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PROCESS FOR ETCHING PRINTED CIRCUITS

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U.S. Cl. 252—79.4 6 Claims

The present invention concerns a process for etching the portions of the copper printed circuits which are not protected by printing ink.

In the production of printed circuits, an insulating backing is first provided with a copper coating 35 or 70 μm. thick which is then printed with an etch resistant printing ink on the portions which should be retained as conductor lines after the etching. After the resist has been printed on, the etching is effected by spraying the printed plates with an etching liquid or by dipping such printed plates in an etching bath in order to dissolve the copper which is not protected by the printed resist.

Usual etching liquids are strong mineral acids such as H_2SO_4 and HNO_3, as well as chromic acid, iron chloride or ammonium persulfate solutions. The use of such solutions, however, entail certain disadvantages.

In order to be able to carry out the etching procedure in an acceptable short period, it is necessary to use the mineral acids in high concentration which requires use of corrosion proof apparatus. This is also true of iron chloride and chromic acid. As it mostly is necessary to operate at higher temperature, the resulting vapors are burdensome to the operating personnel. With iron chloride, which is used at a concentration of 42° Bé. insoluble reaction products are formed which settle out as slime like deposits which when sprays are employed can clog the pumps and/or the spray nozzles. As the sediments in addition have an abrasive action on the resist coatings, such baths usually are only utilized to 60% of their theoretical Cu dissolving capacity.

Recovery of copper from the spent etching solutions or their preparing for satisfactory disposal is very costly, especially with iron chloride or chromic acid etching solutions.

While several disadvantages could be avoided by the use of ammonium persulfate, its use still has several drawbacks. As ammonium persulfate only attacks the copper slowly, it is necessary to add activators or the solution is activated with heat. In spite of this the etching periods necessary, even though not very great, are still longer than those required from iron chloride. Ammonium persulfate solutions can only effectively be used in a concentration range of 150 to 250 g./liter of water. Therefore the capacity of such solutions for take up of Cu is correspondingly smaller than when iron chloride solutions are employed. The recovery of copper from the spent ammonium persulfate solutions is somewhat simpler than from spent iron chloride or chromic acid solutions. It, for example, can be effected by cementation with aluminum or by electrolysis, nevertheless the removal of the remaining ammonium ions requires additional measures.

As dilute mineral acids, such as, dilute H_2SO_4 or HNO_3 only attack copper slowly they do not come into consideration for etching printed circuits where complete dissolution in the shortest time possible is required. It is only through addition of an oxidizing agent, such as, H_2O_2 or other peroxygen compounds, such as, persulfates or perborates that dissolution of copper can be accelerated when dilute mineral acids are used. Baths of this type have been suggested in the literature for the surface treatment of metals especially for polishing such surfaces. See "Surface Treatment of Metals with Peroxygen Compounds," Plating 42, 1955, pages 561–66. In such surface treatments metal ions go into solution which decompose the active oxygen catalytically and in a short time reduce the activity of the baths to a considerable degree. This is especially true when higher temperatures of, for example, 40–60° C. are employed. Application of baths of this composition for etching printed circuits therefore appeared completely out of the question, as in such etching process considerably higher copper concentrations must be reckoned with, especially with a view to the proper industrial efficiency of such process. In order to provide for optimum use of the active substance of printed circuit etching baths copper concentrations of 40 to 60 g. Cu/1 are no rarity. An effective protection of H_2O_2 containing baths against the decomposing action of Cu-ions at such concentration was previously unknown. As a result it previously appeared impossible to employ H_2O_2 containing mineral acid baths for etching of printed circuits.

According to the invention it was found that despite these considerations, H_2O_2 activated mineral acid baths could be successfully used for etching printed circuits when certain definite requirements are met. The essence of the process according to the invention resides in the use of aqueous H_2O_2 containing mineral acid solutions which in addition contain urea or functional urea derivatives, as stabilizers, for the etching of printed circuits.

It was furthermore found that if the etching velocity is to be accelerated still further this can effectively be accomplished by the addition of other activators, namely, salts of heavy metals which are more noble than copper, such as, for example, $HgCl_2$. The activating effects of such heavy metal salts are known in connection with etching processes with ammonium persulfate. The etching baths according to the invention, even in the presence of such additional activators, possess sufficient stability for use in the etching process although it was to be expected that an accelerated decomposition of the bath would take place.

The process according to the invention is illustrated by the embodiments thereof given in the following example.

Example

An etching bath of the following composition per liter was employed:

H_2SO_4 conc. (D=1.84)	kg	0.14
H_2O_2 (35% by wt.)	kg	0.15
Urea	kg	0.05
$HgCl_2$ solution (6.8 g. $HgCl_2$/1. corr. to 5 p.p.m. Hg)	ml	1.0

The printed circuits to be etched were dipped into such bath at a temperature of 49° C. The time required for the etching at the beginning was 3′45″. An ammonium persulfate bath of the usual composition of 250 g./l. required an etching time of 6′. By following the progress of the etching velocity with increasing copper content in the etching bath it was found that the H_2O_2 containing baths still give unobjectionable etching in shorter periods of time than with the normal ammonium persulfate containing etching baths as can be seen from the following table:

G. Cu/l.	Etching time in minutes and seconds	
	Bath according to example	Ammonium-persulfate bath
0	3′45″	6′
10	3′15″	6′
20	3′25″	6′40″
30	4′20″	9′25″
40	6′	18′
50	9′	33′

Analogous results were obtained when the urea in the bath composition was replaced by the following urea derivatives in the quantities given:

	Kg.
Semicarbazide (amino urea)	0.065
Biuret	0.090
Barbituric acid (malonyl urea)	0.100
Proponol (dipropyl barbituric acid)	0.150

Also analogous results were obtained when the $HgCl_2$ solution employed in the bath composition was replaced by the following:

1 ml. $AgNO_3$ solution (9.93 g. $AgNO_3$/l.=6.3 p.p.m. Ag.
1 ml. $Rh_2(SO_4)_3$ solution (3.45 g. $Rh_2(SO_4)_3$.12 H_2O/l.=5 p.p.m. Rh.
1 ml. H_2PtCl_6 solution (2.12 g. H_2PtCl_6.6 H_2O/l.=8 p.p.m. Pt.

The aqueous mineral acid solutions by weight expediently contain 1.5%–10%, preferably, 3.5%–7.0% of H_2O_2 (100%), 1%–15% of urea or functional urea derivative, preferably, 3%–7% of urea and 1 p.p.m.–50 p.p.m., preferably, 5 p.p.m.–10 p.p.m. of heavy metal salt activator.

As mineral acids H_3PO_4 and preferably H_2SO_4 are suitable within the process of this invention. Preferably the etching solution should contain 1.54 g. H_2SO_4 per 1 g. of copper. The content of sulfuric acid within the etching solution is between about 0.01 and about 0.7 kg. per liter of the solution, preferably between about 0.1 and about 0.2 kg.

I claim:

1. In a process for etching printed copper circuits, the step of effecting such etching with a mineral acid solution consisting essentially of water, 0.01 to 0.7 kilogram per liter of sulfuric acid or phosphoric acid, 1.5 to 10% H_2O_2 and 1 to 15% of a stabilizer for the H_2O_2 selected from the group consisting of urea, semicarbazide, biuret, barbituric acid and dipropyl barbituric acid.

2. The process of claim **1** in which said mineral acid solution in addition contains 1–50 p.p.m. of another activator in the form of a heavy metal salt the cation of which is more noble than copper.

3. The process of claim **2** in which said aqueous mineral acid is dilute sulfuric acid the concentration of the sulfuric acid in the etching solution being between about 0.01 and 0.7 kg. per liter.

4. The process according to claim **1** wherein the mineral acid solution also contains 1 to 50 p.p.m. of $HgCl_2$ as an activator.

5. The process according to claim **1** wherein the mineral acid is sulfuric acid and the solution also contains 1 to 50 p.p.m. of a heavy metal salt wherein the heavy metal is selected from the group consisting of silver, mercury, rhodium and platinum and the salt is a chloride, nitrate or sulfate.

6. The process of claim **5** in which the concentration of the sulfuric acid in the etching solution is about 0.1 to 0.2 kg. per liter and said heavy metal salt is a mercury salt.

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