

nitric acid
alkylaryl sulfonate
water immiscible organic liq.
(petr. hydrocarbons or HC derivatives)

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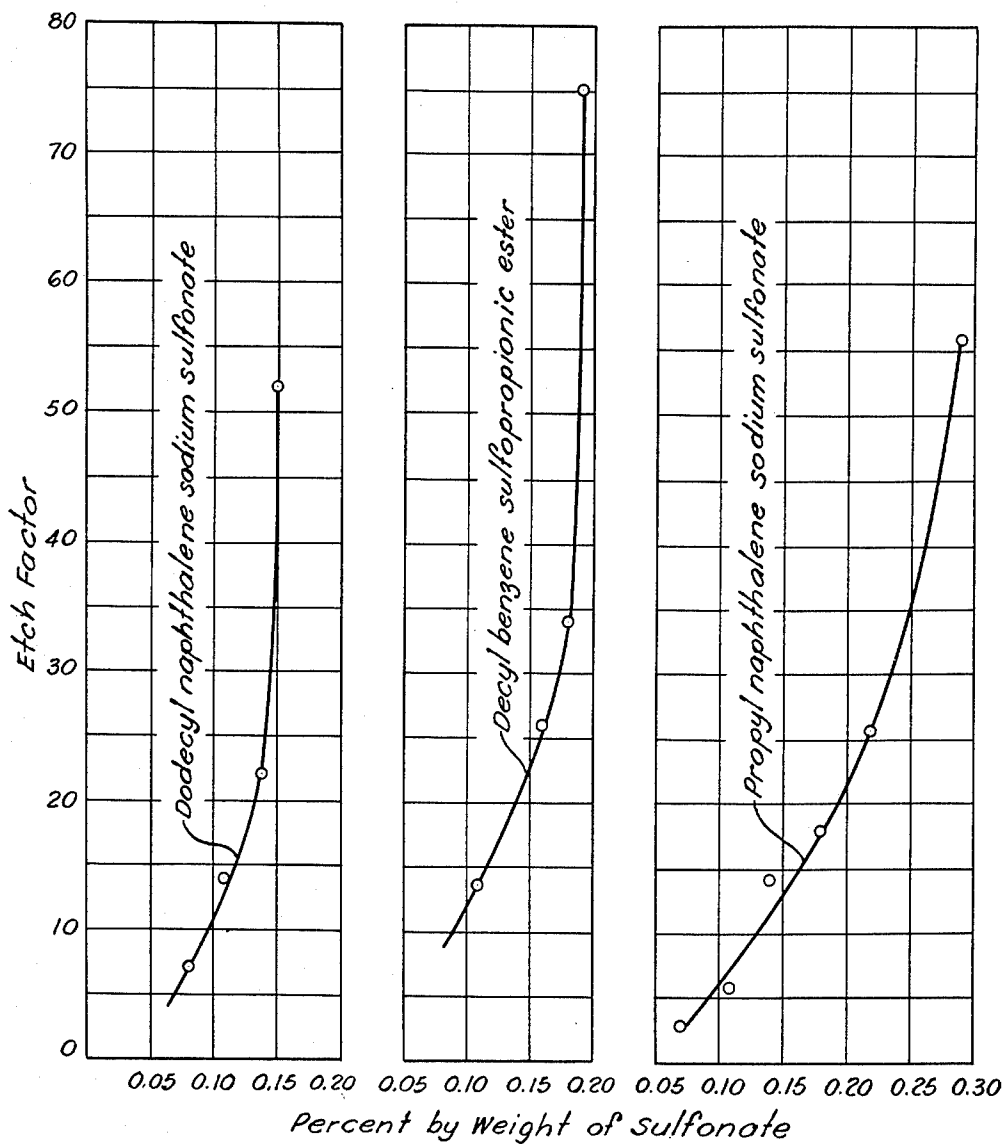
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2,979,387

ETCHING

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0.05 to 0.10



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ETCHING

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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. Other objects and advantages of the present invention will become apparent from the following detailed description thereof when read in conjunction with Figure 1, which comprises a graph showing the relationship between etch factor and concentration of examples of constituents of the improved etching bath under stated conditions.

It has been discovered that by adding certain alkylaryl-sulfonates 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, from 0.1 to 2.0 percent by weight of an alkylaryl-sulfonate selected from the group consisting of the alkylbenzene sulfonates wherein the alkyl portion contains from 8 to 18 carbon atoms and the alkylnaphthalene sulfonates wherein the alkyl portion contains from 3 to 18 carbon atoms, as exemplified in the formula



in which R is an alkyl radical having from 3 to 18 carbon atoms inclusive, A is an aromatic nucleus, e.g. benzene, 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 alkylaryl-sulfonates that may be employed are decylbenzene sodium sulfonate, dodecylbenzene sodium sulfonate, tetradecylbenzene sodium sulfonate, propylnaphthalene sodium sulfonate, amyl-naphthalene sodium sulfonate, diamylnaphthalene sodium sulfonate,

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dodecyl-naphthalene sodium sulfonate. It has been found that the amount of alkylaryl-sulfonate employed is critical and it is essential that this compound be present within the range of 0.1 to 2.0 percent by weight of the total etching bath. Below 0.1 percent by weight of alkylaryl-sulfonate undercutting of the image occurs rapidly and an extremely low etch factor is obtained. Decylbenzene sulfopropionic ester (Surfax 1288 is effective in concentrations of 0.18 to 0.35 percent. 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 percent of the alkylaryl-sulfonate may be employed, although it is preferred not to go above 0.5 percent. 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 percent 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 percent.

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 dipping into the bath composition intermittently throw, by oil, 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 the diethylbenzenes. 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 percent by weight of the total bath. The preferred range is from 4 to 10 percent.

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 procedures 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 Patent No. 2,669,048, issued February 16, 1954, and entitled "Etching Machine." 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

agitation

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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 examples are set forth.

Example 1

An etching solution was prepared in an etching machine of the type set forth in Patent No. 2,669,048, above referred to, having an etching tank with an operating capacity of 5.7 liters, by adding approximately three liters of water to the machine with the circulating pump in operation. Nitric acid of 42° Baumé Technical Grade was then added. The alkylaryl sulfonate, 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 liters. 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.....ml.. 600
Diethylbenzene.....ml.. 400
Dodecyl-naphthalene sodium sulfonate.....grams.. 6
Octyl alcohol (a defoamer).....ml.. 3
Water to make 5.7 liters.

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 percent aluminum, 1.0 percent zinc, 0.10 percent manganese, 0.03 percent 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).....ml.. 600
Diethylbenzene.....ml.. 400
Calcium dodecylbenzene sulfonate.....gms.. 15
Water to make 5.7 liters.

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 Exam-

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ple 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 percent aluminum, 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 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).....ml.. 600
Diethylbenzene.....ml.. 400
Dodecylbenzene sodium sulfonate.....gms.. 8
Water to make 5.7 liters.

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 alkylarylsulfonates falling within the scope of the present invention were tested as in Example 1. The amount of the sulfonate used was adjusted to obtain the most favorable etch factor. The alkylarylsulfonates tested and the average etch factors obtained are set forth in the table:

Alkylarylsulfonate	percent by wt. in bath	average etch factor
amyl-naphthalene sodium sulfonate.....	0.33	27
propyl-naphthalene sodium sulfonate.....	0.24	29
dodecyl-naphthalene sodium sulfonate.....	0.15	40
dodecylbenzene sodium sulfonate.....	0.22	40
di-amylnaphthalene sodium sulfonate.....	0.17	30

Example 6

The effect of the concentration of a number of alkylarylsulfonates 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 alkylarylsulfonate. The sulfonates so tested were dodecyl-naphthalene sodium sulfonate, decylbenzene sulfopropionic ester, and propyl-naphthalene sodium sulfonate. The etch factors obtained in these tests are set forth in the single figure which comprises a graph showing the concentration of the sulfonate as related to the etch factor. It is at once evident from this graph that alkylarylsulfonates in the amounts of 0.05 percent by weight have but little effect in increasing the etch factor of the etching baths. Above about 0.10 percent by weight, however, the alkylarylsulfonates produce a pronounced increase in etch factor of the bath and appear to exert a maximum effect between about 0.15 percent and 0.3 percent 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 alkylarylsulfonates may be dissolved in either or both the water-immiscible organic liquid or the nitric acid solution. In place of the sodium salts the corresponding alkyl aryl sulfonic 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

percent magnesium, zinc, and zinc base alloys containing at least 90 percent 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 practicing 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 alkylarylsulfonate content, and may be used to etch a wide variety of magnesium alloys, especially those which contain no aluminum and which are not readily etchable by known procedures in which powdering is eliminated.

What is claimed is:

1. The method of etching a photoengraving plate consisting of magnesium, magnesium base alloys containing at least 90 percent magnesium, zinc and zinc base alloys containing at least 90 percent zinc, which comprises paddling an etching bath comprising a mixture of (1) an aqueous solution containing from 3 to 20 percent by weight of nitric acid, from 0.1 to 2.0 percent by weight of an alkylarylsulfonate selected from the group consisting of the alkylbenzene sulfonates wherein the alkyl portion contains from 8 to 18 carbon atoms and the alkylnaphthalene sulfonates wherein the alkyl portion contains from 3 to 18 carbon atoms and (2) a water-immiscible organic liquid selected from the group consisting of petroleum hydrocarbons and hydrocarbon derivatives boiling within the range of 70° to 390° C. and substantially unreactive with the aqueous nitric acid solution and present in an amount of from 1 to 14 percent by weight of the aqueous nitric acid solution, said paddling being sufficiently vigorous to intermittently throw the bath against said plate in sheets and continuing this paddling action until the plate has been etched to a satisfactory depth.

2. The method as set forth in claim 1 wherein the water-immiscible organic liquid is a petroleum hydrocarbon.

3. The method as set forth in claim 1 wherein the water-immiscible organic liquid is diethylbenzene.

4. The method as set forth in claim 1 wherein the photoengraving plate consists of an alloy of magnesium containing at least 90 percent magnesium.

5. The method as set forth in claim 1 wherein the photoengraving plate consists of a zinc base alloy containing at least 90 percent zinc.

6. The method as set forth in claim 1 wherein the alkylarylsulfonate is an alkylbenzene sulfonate wherein the alkyl portion contains from 8 to 18 carbon atoms.

7. The method as set forth in claim 1 wherein the alkylarylsulfonate is an alkylnaphthalene sulfonate wherein the alkyl portion contains from 3 to 18 carbon atoms.

8. The method of etching a photoengraving plate consisting of magnesium, magnesium base alloys containing at least 90 percent magnesium, zinc and zinc base alloys containing at least 90 percent zinc, which comprises paddling an etching bath comprising a mixture of (1) an aqueous solution containing from 5 to 12 percent by weight of nitric acid, from 0.1 to 0.5 percent by weight of an alkylarylsulfonate selected from the group consisting of the alkylbenzene sulfonates wherein the alkyl portion contains from 8 to 18 carbon atoms and the alkylnaphthalene sulfonates wherein the alkyl portion contains from 3 to 18 carbon atoms, and (2) a water-immiscible organic liquid selected from the group consisting of petroleum hydrocarbons and hydrocarbon derivatives boiling within the range of 70° to 390° C. and substantially unreactive with the aqueous nitric acid

solution and present in an amount of from 4 to 10 percent by weight of the aqueous nitric acid solution, said paddling being sufficiently vigorous to intermittently throw the bath against said plate in sheets and continuing this paddling action until the plate has been etched to a satisfactory depth.

9. The method as set forth in claim 8 wherein the water-immiscible organic liquid is a petroleum hydrocarbon.

10. The method as set forth in claim 8 wherein the water-immiscible organic liquid is diethylbenzene.

11. The method as set forth in claim 8 wherein the alkylarylsulfonate is an alkylbenzene sulfonate wherein the alkyl portion contains from 8 to 18 carbon atoms and the water-immiscible organic liquid is a petroleum hydrocarbon.

12. The method of etching a photoengraving plate consisting of zinc and zinc base alloys containing at least 90 percent zinc, which comprises paddling an etching bath comprising a mixture of (1) an aqueous solution containing from 5 to 12 percent by weight of nitric acid, from 0.1 to 2.0 percent by weight of an alkylarylsulfonate selected from the group consisting of the alkylbenzene sulfonates wherein the alkyl portion contains from 8 to 18 carbon atoms and the alkylnaphthalene sulfonates wherein the alkyl portion contains from 3 to 18 carbon atoms and (2) a petroleum hydrocarbon boiling within the range of 70° to 390° C. and substantially unreactive with the aqueous nitric acid solution and present in an amount of from 4 to 10 percent by weight of the aqueous nitric acid solution, said paddling being sufficiently vigorous to intermittently throw the bath against said plate in sheets and continuing this paddling action until the plate has been etched to a satisfactory depth.

13. The method of etching a photoengraving plate consisting of magnesium, magnesium base alloys containing at least 90 percent magnesium, zinc and zinc base alloys containing at least 90 percent zinc, which comprises paddling an etching bath comprising a mixture of (1) an aqueous solution containing from 3 to 20 percent by weight of nitric acid, from 0.1 to 0.5 percent by weight of an alkylarylsulfonate selected from the group consisting of the alkylbenzene sulfonates wherein the alkyl portion contains from 8 to 18 carbon atoms and the alkylnaphthalene sulfonates wherein the alkyl portion contains from 3 to 18 carbon atoms and (2) a petroleum hydrocarbon boiling within the range of 70° to 390° C. and substantially unreactive with the aqueous nitric acid solution and present in an amount of from 4 to 10 percent by weight of the aqueous nitric acid solution, said paddling being sufficiently vigorous to intermittently throw the bath against the said plate in sheets and continuing this paddling action until the plate has been etched to a satisfactory depth.

14. An etching bath comprising a mixture of (1) an aqueous solution containing from 3 to 20 percent by weight of nitric acid, from 0.1 to 2.0 percent by weight of an alkylarylsulfonate selected from the group consisting of the alkylbenzene sulfonates wherein the alkyl portion contains from 8 to 18 carbon atoms and the alkylnaphthalene sulfonates wherein the alkyl portion contains from 3 to 18 carbon atoms and (2) a water-immiscible organic liquid selected from the group consisting of petroleum hydrocarbons and hydrocarbon derivatives boiling within the range of 70° to 390° C. and substantially unreactive with the aqueous nitric acid solution and present in an amount of from 1 to 14 percent by weight of said aqueous nitric acid solution.

15. An etching bath according to claim 14 in which the water-immiscible organic liquid is a petroleum hydrocarbon.

16. An etching bath comprising a mixture of (1) an aqueous solution containing from 5 to 12 percent by weight of nitric acid, from 0.1 to 0.5 percent by weight of an alkylarylsulfonate selected from the group consist-

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ing of the alkylbenzene sulfonates wherein the alkyl portion contains from 8 to 18 carbon atoms and the alkyl-naphthalene sulfonates wherein the alkyl portion contains from 3 to 18 carbon atoms and (2) a water-immiscible organic liquid selected from the group consisting of petroleum hydrocarbons and hydrocarbon derivatives boiling within the range of 70° to 390° C. and substantially unreactive with the aqueous nitric acid solution and present in an amount of from 4 to 10 percent by weight of said aqueous nitric acid solution.

17. An etching bath according to claim 16 wherein the alkylarylsulfonate is an alkylbenzene sulfonate.

18. An etching bath according to claim 16 wherein the alkylarylsulfonate is an alkylbenzene sulfonate and the water-immiscible organic liquid is a petroleum hydrocarbon.

19. An etching bath according to claim 16 wherein the alkylarylsulfonate is an alkyl-naphthalene sulfonate and the water-immiscible organic liquid is a petroleum hydrocarbon.

20. A bath solution for a one-stage quick etch on an alloy comprising by weight 3 to 20 parts nitric acid, 1 to 12 parts petroleum solvent, 0.02 to 2.0 parts dodecylbenzene sulfonate and the remainder water.

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21. The process of etching a device composed of metals selected from the group consisting of zinc, magnesium, zinc base alloys and magnesium base alloys consisting in said device having portions of its surface covered with an acid resisting coating to define a design and applying an etching mixture to the remaining exposed or unprotected faces of the device with an etching mixture consisting of between 3 to 20 parts by weight of nitric acid, of between 1 to 12 parts by weight of a petroleum solvent, of between 0.02 to 2.0 parts by weight of a water-soluble alkyl aryl sulphonate constituting a wetting agent selected from the group consisting of the alkylbenzene sulfonates wherein the alkyl portion contains from 8 to 18 carbon atoms and the alkyl-naphthalene sulfonates wherein the alkyl portion contains from 3 to 18 carbon atoms and the remainder water.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,979,387

April 11, 1961

John A. Easley et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 34, for "dipping into the bath composition intermittently throw, by" read -- tions boiling in the range of 70° to 390° C., such as gas- --.

Signed and sealed this 16th day of January 1962.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

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Commissioner of Patents