

## Etching Techniques

Etching is one of the major steps in the chemical processing of the subtractive PCB process. By this process, the final copper pattern is achieved by selective removal of all the unwanted copper to retain the desired circuit patterns. The copper which is not protected by an etch resist is removed by the etching process. The following are the commonly used etching methods:

- Chemical etching or chemical machining;
- Electrochemical etching or chemical milling; and
- Mechanical etching (by milling).



### 9.1 Etching Solutions and Chemistry

Several chemicals are used for etching. The most common etchants are:

- Ferric chloride;
- Ammonium persulphate;
- Chromic acid;
- Cupric chloride; and
- Alkaline ammonia)

The following sections give characteristics, chemistry and process details of these etching methods.



### 9.1.1 Ferric Chloride

(Ferric chloride etching solutions are widely used in the 'print' and 'etch' process) in the PCB industry. Ferric chloride has a high etch rate and high copper dissolving capacity. It is used with screen inks, photo-resist (wet film and dry film) and gold plated boards. As the ferric chloride etchant attacks tin, this is not suitable for tin or tin-lead plated boards.

This etchant is an aqueous solution of 28 to 42 per cent by weight of ferric chloride. The solution has a specific gravity of 1.353 to 1.402. It operates over a wide range of concentration, but is most widely used at about 35 per cent. The ferric chloride solution has free acid due to the following hydrolysis reaction:



In order to prevent the formation of insoluble ferric hydroxide, an excess of hydrochloric acid, upto 5 per cent by weight is usually added, which prevents the spontaneous hydrolysis of  $\text{FeCl}_3$  as per the above equation. Commercial formulations also contain wetting and anti-foam agents.

At the initial stage of the etching process, the concentration of copper dissolved is high due to the high concentration of ferric chloride. As the ferric chloride in the solution gradually gets depleted, the etching time correspondingly increases to the extent that after some time, the solution has to be discarded and replaced by a fresh solution. Better dissolution of copper occurs when the etchant is sprayed perpendicular to the copper surface and the board is moved. The rate of dissolution of copper depends upon the ferric chloride concentration, temperature and agitation rate.

(Ferric chloride is the oldest and perhaps the most common etchant.) It normally comes in crystal form. The crystals are dissolved in de-ionized water to achieve its desired concentration in the solution. This is typically 500 gm of ferric chloride in one litre of water.

#### Chemistry

The ferric ion  $\text{Fe}^{3+}$  oxidizes copper to cuprous chloride ( $\text{CuCl}$ ) as per equation (1). Cuprous chloride is further oxidized to cupric chloride as ( $\text{CuCl}_2$ ) as per equation (2)



In practice, when a solution contains 8 oz./gal (60 g/l) or more of dissolved copper, the etch time becomes longer than desired. However, the ferric chloride can dissolve copper even upto 120 g/l if the prolonged etching time can be tolerated. In order to increase the copper dissolving capacity and to bring down the etching time slightly, hydrochloric acid (upto 10 per cent of the etchant volume) is added after the copper content has reached 80 g/l. The acid also helps to control excessive sludge formation. Figure 9.1 shows the dependence of etching time versus copper content in the etchant.



For monitoring purposes and to know the exact copper concentration in the etchant, a chemical analysis has to be done. A less accurate but practical solution is to use the colorimetric method of colour comparison with standard solutions of known copper content. On an average, to etch 1 kg of copper, 5.1 kg of ferric chloride will be consumed, with etching temperature in the range of 20-45 °C.

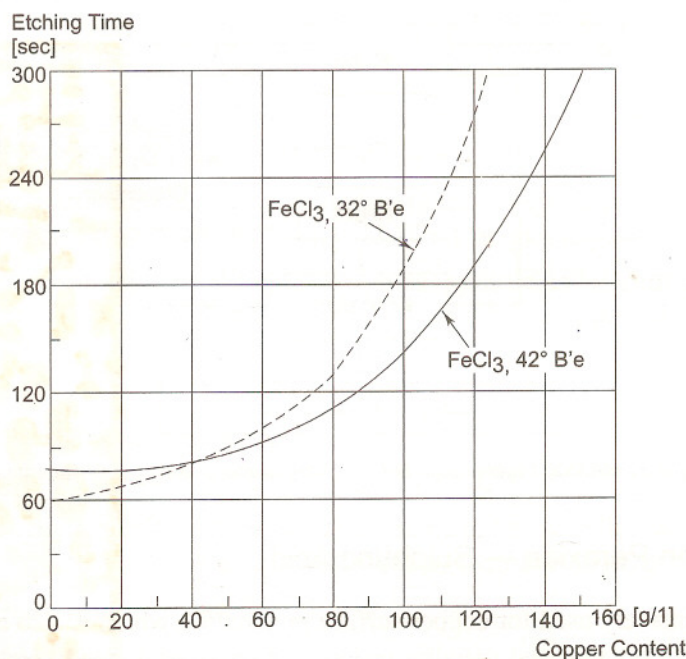


Fig. 9.1 Dependence of etching time with ferric chloride at 43 °C, spray etching, 35 µm Cu (after Bosshart, 1983)

Unfortunately, ferric chloride is corrosive in nature and leaves dark stains. Further, it is normally difficult to regenerate for re-use. If solder or tin is used as a mask, it will attack it.

#### Composition of Ferric Chloride Etchant

- FeCl<sub>3</sub> [ferric chloride] → 450 — 500 g/l
- Specific gravity → 1.35 to 1.4
- Copper dissolving capacity → 120 g/l
- HCl (hydrochloric acid) → 10 ml/lit.
- Temperature → 20-45 °C
- Anti-foaming agent → 3 ml/l

**Process Control and Regeneration:** Regeneration of the solution is almost impossible and its disposal is expensive. Regeneration is carried out only due to the need to separate copper chloride from ferric chloride.



Ferric chloride etchant can be regenerated (Figure 9.2) by passing chlorine gas and to recover copper from the ferric etchant by crystallization. The addition of ammonium chloride and cooling to ambient temperature permit crystallization of a chloride double salt ( $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$ ) and cupra-ammonium chloride complex precipitate.

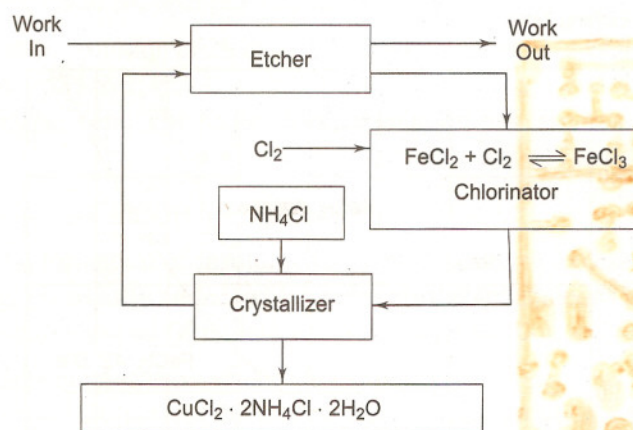


Fig. 9.2 Ferric chloride closed loop regeneration and recovery process using re-crystallization (after Coombs, 1988)

### 9.1.2 Hydrogen Peroxide — Sulphuric Acid

This system is extensively used for copper surface preparation which is also called micro-etching. It is compatible with organic and metallic resists and provides a steady etch rate with optimum undercut. It is a widely accepted system due to its ease of replenishment, closed loop copper recovery and need for simple waste treatment method.

#### Chemistry

Hydrogen peroxide is a strong oxidizing agent. It oxidizes and dissolves the metallic copper. The sulphuric acid makes copper soluble and keep the dissolved copper as copper sulphate in the solution, while copper sulphate helps to stabilize etch and recovery rates. The etching reaction is:



#### Etchant Composition and Process Conditions

• $\text{H}_2\text{SO}_4$ (96 %)	Sulphuric acid	100 ml/lit
• $\text{H}_2\text{O}_2$	Hydrogen peroxide	70 ml/lit
• $\text{CuSO}_4$	Copper Sulphate	60 g/lit
• Temperature		30 to 40 °C



### Process Control and Regeneration

Hydrogen peroxide/sulphuric acid etchant is used in immersion as well as spray etching operations. The process is controlled by composition balance by recovery of copper sulphate as the by-product in closed loop systems. Such systems require continuous re-circulation of the etchant in the etching tank, whereby the etchant replacement is controlled by chemical analysis. The problems commonly encountered include process over-heating, etchant composition balance, etchant contamination and the dangers in handling concentrated peroxide solutions.

#### 9.1.3 Chromic-Sulphuric Acid

Chromic acid mixed with sulphuric acid is used because of its strong oxidizing power and suitability for all kinds of metal resists such as tin, tin-lead, gold, vinyl lacquer and dry or liquid photo-resist.

The etching rate is inconsistent, but it has the advantage of little under-cutting. However, its use is now limited since it is difficult to regenerate and it is highly toxic, polluting and hazardous to health. It is generally not recommended for use.

#### Chemistry

The reaction between chromic acid and copper is



In this system, the etching rate for copper is not very high, but it can be increased with an additive like sodium sulphate. The etch rate can also be increased by increases in temperature and agitation.

#### Composition of Etchant and Process Conditions

- |                   |                         |
|-------------------|-------------------------|
| • Chromic acid    | 200 to 240 g/l          |
| • Sulphuric acid  | 60 to 65 ml/l           |
| • Sodium sulphate | 40 to 45 g/l (additive) |
| • Temperature     | 20 to 30 °C             |

### Process Control and Regeneration

This etchant is used in immersion etching and not in spray etching. The etch rate is controlled by the colorimetric standard method, while the density is measured by a hydrometer. Regeneration is not in common use because of the corrosive nature of the products and handling hazards. For example, chromic acid is an extremely strong oxidizing agent and attacks clothing, plastics and many metals if safety measures are not adopted to keep fumes out of the air through adequate ventilation. Similarly, spent chromic acid also presents a serious disposal problem, which needs to be handled in such a way that it complies with the state pollution control standards.

#### 9.1.4 Cupric Chloride

Cupric chloride offers an economical solution in the etching of print-and-etch type of PCBs on a larger scale. From the pollution point of view, it offers the advantage of easy regeneratability with



the possibility of a relatively easy disposal, high throughput and better material recovery. The dissolved copper capacity, which is upto 150 g/l, is high.

In performance, cupric chloride compares well with ferric chloride, with the advantage that it does not have sludge as ferric chloride does. Basically, it is an aqueous solution having 150-400 grams of cupric chloride. It usually has some hydrochloric acid (HCl) added to it with a large quantity (upto saturation level) of sodium chloride (NaCl) or ammonium chloride ( $\text{NH}_4\text{Cl}$ ).

The cupric chloride etching system is used in the production of fine line multi-layer (inner layers) and print-and-etch boards. It is compatible with resists like screen inks, dry film, liquid film, photo-resist and gold plating, except tin or tin-lead plated resists.

#### Chemistry

The overall etching reaction wherein the cupric chloride ( $\text{CuCl}_2$ ) dissolves copper (Cu) is as follows:



The cuprous chloride is then re-oxidized to regenerate etch-active cupric chloride by the oxygen present in the atmosphere.



In the process, a small amount of solution is continuously drained off to keep the concentration of copper constant. The level is maintained by the addition of a solution of hydrochloric acid, sodium or ammonium chloride and ammonium hydroxide.

#### Etchant Composition

• Cupric chloride	200 g/l
• Hydrochloric acid	200 ml/l
• Water	770 m/l
• Initial copper concentration	40 g/l
• Hydrogen peroxide	30 ml/l (optional)
• Temperature	30° to 40 °C

#### Process Control and Regeneration

The method given in equation (ii) is generally not used for regeneration because the oxygen reaction rate in acids is slow and the solubility of oxygen in hot solution is limited to 4 to 8 ppm. On the other hand, direct chlorination is a preferred technique for the regeneration of cupric etchant because of its low cost, high rate and efficiency in recovery of copper. The chemical reaction of the regeneration process is:





The chlorination process results in:



The process sequence is shown in Figure 9.3. Chlorine, hydrochloric acid and sodium chloride solutions are automatically fed into the system as required. Various process monitoring equipments such as colorimeter, level sensors, and temperature monitoring and control arrangement, etch rate meter, etc, help to achieve optimum results.

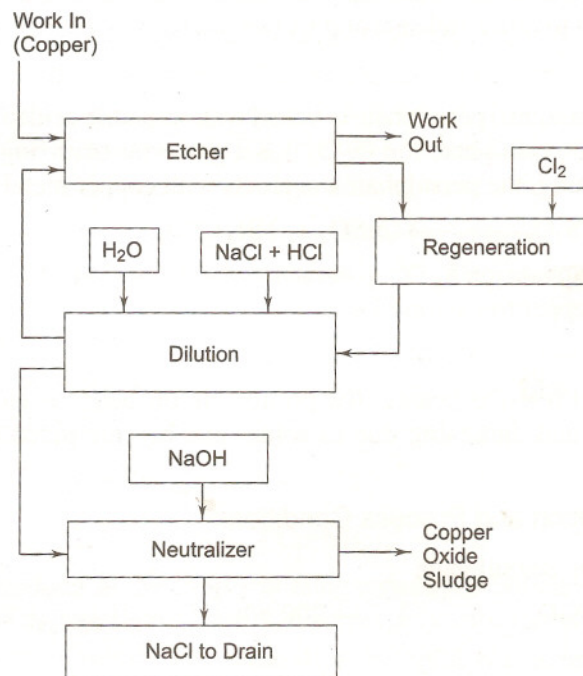


Fig. 9.3 Cupric chloride chlorination regeneration system (after Coombs, 1988)

The above regeneration process is less expensive and has a high rate of copper recovery. Spent etchant can be easily sold for its copper content. There are likely to be several problems with the cupric chloride system if process parameters are not properly controlled. The most significant is the low etch rate which is frequently due to low temperatures, insufficient agitation or lack of solution control. Sludging formation can also take place if the acid concentration is low. Elevated temperatures and the presence of excess acid may lead to the breakdown of photo-resists.

### 9.1.5 Ammonium Persulphate

Ammonium persulphate (APS) is frequently used as an etchant because it does not have most of the disadvantages of ferric chloride. It is also used in the surface preparation for electroless plating, and electroplating prior to oxide coating in multi-layer PCBs. Unfortunately, while ammonium persulphate



is a strong oxidizing agent, it is unstable in solution and decomposes to form hydrogen peroxide, oxygen and peroxydisulphuric acid. The latter is a slow oxidizer at room temperature resulting in a low etch rate, which can however, be accelerated by the addition of a mercuric chloride catalyst when it becomes comparable with chloride etchants. It is compatible to all resists on boards including solder, tin, tin-lead, screen and photo-resist, except gold plated resists.

The formulations of ammonium persulphate containing sulphuric acid and catalysed with mercuric chloride give a good etch factor and easy regeneration in the closed loop system. But this system is costly as compared to other etchants and its use has declined for all practical purposes.

### Chemistry

Ammonium (or potassium) persulphate is mixed with sulphuric acid to get a stable salt of persulphuric acid ( $\text{H}_2\text{S}_2\text{O}_8$ ). The persulphate ion ( $\text{S}_2\text{O}_8^{2-}$ ) is a powerful oxidizing agent and dissolves in water. During copper etching, the persulphate ion reacts with copper metal and the primary reaction is:



In which a persulphate ion  $\text{S}_2\text{O}_8^{2-}$  generates two sulphate ions,  $\text{SO}_4^{2-}$  at the same time oxidizing an atom of metallic copper to a cupric ion:



If tin or tin-lead resist is coated, the printed circuit board is etched in APS. The incomplete etching of copper and darkening due to solder can be eliminated by the addition of 1 per cent phosphoric acid.

### Etchant Composition and Process Conditions

- Ammonium per sulphate
  - $(\text{NH}_4)_2 \text{S}_2\text{O}_8$   $\rightarrow$  200 g/lit
  - Sulphuric acid  $\text{H}_2\text{SO}_4$   $\rightarrow$  10 ml/lit
  - Mercuric chloride  $\text{HgCl}_2$   $\rightarrow$  0.5 ml/lit or 5 ppm
  - Temperature  $\rightarrow$  30° to 40 °C

### Process Control and Regeneration

Ammonium persulphate systems are used in both spray etching and immersion etching operations. The system is controlled by colorimetric measurement. Cooling coils are used to maintain the etchant temperature constant and prevent runaway. The preferred temperature is 45 °C.

The useful capacity of the etchant is about 7 oz./gal copper at 38 to 55 °C. Above 5 oz./gal copper, the temperature of the solution should be maintained at 55 °C to prevent salt crystallization. The etch rate of a solution containing 7 oz./gal of dissolved copper is 0.00027 in./min at 48 °C.

The exhausted etchant consists mainly of ammonium or sodium and copper sulphate with a pH of about 2. Direct discharge of this solution to the sewer is not allowed. Therefore, the dissolved copper must be removed, and subsequently the remaining solution must be diluted, neutralized and discarded.



In general, ammonium, sodium and potassium persulphates, with the addition of certain catalysts, can be used for the etching of copper in PCB manufacturing. However, continuous regenerative systems based on ammonium persulphate have become more common. Persulphate is preferred because it has minimal disposal problems and somewhat higher copper capacity and etch rates.

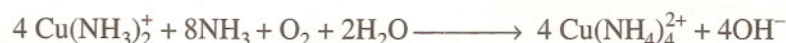
### 9.1.6 Alkaline Ammoniacal/Ammonium Chloride

Alkaline ammoniacal etching system is used in both the batch and conveyor spray etching systems and is compatible with metallic and organic resists. The advantages of this etchant are its minimum undercut, high copper dissolving capacity and fast etch rates. Alkaline etchants provide continuous etching rates of 30-60  $\mu\text{m}$  cu/min at a dissolved copper content of 150 g/l in the etchant.

#### Chemistry

Alkaline etching solutions dissolve exposed copper on PCBs by a chemical process involving oxidation, solubilizing and complexing. Ammonium hydroxide and ammonium salts combine with copper ions to form cupric ammonium complex ions  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , which hold the etched and dissolved copper in solution at 18 to 30 oz./gal.

The oxidation reactions for closed loop systems showing the reaction of cupric ion on copper and air ( $\text{O}_2$ ) oxidation of the cuprous complex ion are:



This process can continue as long as the copper-holding capacity is not exceeded. Due to high copper dissolving capacity, the system (closed loop) is increasingly used in the PCB industry. The functions of different ingredients of this etchant are detailed below.

- $\text{Cu}^{2+}$  (copper ions): act as oxidizing agents and dissolve metallic copper;
- $\text{NH}_4\text{OH}$  (ammonium hydroxide): complexing agent and also holds copper in solution;
- $\text{NH}_4\text{Cl}$  (ammonium chloride): improves the etch rate and copper holding capacity and solution stability;
- $\text{NH}_4\text{HCO}_3$  (ammonium bicarbonate): acts as a buffer to preserve the solder metal surface;
- $\text{NH}_4\text{NO}_3$  (ammonium nitrate): increases the etching speed and preserves the solder metal surface;
- $(\text{NH}_4)_3\text{PO}_4$  (ammonium phosphate): retains clean solder and plated through holes;
- $\text{NaClO}_2$  (sodium chlorite): also an oxidizing agent that reacts and dissolves metallic copper.

#### Composition and Operating Conditions:

- |                        |         |
|------------------------|---------|
| • Ammonium bicarbonate | 75 g/l  |
| • Ammonium nitrate     | 80 g/l  |
| • Cupric chloride      | 200 g/l |



• Ammonium chloride	100 to 110 g/l
• pH	7.8 to 8.2
• Temperature	45 to 55 °C
• Specific gravity	1.2 at 20 °C
• Copper content	150 to 160 g/l

### Process Control and Regeneration

Etching solutions are operated between 50-55 °C and are well suited to spray etching. It is necessary to have an efficient exhaust system to drive away ammonia fumes which are released during operation.

A constant etch rate can be maintained by using automatic feeding controlled by specific gravity or density. In this method, as the printed boards are etched, copper is dissolved in the solution, resulting in increased density of the etching solution. When the quantity of copper in the solution reaches its upper limit, a pump is activated to replenish the etching solution and to simultaneously remove the etchant until the desired density is achieved.

The system is regenerated by removal of the spent etching solution or by chemical restoration of the spent etchant. This process involves mixing spent etchant with hydroxyl oximes (organic solvent), which is capable of extracting copper. This mixture containing copper is mixed with sulphuric acid to get copper sulphate and the copper-free etchant is reprocessed. Alternately, the processed etchant is cooled (chilled) and the precipitate salt is filtered which is followed by re-processing of the solution by adjustment of operating conditions. Regeneration by these methods is, however expensive and is viable only for large printed circuit facilities.



## 9.2 Etching Arrangements

### 9.2.1 Simple Batch Production Etching

Batch etching is applied in laboratories and small industries wherein small series of PCBs have to be etched occasionally. This simple arrangement for etching of PCBs involves the use of the etchant until saturation or until the etching speed becomes too slow. The etchant is then disposed and fresh solution is filled into the etching machine.

When the etching of a new batch of PCBs is started, the optimum etching time must be initially determined. The typical etchant used in this method is ferric chloride.

### 9.2.2 Continuous Feed Etching

In this method, a small steady stream of fresh etchant either continuously or periodically flows into the etchant sump while an equal quantity of partially saturated etchant is simultaneously removed.



Below is given a table showing electrolytes, anodes, metals or articles to be plated and names of plating metals etc.

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Tuesday

Names	Articles or to be plated	Electrolytes	Anode	Some observation	
1. Zinc plating	Strong & heat or wires	Zinc sulphate solution	Zinc	This is galvanised by electro decomposition.	9.00
2. Copper	Plates cast of statues graphite powder.	Copper sulphate solution a little sulphuric acid	Copper plate	A wax impression can also be used.	10.00
					Noon
Nickel	iron or steel	Nickel ammonium sulphate	Nickel block	Acids, even acetic acid dissolves nickel easily.	1.00
					2.00
Chromium	iron or steel	Chromium compound eg (oxides & sulphate) in $H_2SO_4$	Lead anode	A thin layer of copper or nickel is to be deposited first as chromium does not stick well on steel & iron.	3.00
					4.00
Silver plating	knives	solution of potassium argentocyanide sodium compound may also be used.	plate of silver	with silver nitrate solution as electro a coarse and spongy deposit of silver occurs.	5.00
					6.00
					7.00
Gold plating.	Articles expensive metals	Solution of potassium auricyanide	Gold	A very thin layer of gold spreads over the surface making the article highly attractive.	Evening
					appointments