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ETCHING ZINC PLATES

Ernest R. Boller, Cleveland Heights, Ohio, assignor to The Grasselli Chemical Company, Cleveland, Ohio, a corporation of Delaware

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The present invention relates to etching engravers' zinc plates and to novel etching acids comprising nitric acid in which a metal and an organic hydroxy compound is dissolved.

5 I have shown in my co-pending application, Ser. No. 649,731 for "Engraver's etching acid of increased efficiency", filed on even date herewith, that the addition of small amounts of copper, silver or platinum to dilute nitric acid as commonly used for etching zinc plates considerably increases the efficiency of such an etching bath. I have also shown in co-pending application, Ser. No. 649,732 for "Etching of engravers' zinc plates", filed on even date herewith, that the addition to dilute nitric acid as commonly used for etching zinc plates of small amounts of certain organic hydroxy compounds produces an etching bath which produces much smoother and more uniform plates.

20 I have now found that the presence in a dilute nitric acid etching bath of a small amount of an organic hydroxy compound is entirely compatible with the presence therein of a small amount of a metallic addition agent, such as copper, silver or platinum and that a bath which contains both types of addition agents shows the improvements due to both and that their effect seems to be enhanced to a remarkable degree. By the use of an etching bath containing both types of addition agents I am enabled to produce smoother, cleaner etchings with an increased efficiency over the use of a straight nitric acid etching bath or a bath containing one only of these types of addition agents.

35 In the photoengraving art, as at present generally practiced, the etching process may be described essentially as follows: A highly polished zinc plate is coated with a thin layer of an acid resisting enamel, such as glue or shellac, sensitized to light with ammonium chromate, or with a layer of albumin similarly sensitized. The zinc plate thus sensitized is placed back of a glass plate bearing an opaque-translucent mirror-image-negative film of the picture or design to be reproduced, and exposed to a strong light. Where the light strikes the sensitized zinc surface the enamel or albumin is fixed to the surface of the zinc, developing on the zinc a mirror-image-positive of the design being reproduced. In the case of the enamel coating, the unfixed portions of the layer are washed off with water and the zinc plate is ready for etching. In the case of the albumin coating, the plate is covered with a thin layer of ink and the unfixed part of the albumin with overlying ink washed off the plate

with water. The ink remaining on the plate is dusted with an acid resisting resin and the latter burned in by heating the plate to the resin's melting point, after which the plate is ready for etching.

5 The zinc plates to be etched thus have those parts which are to print black covered with an acid resisting coating and the other parts exposed. Those parts of the plate which are protected will hereinafter be referred to as the tops, 10 and the exposed parts as bottoms.

15 The etching process itself consists essentially of exposing the plate prepared as described to a nitric acid solution, taking a suitable procedure to prevent the acid attacking the edges of the tops. This operation is commonly performed by placing the plate vertically in a closed tank and splashing or throwing the acid solution against the plate by means of a paddle arrangement. It is the general practice to use an etching bath 20 containing approximately 10% HNO_3 .

25 When the etching of the zinc plate has proceeded sufficiently far that the bottoms have a noticeable depth, the plate is rinsed, dried and the exposed edges protected against attack by brushing a bank of acid resisting resin against them and fusing this in place by heating the plate to the required temperature. The etching is continued until the edges are again in danger of being undercut, whereupon they are again 30 banked with the acid resisting resin. This procedure is continued until the desired depth is obtained which, of course, varies with the type of reproduction, area of the bottoms and so on.

35 In this procedure it is essential that the bottoms of the plate be quite smooth. Otherwise the irregularities in the surface will catch the acid resisting resin and in the course of the operation build up still larger irregularities, which will interfere with printing from the plate. This coating of resin on the bottoms slows up the operation very considerably. Even on very smooth bottoms there is some such coating, and this must be removed before the actual solution of the zinc underneath can proceed. However, 45 if the acid removes the resin too easily, it will naturally attack the banks on the edges and lead to undercutting before appreciable depth can be obtained.

50 It is equally essential that there be no undercutting of the edges. This is especially true of the work in newspaper plants where paper mattes are made from the engravings for the casting of cylindrical type.

The acid etching bath is used until its action 55

becomes unsatisfactorily slow, as usually evidence by its inability to remove the thin film of resin from the bottoms. This point is commonly reached when the nitric acid concentration has fallen to approximately 5%. It is well known that addition of concentrated acid to a spent bath does not revivify it appreciably; hence, about one-half of the nitric acid required by the industry must be thrown away.

The presence in an engraver's nitric acid of small amounts of copper, silver or platinum increases the efficiency of the bath. By this I mean the amount of zinc which a given quantity of nitric acid at a specified concentration will dissolve at or above a fixed rate, the rate at which it is general practice to discard the bath. A liter of straight 10% nitric acid kept at about 40° C. will dissolve about 17 grams of zinc, after which its rate of dissolving zinc is so slow that it cannot be used further for etching zinc plates and is commonly discarded; its efficiency is rated at 17 grams per liter.

The presence in the engraver's nitric acid of small amounts, for instance from 0.1 to about 2 parts of Cu, Ag or Pt per 100 parts of HNO₃, increases this efficiency. For obvious practical reasons I prefer the addition of copper, though from a purely experimental standpoint silver and platinum produce substantially the same effects as copper.

The addition of small amounts of organic hydroxy compounds to engraver's nitric acid produces a bath which in the first place promotes the formation of a very smooth etched surface, very appreciably smoother than that given by nitric acid alone, thus materially reducing the amount of acid resisting resin which can adhere to the bottoms and practically eliminating the tendency to build up irregularities on the bottoms. In the second place, nitric acid containing a small amount of the organic hydroxy compound removes the thin film of the resin remaining on the bottom when the edges are banked with such resin for protection from undercutting much more readily and quickly than straight nitric acid. These advantages are also present when the etching baths contains copper besides the organic hydroxy compound.

The organic hydroxy compounds which I have found to possess the property of producing the improved etchings as described above are water soluble compounds which contain in their molecule an alcoholic hydroxy group,—OH, and which contain another negative group in their molecule. For purposes of the present invention the OH group contained in aromatic hydroxy compounds, such as phenol, cresol, etc. is considered to be of an alcoholic nature. Representative compounds which satisfy the above definition and which have been found to be useful in my invention are for instance: aliphatic hydroxy carboxylic acids such as citric acid, tartaric acid, lactic acid, mucic acid; aromatic hydroxy carboxylic acids such as salicylic acid; aliphatic polyhydroxy compounds such as ethylene glycol and glycerol; aromatic hydroxy compounds such as phenol, cresol, resorcinol, and their sulfonic acids, saccharids such as glucose, dextrose and sucrose, etc.

Representative negative groups which impart to organic hydroxy compounds the property of improving the etching action of nitric acid upon zinc plates are for instance the benzene nucleus, the carboxylic,—COOH, group, the hydroxyl group itself, the sulfonic acid group, etc.

I have found that straight carboxylic acids, such as acetic acid in which the hydroxy group is not of an alcoholic nature do not have the effect upon an etching bath, as shown by the above alcoholic hydroxy compounds containing a negative group in their molecules; neither is this effect shown in any substantial degree by straight alcohols.

The amount of hydroxy compound to be added to the etching bath to obtain the improved plates according to my invention is not very critical; it will depend to a certain extent upon the specific compound added and upon the nature and character of the zinc plate, type of design to be reproduced, etc. In general the amount should not exceed about 3.5 parts of the addition agent per 100 parts of HNO₃ in the bath. Optimum and maximum amounts are illustrated for a few of my novel addition agents in the following table wherein these amounts are given in parts by weight per 100 parts of HNO₃.

	Optimum	Maximum
Citric acid.....	0.85	1.67
Tartaric acid.....	1.67	3.5
Dextrose.....	0.17	1.67
Phenol.....	0.85	1.67

Amounts of less than 0.05 per 100 HNO₃ are generally not desired.

The metallic and hydroxy addition agents can be incorporated in the etching bath at the time of use or I can also conveniently dissolve the metal or its salt and the hydroxy compound in commercial 40° Bé. nitric acid. This can be shipped without need of particular precautions and all the engraver has to do is to dilute this concentrated acid to the desired strength. In preparing these dual-action etching baths I can in general use more copper than in the absence of the hydroxy compound, whereby I obtain still greater efficiency of the bath without losing the benefit of a smooth, clean etch.

The amounts of the addition agents in respect to each other are otherwise not much different from the amounts I can use in baths containing only one type of addition agent.

I have for instance prepared a very efficient etching bath consisting of a 10% nitric acid in which copper sulfate was dissolved in an amount corresponding to 0.167 parts Cu per 100 parts HNO₃ and to which about 0.85 parts citric acid per 100 parts HNO₃ was added. The zinc efficiency of this bath was 21.4 grams per liter. It produced very clean, bright and smooth etchings.

The efficiency of a similarly prepared 10% nitric acid etching bath containing 0.33 Cu and 1.67 parts tartaric acid per 100 HNO₃ was 25.2 grams per liter and it produced exceedingly smooth and bright etchings.

A commercial newspaper photoengraving plant was run for 3 weeks using an etching bath of 10% nitric acid containing 0.167 parts Cu and 0.85 parts citric acid per 100 parts HNO₃. Approximately 67,000 sq. in. of surface were etched with this bath and 1300 lbs. of 40° Bé. nitric acid consumed during the time of the test.

Under identical conditions this same plant required for the production of 22,000 sq. in. of etched surface 580 lbs. of 40° Bé. nitric acid containing no addition agents; and the plates produced with my novel etching bath were much smoother and brighter and could easily be distinguished by visual examination from those produced without the addition agents.

I claim:

1. An engraver's etching bath for zinc plates comprising nitric acid and dissolved therein a small amount of a metal of the group of metals consisting of copper, silver and platinum, and a water soluble, organic, alcoholic hydroxy compound containing a negative group in its molecule.
2. An engraver's etching bath for zinc plates comprising nitric acid and dissolved therein a small amount of copper and a small amount of an organic hydroxy compound selected from the group consisting of hydroxy-carboxylic acids, aromatic hydroxy compounds and their sulfonic acids, aliphatic poly-hydroxy compounds and saccharids.
3. An engraver's etching bath for zinc plates comprising nitric acid and dissolved therein from about 0.1 to 2 parts of copper per 100 parts HNO_3 and from about 0.05 to 3.5 parts per 100 parts HNO_3 of an organic hydroxy compound selected from the group consisting of hydroxy-carboxylic acids, aromatic hydroxy compounds and their sulfonic acids, aliphatic poly-hydroxy compounds and saccharids.
4. An engraver's etching bath for zinc plates comprising nitric acid and dissolved therein a small amount of copper and a small amount of an aliphatic hydroxy carboxylic acid.
5. An engraver's etching bath for zinc plates comprising nitric acid and dissolved therein a small amount of copper and a small amount of citric acid.
6. A process of etching a zinc plate which comprises treating the prepared plate with an etching bath comprising nitric acid and dissolved therein a small amount of a metal of the group of metals consisting of copper, silver and platinum, and a water soluble, organic alcoholic hydroxy compound containing a negative group in its molecule.
7. A process of etching a zinc plate which comprises treating the prepared plate with an etching bath comprising nitric acid and dissolved therein a small amount of copper and a small amount of an organic hydroxy compound selected from the group consisting of hydroxy-carboxylic acids, aromatic hydroxy compounds and their sulfonic acids, aliphatic poly-hydroxy compounds and saccharids.
8. A process of etching a zinc plate which comprises treating the prepared plate with an etching bath comprising nitric acid and dissolved therein from about 0.1 to 2 parts of copper per 100 parts HNO_3 and from about 0.05 to 3.5 parts per 100 parts HNO_3 of an organic hydroxy compound selected from the group consisting of hydroxy-carboxylic acids, aromatic hydroxy compounds, and their sulfonic acids, aliphatic poly-hydroxy compounds and saccharids.
9. A process of etching a zinc plate which comprises treating the prepared plate with an etching bath comprising nitric acid and dissolved therein a small amount of copper and a small amount of an aliphatic hydroxy-carboxylic acid.
10. A process of etching a zinc plate which comprises treating the prepared plate with an etching bath comprising nitric acid and dissolved therein a small amount of copper and a small amount of citric acid.
11. An engraver's etching bath for zinc plates comprising nitric acid and dissolved therein a small amount of copper and a small amount of tartaric acid.
12. A process of etching a zinc plate which comprises treating the prepared plate with an etching bath comprising nitric acid and dissolved therein a small amount of copper and a small amount of tartaric acid.

ERNEST R. BOLLER.