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ETCHING BATH COMPOSITION

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1 Claim. (Cl. 252—79.4)

This invention relates to the etching of metal and, more particularly, to a novel etching bath composition capable of effecting controlled etching of metal surfaces.

Controlled etching of a metal surface is required in a number of arts. For example, in the production of photoengraving metal printing surfaces, the surface is covered with a light-sensitive coating, the coating is exposed to light through a negative of the desired image, and then the exposed surface is heated to develop the image on the metal surface in the form of an acid-insoluble residue called the "resist." If the resist-bearing metal surface is bathed by splashing over it a corrosive acid mixture of proper composition, the corrosion of the metal not protected by the resist can be controlled so as not to undercut the metal lying under the resist. A similar type of controlled etching is required in the production of printed electronic circuits and chemical milling.

Controlled etching bath compositions are described in United States Patents Nos. 2,640,763, 2,640,764, 2,640,765, 2,640,766, 2,640,767, 2,763,536, 2,828,194, 2,940,836, 2,979,387 and 3,023,138. The effectiveness of the baths described in all of these patents is based upon the use of nitric acid as the corrosive medium. I have now discovered that an aqueous mixture of sulfuric acid and hydrogen peroxide can be substituted for the aqueous nitric acid solution in each of the aforementioned patents and that the corrosion inhibitors described in those patents are effective, in combination with an aqueous sulfuric acid-hydrogen peroxide solution, in forming an etching bath capable of controlled etching of the surface of zinc, magnesium, copper, nickel and iron, and alloys based on these metals, for producing photoengraving and printed circuit sheets, and the like. Thus, the novel etching bath of the present invention comprises a mixture of an aqueous solution of sulfuric acid and hydrogen peroxide with an organic corrosion inhibitor.

The sulfuric acid content of the aqueous corrosion medium of the new etching bath is effective within the range of about 4% to about 20% by volume of H_2SO_4. Within this range, the optimum acid concentration varies with the metal to be etched. For example, in etching zinc an acid concentration of about 5 to 7% is particularly satisfactory, and for etching copper an acid concentration of about 8 to 12% is presently preferred. The sulfuric acid need not, of course, be added as 100% acid but can be used in any concentration capable, considering the water content of the added hydrogen peroxide component, of establishing the H_2SO_4 content within the aforementioned prescription.

The hydrogen peroxide content of the aqueous corrosion medium is effective within a range of about 4% to about 15% by volume of H_2O_2. Within this range the optimum concentration varies with the metal being etched and can be readily determined by simple testing. For example, in etching zinc, concentrations of about 5% to about 8% are particularly satisfactory, and a concentration of about 5 to 6% is presently preferred. The hydrogen peroxide is advantageously added in the form of a 50% aqueous solution, but other concentrations of the hydrogen peroxide component can be used provided that they are sufficiently high to permit the formation of an aqueous corrosion medium containing both the sulfuric acid and the hydrogen peroxide within the recited ranges of concentrations.

To the aqueous corrosion medium consisting essentially of the sulfuric acid and hydrogen peroxide solution, there is admixed an organic corrosion inhibitor such as any of those referred to in the aforementioned patents. Thus, the inhibitor can be (a) a saturated aliphatic monobasic or polybasic acid or its metal salt, advantageously limited to those containing 5 to 26 carbon atoms, in which at least one carboxylic group is present, such, for example, as oleic and stearic acids, metal oleates and stearates, etc., (b) an ester of such an aliphatic acid and a polyhydric aliphatic alcohol, (c) an ester of sulfosuccinic acid and an aliphatic alcohol, (d) a petroleum sulfonate such as a petroleum sulfonic acid or a mahogany soap, (e) a water-soluble anionic surface-active agent containing a sulfate radical with at least about 8% sulfation such, for example, as sulfated tall oil, sulfated castor oil, etc., (f) alkylarylsulfonates such as alkylbenzene and alkylnaphthalene sulfonates in which the alkyl group contains 8 to 18 carbon atoms, and (g) halogenated diaryloxide sulfonic acids and their salts, such as those described in United States Patent No. 2,081,876.

The amount of organic corrosion inhibitor useful in practicing the invention generally does not exceed about 1.5% by weight of the aqueous sulfuric acid-hydrogen peroxide solution and at present is used in amounts less than about 1% but not less than about 0.1% by weight of the aqueous corrosion medium. The optimum specific amount of any such organic corrosion inhibitor used in the practice of the invention depends upon the concentration of the sulfuric acid and hydrogen peroxide components of the aqueous corrosion medium, the temperature of this medium used in the etching operation, the composition of the metal being etched, and the design of the vessel and etchant-splashing device used for the etching operation. Moreover, the inhibitor action can be modified by further addition to the etching bath of a water-insoluble organic liquid such as kerosene, gasoline, benzene, coal oil and lubricating oils, in amounts ranging from about 0.1 to about 10% by volume of the aqueous corrosion medium, and the presence of such an organic liquid in the etching bath will also affect the optimum amount of organic corrosion inhibitor.

The etching bath compositions of the present invention are useful in effecting controlled etching of such metals as zinc, copper, magnesium, nickel and iron, as well as alloys based on these metals.

The following example is illustrative of the practice of the invention:

EXAMPLE

A zinc-base alloy of the type used for commercial photoengraving was conventionally exposed and developed by etching in a standard photoengraving etching machine. The aqueous etching bath, having a total volume of 78 liters, was prepared by adding to the water component 6% by volume of C.P. H_2SO_4, 5% by volume of H_2O_2 (added as 10% by volume of a 50% aqueous solution of H_2O_2), 0.27% of sulfonated castor oil (American Cyanamid's AR90), 0.047% of a petroleum sulfonate having a molecular weight range of about 200–600, and 0.013% of commercial grade oleic acid. The plate was etched in this bath in the machine for 20 minutes, follow-

ing which the plate was washed and dried. The etched plate showed controlled etching of the metal with lines and half-tones representative of the image being reproduced.

I claim:

1. A metal controlled-etching bath consisting essentially of an aqueous solution containing by volume about 5 to 7% H_2SO_4 and about 5 to 6% H_2O_2, said solution further containing about 0.1 to 1% by weight of an organic corrosion inhibitor.

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