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ETCH FOR OFFSET PLATE MAKING

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This invention relates to the art of lithographic printing, and is directed at the production of a material which will dissolve chromium without attacking either copper or a light hardened bichromated gum arabic solution.

In my U. S. Patent No. 2,291,854, issued August 4, 1942, there is described a lithographic plate consisting of a grained copper surface coated with chromium in all but the printing areas. The plate is made from a blank in which a continuous chrome layer covers the copper; this plate is coated with a bichromated gum arabic solution, exposed through a positive to harden the non-printing areas, developed with a conventional developer which removes the unhardened gum coating without attacking the light-hardened portion, and then treated with an etching solution whose function it is to dissolve the chromium in the portions where it has been laid bare by the developer, without attacking the copper or the light-hardened gum film.

In the past, this etch has consisted of various chemicals which yield hydrochloric acid, which reacts vigorously with chromium but does not attack copper. Unfortunately, such etches fume badly, making it disagreeable to work over the plate unless special fume control is provided.

A number of materials which do not fume have been developed, but they either act very slowly on the chromium or they produce difficulties by attacking either the resist or the copper.

I have discovered a non-fuming etch which attacks chromium without attacking copper, and which does not attack the resist for a much longer period than is required for complete etching of the chromium. My new etch consists of a concentrated aqueous solution of a water-soluble chloride of the group consisting of calcium and magnesium chlorides, a small amount of acid, and a minor proportion of a chromic, or stannic salt.

The essential base of my etch is a rather concentrated aqueous solution of a very water-soluble chloride; these concentrated solutions are widely used in offset plate making, since they reduce the solubility of the hardened gum solution in the aqueous system. Calcium chloride seems to give me best results, with magnesium chlorides reasonably close to it in action. The alkali metal, barium, strontium and aluminum chlorides do not yield solutions which are sufficiently inert to the hardened gum solution; the same applies to most other chlorides except zinc, which I have found is an inhibitor for the etching of chromium, and ferric chloride, which attacks copper.

To the base I add a small amount of an acid;

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about 2 liquid ounces of commercial acid per gallon of chloride solution seems to be an optimum quantity. Less acid tends to slow down etching time, while more acid does not speed it up. However, etching is obtained with any quantity from 1 ounce per gallon up (pH below 2.0). I have used hydrochloric, nitric, sulphuric, acetic, phosphoric, lactic, hydroxy acetic, citric, oxalic, and tartaric acids, and even resorcinol to get the necessary acidity; while some acids (e. g. acetic, phosphoric) are slightly slower, and some give precipitates (e. g. sulfuric with $CaCl_2$) they all can be used.

What makes my new etch effective is the use of a minor proportion of a control agent of the group consisting of a stannic or chromic salt, which will react with the nascent hydrogen formed by the reaction of the hydrochloric acid in the etch with chromium, to regenerate hydrochloric acid. This prevents the ebullition of gases, and thus no fuming occurs.

I have found chromic and stannic salts (which are preferably present as the chloride) to be unique in their action; other easily reducible salts are either not sufficiently soluble, or reduce to the metal and plate out, or attack the copper or the resist, or both. I have unsuccessfully tried to use, among others, antimonic, ferric, silver, mercuric and cobaltic chlorides.

Typical satisfactory etches include the following:

Example 1

16 liquid ounces 41.5° Bé. calcium chloride solution (79% $CaCl_2 6H_2O$)
4 liquid ounces 45° Bé. chromic chloride solution (saturated solution)
¼ liquid ounce concentrated nitric acid

This etches chromium rapidly without fuming, and without attacking copper.

Example 2

Like Example 1, but replacing the concentrated nitric acid by concentrated hydrochloric acid. Works equally well.

Example 3

Like Example 1, but substituting concentrated magnesium chloride solution of the calcium chloride.

Example 4

16 liquid ounces 41.5° Bé. calcium chloride solution
4 liquid ounces 65° Bé. stannic chloride solution (64% $SnCl_4$)
¼ liquid ounce concentrated hydrochloric acid

As will be noted, the etches consist of essentially concentrated solutions, a major proportion of calcium or magnesium chloride, a minor proportion of tin or chromic chloride, and a small amount of acid sufficient to get the pH down below 2.0.

Obviously, examples can be multiplied, without departing from the spirit of the invention, which is set forth in the claims.

I claim:

1. An etch which dissolves chromium without attacking copper, and which has relatively slow action on a light-hardened bichromated gum arabic film, consisting of a concentrated solution of a chloride of the group consisting of calcium and magnesium chlorides, a minor proportion of a concentrated solution of a chloride of the group consisting of stannic and chromic chlorides, and a small amount of acid sufficient to reduce the pH to below 2.0.

2. An etch which dissolves chromium without attacking copper, and which has relatively slow action on a light-hardened bichromated gum arabic film, consisting of a concentrated solution of calcium chloride, a minor proportion of a concentrated solution of a chloride of the group consisting of stannic and chromic chlorides, and a small amount of acid sufficient to reduce the pH to below 2.0.

3. An etch which dissolves chromium without attacking copper, and which has relatively slow action on a light-hardened bichromated gum arabic film, consisting of a concentrated solution of calcium chloride, a minor proportion of a concentrated solution of stannic chloride, and a small amount of acid sufficient to reduce the pH to below 2.0.

4. An etch which dissolves chromium without attacking copper, and which has relatively slow action on a light-hardened bichromated gum arabic film, consisting of a concentrated solution of calcium chloride, a minor proportion of a concentrated solution of chromic chloride, and a small amount of acid sufficient to reduce the pH to below 2.0.

5. An etch which dissolves chromium without attacking copper, and which has relatively slow action on a light-hardened bichromated gum arabic film, consisting of a concentrated solution of calcium chloride, a minor proportion of a concentrated solution of a chloride of the group consisting of stannic and chromic chlorides, and hydrochloric acid sufficient to reduce the pH to below 2.0.

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