

Electrochemical Regeneration of Acid Copper Etchants

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Various types of acid copper etching solutions are used in the manufacture of PW boards: cupric/cuprous chloride, ferric/ferrous chloride, hydrogen peroxide or persulfate salt/sulfuric acid. Their service period is limited due to built-up of copper ions. A removal of excessive copper ions is accomplished by means of cathodic deposition either directly from the etchant (*e.g.* copper-chloride type) or after the transfer of copper ions from the etchant (*e.g.* persulfate or hydrogen-peroxide type) through a membrane. Reoxidation of etching agents (Cu⁺ to Cu²⁺ or Fe²⁺ to Fe³⁺) can be made by anodic treatment of the solution.

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Introduction

Etching of copper is one of important stages in the manufacture of printed wiring boards. Both acid and alkaline etchants are used on industrial scale. Irrespectively of the type of the particular solution etching reaction is the oxidation of copper by some oxidant:

 $Cu + Ox \rightarrow Cu^{2+} + or Cu^{+} + R$

(1).

The oxidant, Ox, is reduced into R. Therefore, any regeneration process should include conversion of R back into Ox, and removal of etched copper as Cu^{2+} or Cu^{+} .

Conversion of R into Ox is always an oxidation reaction, while the removal of etched copper is possible by means of a reduction process, i.e. conversion into copper metal. In many cases the activity of copper etchants is maintained by using an additional oxidizer to convert R into Ox (by atmospheric oxygen or hydrogen peroxide) while an excessive growth of copper content in the etchant is prevented by adding some water, e.g., in the forms of hydrogen peroxide solution or rinse water. In both cases the overall volume of the solution is permanently increasing, and excessive amounts are subjected to utilization.

In all chemical regeneration and utilization processes additional chemicals are consumed and equivalent amounts of waste are formed. Electrochemical regeneration is supposed to be wasteless, consuming only electric energy. Alkaline etchants have been successfully regenerated in industry for already several decades.

Electrochemical regeneration of acid etchants includes few problems to be discussed here in more detail.

Major types of acid etchants and reactions involved

There are four major types of acid copper etchants used in the manufacture of printed wiring boards.

I. cupric/cuprous chloride: $Cu + Cu^{2+} \rightarrow 2Cu^{2+}$	(1)	
II. ferric/ferrous chloride: $Cu + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+}$	(2)	
III. persulfate: $\text{Cu} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Cu}^{2+} + 2\text{SO}_4^{2-}$		(3)
IV. hydrogen peroxide: $Cu + H_2O_2 + 2H^+ \rightarrow Cu^{2+} + 2H_2O$	(4)	

If electric current is passed through a cell containing these etching solutions, following cathodic reactions may occur:

$Cu^{2+} + 2e^{-} \rightarrow Cu$			(5)	
$Cu^+ + e^- \rightarrow Cu$				(6)
$Cu^{2+} + e^- \rightarrow Cu^+$			(7)	
$2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{H}_2$			(8)	
$Fe^{3+} + e^- \rightarrow Fe^{2+}$			(9)	
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$				(10)
$\mathrm{H}_{2}\mathrm{O}_{2} + 2\mathrm{e}^{-} + 2\mathrm{H}^{+} \rightarrow 2\mathrm{H}_{2}\mathrm{O}$			(11)	
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Reactions (5) to (8) may proceed in all types of etchants and (9) to (11) only in solutions containing corresponding compounds.

Among these 7 cathodic reactions only (5) and (6) are desirable. They represent the cathodic part of the whole regeneration process: reaction (5) – for solutions II, III and IV, reaction (6) – for solution I.

Side reactions (7) to (11) not only decrease cathodic current efficiency, but also destroy oxidants in the etching solutions. The fact that cathodic current efficiency for copper metal may be lower than 100% due to side cathodic reactions leads to the following important conclusion: actual number of amperehours necessary for the removal of a certain amount of copper ions from the etching solution will always exceed theoretical value calculated from the Faraday's law.

Anodic reactions

Following anodic reactions may proceed on insoluble anodes in solutions I to IV:

$Cu^+ \rightarrow Cu^{2+} + e^-$	(12)
$\mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+} + \mathrm{e}^{-}$	(13)
$2\mathrm{SO_4}^{2-} \rightarrow \mathrm{S_2O_8}^{2-} + 2\mathrm{e}^{-}$	(14)
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	(15)
$2\mathrm{CI}^{-} \rightarrow \mathrm{CI}_2 + 2\mathrm{e}^{-}$	(16)
$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	(17)

Reactions (12), (13) and (14) represent anodic regeneration of the oxidant in the solutions I, II, and III respectively. Side anodic reactions (15), (16) and (17) lead to losses of anodic amperehours, decreasing anodic current efficiency for the reactions (12) to (14). In addition to that reaction (17) destroys the oxidant and in reaction (16) poisonous chlorine gas is formed. It should be noted that the regeneration of hydrogen peroxide does not happen and the anodic regeneration of persulfate needs much higher concentrations of sulfate ions (strictly speaking HSO_4) in the etching solution than those used in practice. Thus, in solutions III and IV only copper ions can be removed by cathodic deposition of copper and there is no anodic regeneration of the oxidant.

The Use of Ion-selective Membranes

In order to prevent cathodic destruction of the oxidant the etching solutions III and IV should not have direct contact with the cathode. Therefore they are separated from the catholyte by a cationic membrane. Under such conditions the steady-state current efficiency for copper metal is determined by the transport number, t, of copper ions in the cationic membrane: $CE_{Cu} \approx 100t_{Cu^{2+}}$ (18).

Similar situation takes place in the process developed by Finishing Services Ltd (UK) for the regeneration of the solution I. In order to prevent anodic destruction of hydrogen peroxide in the solutions IV and III (where it is formed from persulfate) cationic membrane should separate the anolyte from these etching solutions.

Electrochemical regeneration of solutions I and II is possible in a non-divided cell using very high current densities. Under such conditions an overall cathodic current density, i_{Σ} , is a sum of partial currents for all reactions taking place simultaneously:

Solution I: $i_{(\Sigma)} = i_{(5)} + i_{(6)} + i_{(8)}$

(19)

Solution II:
$$i_{(\Sigma)} = i_{(5)} + i_{(8)} + i_{(9)}$$
 (20).
In both cases current efficiency should be equal to:
 $CE = 100 \frac{i_{(5)}}{i_{E_{1}}}$ (21)

provided there are no losses of copper metal due to dissolution. Fast dissolution happens immediately as soon as cathodic protection created by negative potential is eliminated. There are two causes for this:

(1) Decreasing the current density below limiting values for $(i_{(5)} + i_{(6)})$ or $(i_{(5)} + i_{(9)})$ resulting from the formation of dendritic deposits with much higher true surface area.

(2) Separation of copper dendrites from the cathode surface.

An interesting solution for this problem consisted in the use of a rotating cylinder as the cathode (Fig. 1). Copper sponge formed on the lower part of the cylinder below the level of the solution is continuously removed before it enters the solution again.



Fig. 1. Regeneration cell with rotating cathode cylinder. 1, copper sponge; 2, cathode; 3, anode

However, intensive and unavoidable evolution of chlorine formed at the anode is very important disadvantage of the process. The use of electrolytic cells equipped with one (solutions I and II) or two (solutions III and IV) cationic membranes eliminates the above restrictions concerning the cathode current density.

As has already been mentioned above there are two different types of the catholyte:

(1) an auxiliary solution (hydrochloric acid for solution I and II sulfuric acid for solutions III and IV);

(2) etching solutions I or II.

Thus, for solutions I and II both types of the catholyte are possible and for etchants III and IV only auxiliary solution can be used as the catholyte.

An important advantage of the operation (2) is easy compensation of the effects of ionic transport through the membranes, provided same solution passes first through the cathode compartment and then through the anode compartment (see Fig. 2).



Fig. 2. Circulation of the etchants I or II through the catholyte (1), the analyte (2) and the etching unit (3).

Problem of Chlorine Gas Evolution

An important feature of chloride-based etchants I and II is the discharge of chloride ions at the anode and the evolution of chlorine gas. According to the claims of manufacturers of regeneration cells for solutions I and II it is possible to prevent evolution of chlorine by maintaining anode potential below certain value. Indeed, the discharge of chloride ions starts at much higher potentials than the anodic oxidation of Cu^+ to Cu^{2+} or Fe^{2+} to Fe^{3+} (Fig. 3).



Fig. 3. Anodic polarization curve obtained in the etching solution containing (g/l): HCI 2,55; Cu^{2+} 182,4; Cu^{+} 57,5; CI 238,2. Copper cathode; platinum anode (4 cm²); potentiodynamic operation with potential sweep of 1 mV/s.

Therefore, potentiostatic control of the anode reaction actually allows to avoid the evolution of chlorine gas. Anodic current under such conditions will always be somewhat lower than the diffusion current for the oxidation of Cu^+ to Cu^{2+} (a horizontal part of the polarization curve in Fig. 3). As the diffusion current is proportional to the concentration of Cu^+ (or Fe²⁺), it will approach zero when nearly all Cu^+ (or Fe^{2+}) ions will be converted to Cu^{2+} (or Fe^{3+}). Since the number of amperehours passed through the cathode and the anode is the same, the amount of copper metal deposited at the cathode will be equivalent to the amount of Cu⁺ oxidized at the anode to Cu^{2+} (or Fe²⁺ to Fe³⁺). However considerable part of Cu^{+} (or Fe²⁺) is already oxidized by atmospheric oxygen in the course of etching. So, there is a considerable disbalance between the number of amperehours necessary for the electrodeposition of copper metal and for the anodic oxidation of Cu^+ or Fe^{2+} . Cathodic reduction of Cu^{2+} to Cu^+ or Fe^{3+} to Fe^{2+} should not be taken into account in these calculations, since the equivalent amount of amperehours will be spent for the reversed process at the anode. An additional consumption of cathodic amperehours for possible evolution of hydrogen at the cathode by reaction (8) should be added to this disbalance. Thus, the theoretical number of moles of chlorine gas, n_{CL} , formed at the anode per one mole of copper metal deposited at the cathode is equal to the sum:

$$n_{Cl} = 2n_{OX,Ab} + n_H - 2n_{OX,Ev}$$
(22)

where $n_{OX,Ab}$ is the number of moles of atmospheric oxygen absorbed by the etchant, n_H is the number of moles of hydrogen formed at the cathode and $2n_{OX,Ev}$ is the number of moles of oxygen evolved at the anode simultaneously with chlorine.

Minimization of chlorine amounts at a given value of $n_{OX,Ab}$ is achieved by preventing the evolution of hydrogen by maintaining an appropriate value of the cathode potential (Fig. 4) and by decreasing the fraction of chlorine, f, in the chlorine +oxygen mixture:

$$f = \frac{n_{Cl}}{n_{Cl} + 2n_{OX}}$$

(23).



Fig. 4. Cathodic polarization curve obtained in the etching solution I diluted by 70 times with 1 N HCl. Copper anode, copper cathode 4 cm²; potentiodynamic operation at potential sweep of 1 mV/s.

A radical way for a considerable f decreasing is the use of an auxiliary analyte - e.g. a solution of sulfuric acid, so the f value will be equal in this case to the transport number of chloride ions in the cationic membrane, which does not exceed usually 0.01.

Energy consumption and cost of the process

Catodic current efficiency for copper metal may change from 10-20% to 80-95% and cell voltage from 2.5-3.0 to 15-20 volts. This means that specific energy consumption may vary over very wide range: from 2.5 up to 20 amperehours per one gram of copper. Most easy and inexpensive equipment is required for the removal of copper ions from solutions III and IV. For solutions I and II chlorine problem creates additional costs. Among these two etchant solution I is preferable due to lower cell voltage, since in the presence of ferric ions cell voltage may rise considerably due to the formation of iron oxides on the cathodic side of the membrane.

Utilization of spent etchants by electrochemical and chemical methods

Utilization of solutions III and IV by electrolysis in a nondivided cell allows to recover practically 100% of etched copper, and to produce waste solution containing only relatively harmless components: ammonium sulfate and diluted sulfuric acid. Non-electrochemical utilization processes seem preferable for spent etchants I and II because of chlorine problem. There are two major versions of such processes: conversion of cupric chloride into copper-based fungicides such as cupric oxichloride and recovery of copper metal by cementation with iron.

Summary

Both environmental and economic factors should be taken into account in the selection of preferable process for the regeneration or utilization of a particular acid copper etchant. Because of low energy consumption and cheep materials used in nonelectrochemical process the advantages of electrochemical method are not so obvious as is the case of chromate-based solutions used in plating industry.