; 705,004; 703,815; 703,814 and 709,315 an unusually pronounced improvement in the etching action has been noted with baths such as those defined in Patent No.

703,814. These baths comprise a mixture of an aqueous solution containing nitric acid, an ester of sulphosuccinic acid and an aliphatic alcohol having from 4 to 12 carbon atoms, and a water-immiscible organic liquid substantially unreactive with the aqueous nitric acid solution.

In applying baths comprising the present invention to the etching of combination plates, it has been found necessary to maintain an extremely delicate balance between a number of factors in order to produce commercially acceptable plates. For this purpose, the commercially operable baths are those wherein the ingredients are maintained within quite narrow limits.

Experimentation has shown that when this bath is to be employed in the etching of combination plates the nitric acid content should be maintained between 3 and 15 per cent by volume measured as 42° Baume acid. As used in this description and in the attached claims the term "per cent by volume" refers to the total volume of the etching bath. "Nitric acid" as used herein refers in each instance to 42° Baume acid and "concentrated sulphuric acid" is defined as reagent grade acid having a specific gravity of 1.84. When the concentration of the nitric acid falls below 3 per cent the time required for etching the plate is unduly increased, while above 15 per cent undercutting of the image area may occur. It is preferred that the nitric acid content be maintained in the range of 5.0 to 11.0 per cent by volume.

As above set forth, the wetting agents that we prefer to employ are those described and claimed in Patent No. 703,814. When the bath is to be used to etch combination plates, however, it is necessary to limit these wetting agents to an ester of sulphosuccinic acid and an aliphatic alcohol having from 7 to 9 carbon atoms. Of these esters, we prefer to employ dioctyl sodium sulphosuccinate. The amount of wetting agent employed ranges from 2.0 to 10.0 grams per litre. Below 2 grams per litre of wetting agent, undercutting may occur. When the wetting agent is employed in amounts greater than 10.0 grams per litre of bath solution, a rough uneven etching of the metal surface may occur.

For general purposes, any water-immiscible organic liquid which is substantially unreactive with the aqueous nitric acid solution may be employed. For combination plates, however, it is preferred to employ liquid alkylbenzenes, or mixtures thereof, wherein the alkyl portion is composed of one or more alkyl groups having a maximum of 4 carbon atoms per group and the total number of carbon atoms in the alkyl portion does not exceed 10. These liquid alkylbenzenes include such compounds as monoethylbenzene, the diethylbenzenes, the dimethylbenzenes, the tetramethylbenzenes, the tetraethylbenzenes and the monobutylben-



sulphuric

zenes. The amount of alkylbenzene employed may vary from 2.0 per cent to 4.5 per cent by volume. An uneven etching with excessive filming is obtained when less than 2.0 per cent by volume of alkylbenzene is employed and a minimum of 2.5 per cent is preferred. When more than 3.3 per cent alkylbenzene is used an inadequate depth of etch is generally obtained in the half-tone areas, although up to 4.5 per cent by volume of alkylbenzene can be used and still produce acceptable combination plates under some conditions.

In etching photoengraving plates with baths of the present invention, commercial practice has shown that it is generally necessary to condition the baths by dissolving magnesium therein in order to obtain a plate that will be satisfactory for printing purposes. Although continued use of the bath will itself effect the required conditioning, initial conditioning is essential if the first few plates etched in the bath are to be commercially useable. It has been discovered that the addition of a soluble nitrate salt, such as magnesium nitrate or sodium nitrate, will also condition the bath. When magnesium is dissolved in the bath, some of the nitric acid is used up. The addition of a soluble nitrate does not alter the nitric acid content of the bath, so that somewhat lower acid concentrations can be used with soluble nitrates as conditioning agents than those acid concentrations set forth above, which are intended for use when the bath is conditioned by dissolving magnesium in the bath. The amount of magnesium dissolved in the bath for conditioning purposes will range from about 3 to 5 grams per litre. The best manner of defining this bath conditioning factor is by reference to the molar ratio between the hydrogen content of the nitric acid and the total nitrate radical present in the bath. The nitrate addition, or dissolution of magnesium, should be so regulated that this molar ratio of hydrogen to nitrate will range from 0.3 to 0.9 and preferably between 0.4 and 0.8.

The temperature of the bath is preferably maintained between 70 and 75° F. It will be apparent to those skilled in the art that as the temperature varies, the composition of the bath must be altered to compensate for higher or lower temperatures. The length of time required to etch a combination plate using the preferred bath compositions above set forth will vary from 7½ minutes in a fresh bath to 15 minutes in a used bath. A deep etch bath, such as that disclosed in Patent No. 703,814, may be employed to increase the depth of etch in the line areas and open areas.

Following is a description by way of example of methods of carrying the invention into effect:—

EXAMPLE 1

A plate 18 inches by 24 inches by 0.064 inch formed of a magnesium-base alloy having

a nominal composition of approximately 3.0 per cent aluminium, 1.0 per cent zinc, 0.06 per cent manganese, 0.025 per cent calcium and minor traces of other impurities, the balance being magnesium, was coated with a conventional polyvinyl alcohol photo-resist and exposed through a photographic negative having images including a 65 screen half-tone area with some highlight drop out areas and line areas comprising type lines and illustrations. After the exposure, the plate was developed, leaving a resist corresponding to the image of the printed matter and the half-tone area, the remainder of the plate being bare. The resist image on the plate was set by heating the plate in an oven for six minutes, the oven temperature being maintained at 450° F. Scum was removed from the plate by a 2 minute immersion in an aqueous solution consisting of 12 oz./gal. of potassium hydroxide and 2 oz./gal. of potassium permanganate. An etching bath was made up having the following formulation:—

nitric acid (42° Be.)	-	16	litres
dioctyl succinate ester*	-	900	grams
diethylbenzene	-	3.3	litres
H ₂ SO ₄ (1.84 sp.gr.)	-	6	c.c.

*a material comprising 75 per cent by weight of dioctyl-sodium sulphosuccinate, 20 per cent water and 5 per cent ethyl alcohol.

The bath was conditioned by etching an 18 inch by 24 inch sheet of magnesium photoengraving plate for about 18 minutes at 600 r.p.m. paddle speed and thus dissolving 600 grams of magnesium in the bath.

The above bath formulation was placed in an etching machine corresponding to that disclosed in Patent No. 725,110 and maintained at a temperature 72° F. The plate was held with the image bearing side down at a height of about 3 inches above the uppermost point of travel of the tips of the paddles. These paddles were positioned in the bath and splashed the bath upwardly against the image-bearing side of the plate. The paddles were rotated for an initial period of 2 minutes at 600 r.p.m. and the speed was then dropped to 500 r.p.m. for one-half minute, with final reduction in paddle speed to 380 r.p.m. for a period of 7 minutes. The etched plate was rinsed and dried and the large bare portions thereof were found to be etched to a depth of .016 inch. The half-tone area was etched to a depth of .006 inch in the highlight areas and showed no undercutting or loss of dots. In type of about 8 point size there was an etch depth of .015 inch in the area between the lines.

EXAMPLE 2

Using a plate 18 inches by 6 inches by 0.064 inch of the same magnesium-base alloy and coated with the same resist as defined in Example 1, all of the procedures of Example 1 were followed except for a different etching

bath and some variation in the paddle speed employed. The bath used had the following composition:—

	nitric acid (42°Be.) - -	16	litres
5	dioctyl succinate ester* -	950	grams
	diethylbenzene - - -	4.15	litres
	sodium sulphate (anhydrous) - - -	50	grams

*as defined in Example 1

10 The paddle speed initially was 600 r.p.m. for 2 minutes, followed by one minute at 500 r.p.m. and finally 6½ minutes at 380 r.p.m. Substantially identical depths of etch were obtained as in Example 1.

15 The amount of sulphur-containing compound, calculated on the basis of sulphur content, was 0.0268 grams/litre in Example 1 using H₂SO₄ and 0.084 grams in Example 2 using sodium sulphate (anhydrous). The

20 amount of sulphur-containing compound, nitric acid, wetting agent and water-immiscible organic liquid may be varied within the ranges above set forth. Plates of various compositions may be employed including zinc plates,

25 plates composed of zinc alloys containing over 90 per cent zinc, magnesium plates, and plates composed of magnesium alloys containing over 80 per cent magnesium.

30 It will be apparent to those skilled in the art that the invention above described may be used to advantage in a variety of ways. The bath comprising the present invention may be employed to etch combination plates, plates containing only line areas, and plates contain-

35 ing only half-tone areas, although it is unusually effective in etching combination plates. By the combination of an enhanced etching action arising from the addition of the sulphur-containing compound to the bath and by careful control of the velocity with which the bath

40 impinges upon the plate to be etched, combination plates have been etched without requiring any powdering. This is achieved by operating the paddles in the bath at a relatively

45 high velocity in the initial stages of etching, this velocity of impingement of the bath on the plate being sufficient to rapidly etch the half-tone area. When these half-tone areas have been etched to a satisfactory depth, which

50 is normally from 0.0025 inch to 0.007 inch, the speed with which the paddles are rotated in the bath may be reduced so that the velocity of impingement of the bath on the plate is such that the etching of the line areas is continued and substantially no etching occurs in the half-tone area. This selective etching of the action bath is critical in producing commercially acceptable plates.

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WHAT WE CLAIM IS:—

1. An etching bath comprising a mixture of an aqueous solution containing nitric acid, a wetting agent comprising succinic acid esters, petroleum sulphonates, saturated aliphatic acids, or esters of polyhydric alcohols and ali-

phatic acids, and from 0.02 to 0.3 grams per litre of bath solution of a sulphur-containing compound selected from the group consisting of sulphuric acid, inorganic sulphates, organic sulphates or organic sulphonates wherein the organic portion of the molecule consists of alkyl radicals containing not more than 8 carbon atoms, naphthenic radicals, phenyl radicals, or alkylphenyl radicals wherein the alkyl portion comprises one or more alkyl groups and contains a maximum of 6 carbon atoms, and a water-immiscible organic liquid substantially unreactive with the aqueous nitric acid solution.

2. A bath as claimed in Claim 1 wherein the wetting agent is an ester of sulphosuccinic acid and an aliphatic alcohol having from 4 to 12 carbon atoms.

3. A bath as claimed in Claim 2 wherein the aqueous solution contains from 2 to 10 grams per litre of the ester of sulphosuccinic acid.

4. A bath as claimed in any one of the preceding claims wherein the aqueous solution contains from 3 to 15 per cent by volume of nitric acid.

5. A bath as claimed in any one of Claims 1 to 3 wherein the aqueous solution contains from 5 to 11 per cent by volume of nitric acid.

6. A bath as claimed in any one of Claims 1 to 5 wherein the sulphur containing compound is present in amount such as to provide a sulphur content in the bath ranging from 0.04 to 0.95 grams per litre thereof.

7. A bath as claimed in any one of the preceding claims wherein the mixture contains from 2 to 4.5 per cent by volume of a liquid alkyl benzene in which the alkyl portion is composed of one or more alkyl groups having a maximum of four carbon atoms per group and the total number of carbon atoms in the alkyl portion does not exceed ten.

8. A bath as claimed in Claim 7 wherein the alkyl benzene is present in an amount ranging from 2.0 to 3.3 per cent by volume.

9. A bath as claimed in Claim 7 or Claim 8 wherein the alkyl benzene compound is diethyl benzene.

10. A bath as claimed in any one of Claims 3 to 9 wherein the ester of sulphosuccinic acid is formed with an aliphatic alcohol having from 7 to 9 carbon atoms.

11. A bath as claimed in any one of the preceding claims wherein the sulphur-containing compound is sulphuric acid.

12. A bath as claimed in any one of Claims 1 to 9 wherein the sulphur-containing compound is sodium sulphate.

13. A bath as claimed in any one of the preceding claims wherein the molar ratio of hydrogen in the nitric acid to the total nitrate radical in the bath ranges from 0.3 to 0.9.

14. A bath as claimed in Claim 13 which contains magnesium dissolved therein in an amount such as to maintain the ratio of hyd-





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bath and some variation in the paddle speed employed. The bath used had the following composition:—

- 5 nitric acid (42°Be.) - - 16 litres
 dioctyl succinate ester* - 950 grams
 diethylbenzene - - - 4.15 litres
 sodium sulphate (anhydrous) - - - 50 grams

*as defined in Example 1

- 10 The paddle speed initially was 600 r.p.m. for 2 minutes, followed by one minute at 500 r.p.m. and finally 6½ minutes at 380 r.p.m. Substantially identical depths of etch were obtained as in Example 1.

- 15 The amount of sulphur-containing compound, calculated on the basis of sulphur content, was 0.0268 grams/litre in Example 1 using H₂SO₄ and 0.084 grams in Example 2 using sodium sulphate (anhydrous). The

- 20 amount of sulphur-containing compound, nitric acid, wetting agent and water-immiscible organic liquid may be varied within the ranges above set forth. Plates of various compositions may be employed including zinc plates, 25 plates composed of zinc alloys containing over 90 per cent zinc, magnesium plates, and plates composed of magnesium alloys containing over 80 per cent magnesium.

- 30 It will be apparent to those skilled in the art that the invention above described may be used to advantage in a variety of ways. The bath comprising the present invention may be employed to etch combination plates, plates containing only line areas, and plates containing 35 only half-tone areas, although it is unusually effective in etching combination plates. By the combination of an enhanced etching action arising from the addition of the sulphur-containing compound to the bath and by careful control of the velocity with which the bath 40 impinges upon the plate to be etched, combination plates have been etched without requiring any powdering. This is achieved by operating the paddles in the bath at a relatively 45 high velocity in the initial stages of etching, this velocity of impingement of the bath on the plate being sufficient to rapidly etch the half-tone area. When these half-tone areas have been etched to a satisfactory depth, which 50 is normally from 0.0025 inch to 0.007 inch, the speed with which the paddles are rotated in the bath may be reduced so that the velocity of impingement of the bath on the plate is such that the etching of the line areas is continued and substantially no etching occurs in 55 the half-tone area. This selective etching of the action bath is critical in producing commercially acceptable plates.

WHAT WE CLAIM IS:—

- 60 1. An etching bath comprising a mixture of an aqueous solution containing nitric acid, a wetting agent comprising succinic acid esters, petroleum sulphonates, saturated aliphatic acids, or esters of polyhydric alcohols and ali-

phatic acids, and from 0.02 to 0.3 grams per 65 litre of bath solution of a sulphur-containing compound selected from the group consisting of sulphuric acid, inorganic sulphates, organic sulphates or organic sulphonates wherein the organic portion of the molecule consists of 70 alkyl radicals containing not more than 8 carbon atoms, naphthenic radicals, phenyl radicals, or alkylphenyl radicals wherein the alkyl portion comprises one or more alkyl groups and contains a maximum of 6 carbon atoms, 75 and a water-immiscible organic liquid substantially unreactive with the aqueous nitric acid solution.

2. A bath as claimed in Claim 1 wherein the wetting agent is an ester of sulphosuccinic acid 80 and an aliphatic alcohol having from 4 to 12 carbon atoms.

3. A bath as claimed in Claim 2 wherein the aqueous solution contains from 2 to 10 85 grams per litre of the ester of sulphosuccinic acid.

4. A bath as claimed in any one of the preceding claims wherein the aqueous solution 90 contains from 3 to 15 per cent by volume of nitric acid.

5. A bath as claimed in any one of Claims 1 to 3 wherein the aqueous solution contains 95 from 5 to 11 per cent by volume of nitric acid.

6. A bath as claimed in any one of Claims 1 to 5 wherein the sulphur containing compound is present in amount such as to provide 100 a sulphur content in the bath ranging from 0.04 to 0.95 grams per litre thereof.

7. A bath as claimed in any one of the preceding claims wherein the mixture contains 105 from 2 to 4.5 per cent by volume of a liquid alkyl benzene in which the alkyl portion is composed of one or more alkyl groups having a maximum of four carbon atoms per group and the total number of carbon atoms in the 110 alkyl portion does not exceed ten.

8. A bath as claimed in Claim 7 wherein the alkyl benzene is present in an amount 115 ranging from 2.0 to 3.3 per cent by volume.

9. A bath as claimed in Claim 7 or Claim 8 120 wherein the alkyl benzene compound is diethyl benzene.

10. A bath as claimed in any one of Claims 3 to 9 wherein the ester of sulphosuccinic acid 125 is formed with an aliphatic alcohol having from 7 to 9 carbon atoms.

11. A bath as claimed in any one of the preceding claims wherein the sulphur-containing compound is sulphuric acid.

12. A bath as claimed in any one of Claims 1 to 9 wherein the sulphur-containing compound is sodium sulphate. 130

13. A bath as claimed in any one of the preceding claims wherein the molar ratio of hydrogen in the nitric acid to the total nitrate 135 radical in the bath ranges from 0.3 to 0.9.

14. A bath as claimed in Claim 13 which contains magnesium dissolved therein in an amount such as to maintain the ratio of hyd-



etched

rogen to nitrate radical within the range specified.

- 5 15. A process for etching a developed photoengraving plate containing both line and half-tone images thereon and comprising essentially a metal consisting of magnesium, magnesium-base alloys containing over 80 per cent magnesium, zinc, or zinc-base alloys containing over 90 per cent zinc, which process comprises causing an etching bath as claimed in 10 any one of the preceding claims to impinge upon the surface thereof at a velocity sufficient to etch rapidly the half-tone areas, and continuing to cause the bath to impinge on the 15 plate until the half-tone areas have been etched to a satisfactory depth, and then reducing the velocity at which the bath is caused to impinge

on the plate to a point such that the etching of the line areas is continued and substantially no etching in the half-tone area occurs.

16. A process according to Claim 15 using an etching bath as claimed in Claims 3, 4, 7, 10, 12 and 13.

17. A process for etching developed photoengraving plates substantially as described in either of the specific examples hereinbefore set forth.

18. Etched photoengraving plates when prepared by the process claimed in any one of Claims 15, 16 or 17.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1959.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.



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