

Chapter 13

Electroless Copper

In Printed Wiring Board Fabrication

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Electroless copper is employed in the manufacture of printed circuit boards that will ultimately have plated-through holes. Its purpose is to make this hole path conductive enough to permit further build-up of this path with copper metal deposited electrolytically to the thickness specified by the board designer, usually 1 mil (0.001 in.) or slightly more, or to build the entire circuitry on its own. The electroless copper process is a series of steps required to accomplish electroless copper deposition. Each step is critical to the overall process.

The purpose of this chapter is not to detail the fabrication of printed wiring boards, but rather to detail the important aspects of electroless copper deposition as they relate to PWB fabrication. Those readers who want to know how to make a PWB are advised to consult other texts, some of which are listed in the bibliography section of this chapter.

The concept of "plated-through-hole" centers around one or both of the following purposes:

- To hold a component lead wire.
- To interconnect circuitry or "printed wires".

A printed circuit board is simply a non-conductive composite substrate material (epoxy-glass, phenolic-paper, polyester-glass, etc.) upon which circuitry is either etched (if the composite was copper-clad to begin with) or plated (if the composite was not copper-clad).

Some typical composites used in circuitry manufacturing are:

Polyimides—For flexible circuitry or for high-temperature applications.

Paper/phenolic—Can be punched; NEMA grades FR-2, XXX-PC.

Paper/epoxy—Better mechanical properties than paper/phenolic; NEMA grades CEM-1, FR-3.

Glass/epoxy—Woven glass fabric—good mechanical properties; NEMA grades FR-4, FR-5, G-10, G-11.

Random glass/polyester—Suitable for some applications; NEMA grade FR-6.

Table 13.1
Electroless Copper
Foil Thicknesses

Oz/ft ²	Foil thickness
0.5	0.7 mils (17.5 μm)
0.25	0.35 mils (8.75 μm)
1	1.4 mils (35 μm)
2	2.8 mils (70 μm)

Holes through the nonconductive substrate (dielectric) are made conductive to either interconnect both sides, better solder in the joining operation, or for *both* reasons. Internal to the dielectric there may exist internal layers of circuitry—etched circuits that were prepared prior to the lamination of the dielectric composite. In this case, the result is what is termed a “multilayer” board. In the case of a multilayer composite, the plated-through hole serves not only to connect the two external sides, but also to interconnect with the internal layer(s) if this is desirable in a particular hole through the dielectric.

Most printed circuit boards presently produced are *subtractive* in process characteristic. That is, the external layers of the dielectric material are supplied clad with a certain thickness of electrolytically produced copper foil. The foil thickness is designated by ounces of copper metal per square foot or fractions or multiples thereof. These designations translate into actual foil thickness as shown in Table 13.1.

The dielectric thickness may also vary, so that we may have a very rigid substrate or even one that is so thin that it is flexible.

If the substrate is non-copper clad to begin with, as for *additive* processing, then the function of the electroless copper is not only to make the holes conductive, but to make the surface conductive as well, for either further electroplating or for full electroless deposition to the full thickness desired, and to the full surface circuit pattern desired.

Since most boards presently produced are of the subtractive processing variety, whether double-sided or multilayer, the discussion will begin with attention to subtractive-type processing; most of the principles involved in pretreatment for electroless deposition as well as some of the principles discussed relative to the electroless copper bath itself, will pertain, whether subtractive processing or additive processing is being considered.

SUBSTRUCTIVE PROCESSING

Since the through-hole processing of multilayer boards with electroless copper brings some extra factors into consideration, a sketch of multilayer processing

Drilling or Punching

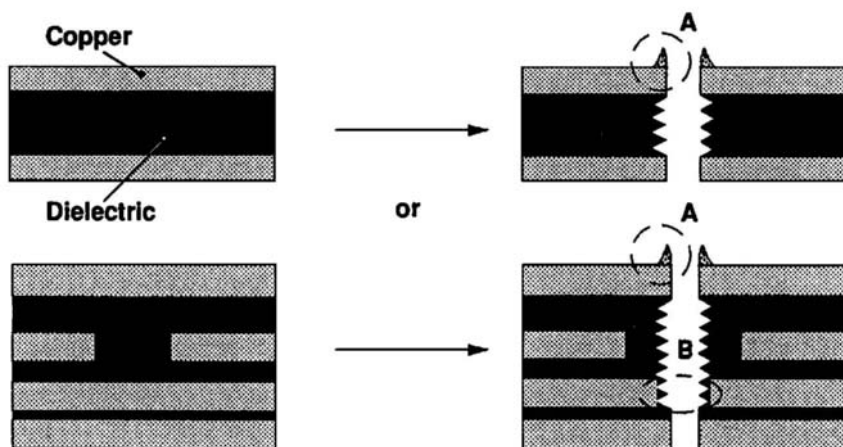


Fig. 13.1—Burr and smear.

will be carried through this presentation where pertinent. The complete, complex aspects of multilayer board production will not be covered in this chapter.

So, the process then starts with a sheet of laminate, copper-clad both sides, which may or may not contain an internal layer or layers of circuitry (previously prepared).

The first step is to produce the holes, in designated positions, by either drilling or punching through the copper cladding and through the dielectric material. Whether to drill or to punch is determined by the thickness of the sandwich, the ease of punching or drilling the particular dielectric material, the quality obtained by either choice, and in some cases, the quantities of material to be perforated (amortization of die costs, etc.).

Once the holes have been produced, a few things should be taken care of before proceeding to the wet processing involved in plated-through-hole electroless copper deposition (see Fig. 13.1).

First of all, after drilling or punching, burrs of copper (A) will exist on the copper on the external copper layers of the sandwich. These should be removed prior to further processing to avoid plating nodulation at the burr site, tearing problems in dry-film lamination, or screen damaging if screen pattern generation is used. The burrs are indicated by Area A in Fig. 13.1. The burrs are generally removed by wet sanding using a polymeric brush with abrasive tips. Area B will be referred to later.

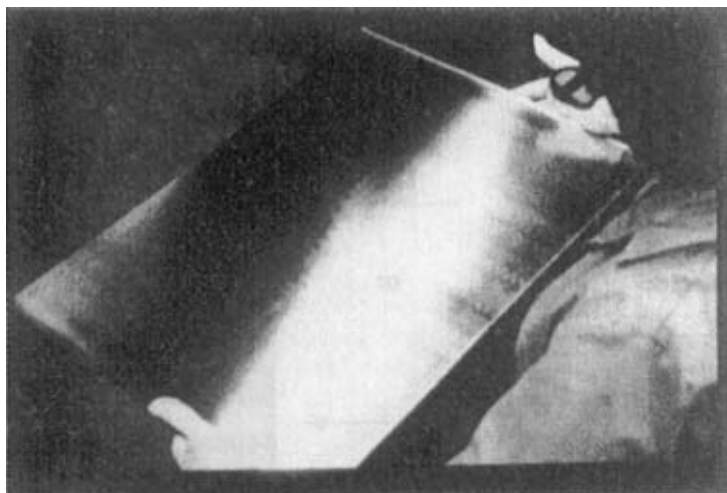


Fig. 13.2—Wet sanding.

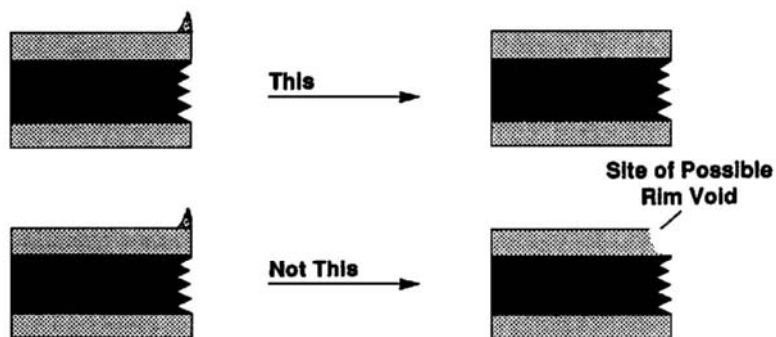


Fig. 13.3—Rim voids.

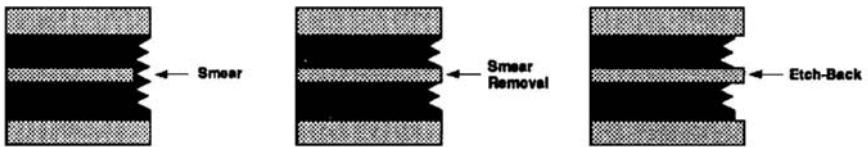


Fig. 13.4—Smear removal.

In wet sanding (Fig. 13.2), care must be taken not to apply too much pressure at this step, to avoid rounding the corner of the hole and exposing bare dielectric material, since the adhesion of the electroless copper subsequently deposited will not be very good to bare surface dielectric substrate and later rim-voids may be apparent (see Fig. 13.3).

Secondly, the purpose in plating through the hole produced is to make this path conductive to the external copper layers, and, in the case of multilayers, to those internal layers of copper that abut the pierced hole. When drilling or punching through any copper-polymer-copper sandwich, particularly in the case of multilayer boards where there are copper layers internal to the sandwich, there is a high degree of probability that polymer will be smeared over the copper edges internal to the hole (Fig. 13.1, Area B). The "smear" must be removed, particularly from the internal copper abutting the hole, to insure electrical continuity between the laminated internal layers and the copper that will ultimately be plated through the hole.

Sometimes it is desirable to "etch-back" a small amount of resin also, to produce a tiny protrusion of the inner-layer copper *into* the hole, thereby creating a better bond of plated-through copper to the inner layer copper.

Smear removal (Fig. 13.4) may be accomplished by the same techniques as used for etch-back. Smear removal alone may be accomplished mechanically by "wet-blasting" or vapor-honing; these techniques employ fine abrasives, such as glass beads or alumina, in a wet slurry that is nozzle-blasted through the holes. The chemical materials employed for both etch-back and/or smear removal

dissolve polymer resin. Commonly (for epoxy resin systems) either concentrated sulfuric acid or concentrated water solutions of chromic acid are used. Both chemical methods require post-attention so that problems with through-hole electroless deposition are not *created* by wet processing for smear removal.

Sulfuric Acid

It is important to follow this solution with a very good water rinse, preferably using warm water, and to avoid, if possible, rinsing in any *strongly* alkaline solution. The formation of sodium salt of any residual sulfonated epoxy resin in the hole is undesirable, since this compound is very hard to remove by rinsing, once formed. Its presence in the hole as a residual will cause plating difficulties.

Chromic Acid

The presence of residual Cr^{+6} in the pierced hole will cause coverage problems, since it will tend to destroy the tin-palladium activation by an oxidation mechanism, and interfere with electroless copper reduction. Voids are a typical result of this interference. A second pass through the activation step will usually correct this problem, but second passing is cumbersome, particularly in automatic processing, and at best—expensive.

It is typical to follow chromic acid with a neutralization step, typically using NaHSO_3 (sodium bisulfite) to reduce any Cr^{+6} to Cr^{+3} . This is best accomplished by using warm water (100° F) solutions of sodium bisulfite, and following the neutralization with a hot water rinse (120 to 150° F) to prevent interference with activation later on by any *bisulfite* that may otherwise tend to be dragged into other process solutions.

Other Systems

Several other chemical methods are in common usage for etch-back/desmar. Among these are systems that employ a combination of organic solvents (to swell the polymer) and permanganate, used either after treatment with concentrated sulfuric acid, or even instead of either sulfuric acid or chromic acid.

THE ELECTROLESS COPPER PROCESS

Prior to the actual *plating* of electroless copper, some pretreatment of the parts to be plated is necessary to insure:

- Adhesion of electroless copper (in holes) to the dielectric material.
- Continuity of the electroless copper deposit.
- Adhesion of electroless copper to the copper cladding external to the laminate sandwich.
- Adhesion of electroless copper to any internal layers of copper.

The classical steps of pretreatment will now be taken in sequence.

Cleaning

The first step in any pretreatment line is to clean the entire composite—the laminated copper and the pierced dielectric material. The cleaner is typically alkaline in nature, although neutral or acidic materials may also suffice if not much classical “cleaning” is required. The purpose of the cleaning step or steps are:

- Remove soil from the copper foil and the holes (the dielectric).
- Remove light oils from the copper foil and the holes.
- Help remove stains and heat-treatment oxides from the copper foil.
- Roughen slight smear from drilling (existent on the polymer resin).
- Remove impacted drilling debris from the holes.

The cleaning solution is one of the key solutions in the pretreatment line. Inadequate cleaning can give rise to a number of problems, as illustrated in Fig. 13.5 and the following two figures.

The contaminated area will not adequately hold the needed activator to allow coverage with electroless copper—and a “void” or non-plated area will result. Tiny voids after electroless copper may bridge-over with electroplate, but in that case there is no adhesion of the electroplate to anything underneath it. In this case, a pull-away or blow-holing may be the ultimate result.



Fig. 13.5—Inadequate cleaning—voids.

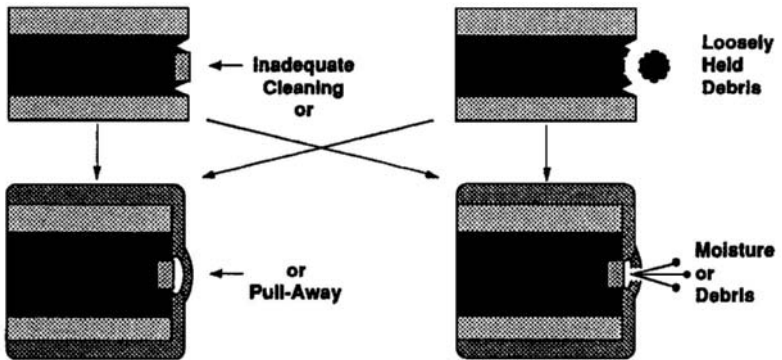
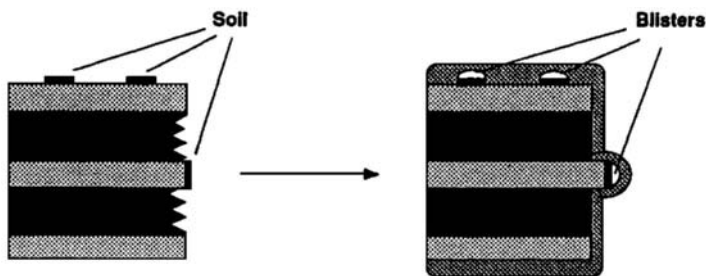


Fig. 13.6—Inadequate cleaning—pull-away or voiding.



poor adhesion due to residual soil or lack of proper etch due to residual soil not removed until partway through etching

Fig. 13.7—Inadequate cleaning of copper.

The mechanical stresses within the electroplated deposit put on after electroless copper or the force of any moisture entrapped in the laminate as a result of plating that will tend to stress the plated deposit from behind during any operation involving *heat* (baking of resists, solder fusion, etc.) tend to pull the plating away from the dielectric, resulting in what would be termed "hole-wall pull-away". By the same measure, loosely-held debris that is not removed in the cleaning step will be plated over, meaning that the plate has adhered to a structure that itself is not adhering too well to the side of the hole. Pull-away may again be the ultimate result in this case. For both cases in Fig. 13.6, whether pull-away is evident or not, the adhesion may be so poor and the stresses on this area so great during any thermal shock, that the plating continuity may be destroyed, particularly in a solder fusing or wave-solder operation, and the result will be what is called a blow-hole, due to out-gassing from the dielectric behind this weakened area.

If the electroless copper is deposited over soil existent on either the copper laminate or copper protruding to the hole, as in the case of multilayers, then the bond between the electroless plate and the underlying copper will not be as good as if the underlying copper were clean. Bond failure may result, evidenced as blisters if the soil is spotty, or peeling electroless deposition, if the soil is more widespread (see Fig. 13.7).

Important factors to be considered about the cleaning solution are:

- Proper cleaner choice to do the job.
- Temperature of cleaner.
- Concentration of cleaner.
- Time in the cleaner.
- Work agitation in the cleaner.
- Cleanliness of the cleaner—when to dump.
- Rinsing after cleaning.

Temperature is a key factor that is often overlooked in cleaner operation. Most cleaners have a lower limit of temperature operation below which they rapidly lose effectiveness.

Rinsing of the cleaner from the work in process is actually as important a step as the cleaner-solution step itself. Residual cleaner left on the printed circuit board can act as a contaminant to the board itself, as well as a contaminant to other key process solutions—namely, the etch solution and the activator solution. The best type of rinse at this stage would be a rinse that is (a) not ice cold (preferably 60° F or higher), (b) aerated, and (c) equipped with spray nozzles to run fresh water over the boards as they exit the rinse. Condition C is not often used, but Conditions A and B should be easily achievable (see Fig. 13.8).

An adequate flow of fresh water must enter the rinse. The fresh water flow to the rinses (all rinses in general) will be predicated upon the following factors:

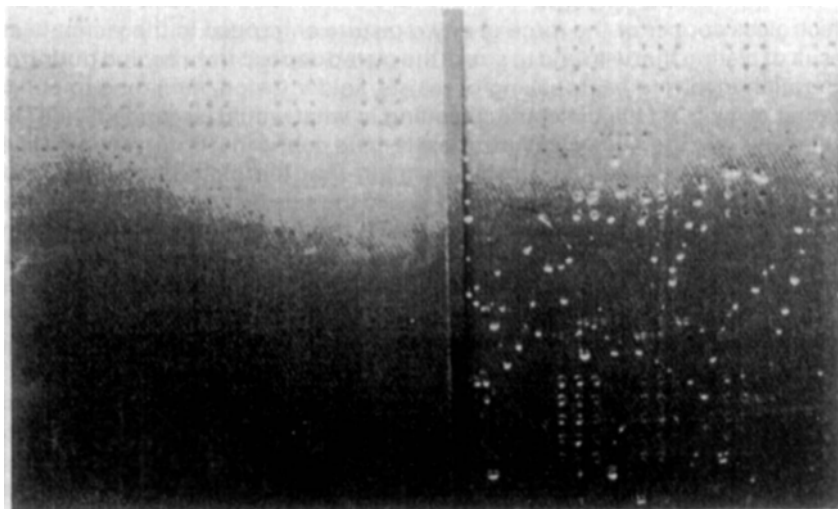


Fig. 13.8—Boards emerging from cleaner: (left) normally adequate cleaning and rinsing; (right) probably inadequate cleaning and rinsing.

- The drag-out from the process tank (mL/rack).
- The work load to be rinsed (ft²/rack).
- Whether the rinse is to be followed by another rinse, which will be cleaner than the rinse preceding it (cascading rinse system).

Conditioning

Following classical cleaning, some processes, and indeed some particular laminate types (notably multilayers, because of the resin-altering nature of the etch-back chemistries), require the use of a step called *conditioning*. The function of the conditioners is to "super-wet" the dielectric material, and in some cases, to provide this surface with a uniformity of polarity such that the later adsorption of activator will be more easily facilitated (see Fig. 13.9).

Sometimes conditioning materials are built into the cleaner formulation, resulting in what is termed a cleaner/conditioner, although the separation of the two functions into two separate process steps, with water rinsing in-between, is generally more effective for both cleaning and conditioning. Conditioning materials typically contain surfactants to do the job intended. Rinsing after this step is an *extremely* important consideration, since too little rinsing can allow the surfactant to remain on the laminated copper surfaces throughout the rest of the process and act as an interference to etching, activation, and the ultimate copper-to-copper bond—resulting in poor electroless copper to laminate-copper bond. Care must be taken to avoid too cold a rinse water temperature and to allow for *sufficient* rinsing quantities of water. The concentration of the

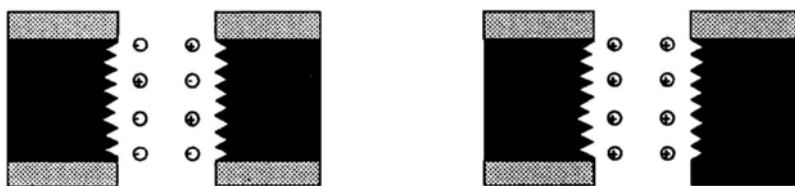


Fig. 13.9—Hole conditioning.

conditioning solution has to be watched carefully—too strong a conditioner solution should be avoided—a little bit usually goes a *long* way.

Etching

The next step in the electroless deposition line is the micro-roughening or micro-etch stage. The purpose of this step is primarily to give a micro-toothed surface structure to all copper surfaces that will ultimately be plated-over with electroless copper. Without proper etching, the bonds obtained between electroless copper and the laminated copper are usually very poor.

The etched surface serves a number of purposes:

- The surface area of the copper laminate is substantially increased, providing more opportunity for intimate contact between the electroless copper and the laminated copper.
- Some residual surface contamination may be removed in the etch, being undermined by the action of the etch on the underlying copper, if the contamination was not totally removed in the soak cleaner. Relying on the etch to do a substantial amount of cleaning is *not* good practice, however, since uneven etching is generally the result. This is because the residual contaminant does not allow the etch to start working on the underlying copper at the same time it starts to work on uncontaminated copper areas.

- A properly etched surface will provide anchoring sites for the activator (catalyst) material, which can now mechanically “bond” to the laminated copper surface.

- The deposited electroless copper can mechanically “bond” to the laminated copper by “keying” into a satisfactorily etched surface (see Fig. 13.10).

To accomplish what is desired, the depth of etch as well as the type of etch must be correct. Usually a minimum depth of 0.1 mil is recommended, although lesser depths can give satisfactory results under ideal circumstances existent in the rest of the total process line.

Copper removal *alone* from the laminate is not really all that is required. Some etchant chemicals may remove the proper amount of copper, but leave a polished surface. This is contrary to our goal. A *matte* or micro-roughened surface is needed. Some etchants that work well when their copper content is low tend to become micropolishers when their copper content becomes too high.

Temperature is an important parameter with etch solutions. Too low a temperature can result in little or no etching, or a micropolishing effect. Too high a temperature can result in runaway etch activity or etching solution decomposition, with a correspondingly difficult-to-control exotherm.

Too vigorous an etch is undesirable from two standpoints, as shown in the next two figures.

In Fig. 13.11, the adhesion of electroless copper to dielectric at Point A will most likely be less than adequate, and will fail if tested. The dielectric at Point A has not been roughened as it has in the drilled hole.

In Fig. 13.12, the inner-layer copper has been severely etched so that it is receded into the dielectric. This phenomenon is termed *reverse etch-back* and is undesirable from the standpoint that less sure-fire bonding of electroless copper to inner-layer copper can result.

Poor electroless copper adhesion to the copper surfaces of the laminate is generally the result of inadequate etching. Tape testing for adhesion after electroless copper deposition, as a once or twice a day routine quality control test, can help ward off potential problems. Unfortunately, most shops tape test only when they are fairly sure that a problem exists—then the tape test merely confirms everyone’s fears.

The tape test best suited for most shops uses a six inch strip of ½- to 1-inch-wide tape, sticky enough for the purpose and strong enough to be rapidly ripped away from the copper surface without tearing or breaking. The tape should be applied to the copper surface (after electroless deposition, rinsing, and drying) across flat areas and some holes, by pressing and rubbing with the edge of one’s thumbnail or a coin. The tape is removed with a quick snap motion, and with enough force so that the board has to be held down tightly with the hand that is not pulling the tape. If any copper is removed, it will be observed on the tape.

Copper removal around a hole may indicate an over-etching condition. Copper removal elsewhere may indicate under-etching or *other* problems, such as residual wetting agents on the board, overactivation, or a poorly cohesive electroless copper deposition.



Fig. 13.10—Micro-roughened switches.

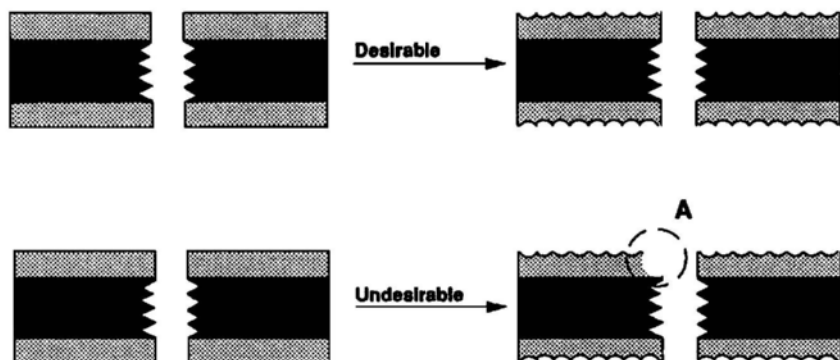


Fig. 13.11—Bare dielectric exposure.

Rinsing prior to etching is important to insure that residual cleaning agents from the cleaner are not dragged into the etch nor are residual to the copper surface. With all etchant materials, the introduction of alkaline components will dramatically reduce their effectiveness.

Other precautionary steps are:

- The electroless plating racks should be stripped in a separate step because all etchant materials are sensitive to the introduction of metals like palladium, which promote etchant decomposition.
- A good rinse after etching is also desirable so as not to drag copper down the electroless processing line.

Typical chemicals employed as etchants in the electroless line are: ammonium persulfate, sodium persulfate, other sulfuro-oxide type-oxidants (all typically 1-½ lb/gal with 1% sulfuric acid added), and peroxide-sulfuric-type etchants. Cupric chloride is not used due to the fact that it leaves a very difficult to remove residue on copper surfaces.

Depending on the type of etch used, the processing steps prior to and after the etch step may vary slightly, as in the following:

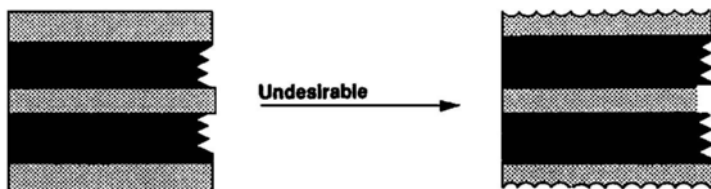


Fig. 13.12—Inner-layer copper attack.

Persulfate Type Etch

- 1. Cleaner
- 2. Rinse
- 3. Conditioner (optional)
- 4. Rinse (optional)
- 5. Etch
- 6. Rinse
- 7. Dilute sulfuric acid
- 8. Rinse

Peroxide-Sulfuric-Type Etch

- 1. Cleaner
- 2. Rinse
- 3. Conditioner (optional)
- 4. Rinse (optional)
- 5. Dilute sulfuric acid
- 6. Rinse (optional)
- 7. Etch
- 8. Rinse

With the peroxide-sulfuric-type etchants, all of which operate at elevated temperatures, it is usually recommended to insert a sulfuric acid immersion step after cleaning and prior to the etch step, to keep the etch solution free of dragged-in alkaline materials.

With other types of etchants, the etch will be followed by a sulfuric acid immersion step, following etch rinsing, to remove etch residues. This is generally not necessary with the peroxide-sulfuric acid-type etchants.

If a persulfate-type etch is used, a dilute sulfuric acid (10 to 15 percent by vol.) dip is recommended to remove etch residues, followed by a satisfactory rinse. As with all acids to be used in the electroless line, care should be taken that the acid is free of heavy metals, to prevent an adhesion-disrupting immersion deposit onto the copper surface.

Activator Pre-Dip Solutions

Prior to the activation step, it is most common to immerse the work into a solution containing ions common to those of the activator itself. After this *pre-dip*, the work is then brought directly to the activating bath *without* an intervening water rinse. Since most activating solutions are chloride-ion based, most *pre-dips* are based upon chloride ions. In this fashion, the work that is brought to the activating solution is residual with an ion and has a pH common to the activator.

Every time a copper-clad laminate enters rinse water, a slight surface oxide will develop, particularly if the work is being rinsed of an acid. Immersion *into* any mildly acidic pre-dip solution will remove slight amounts of copper oxide and therefore put copper ions into this solution. Activators are usually acidic to

some degree. Therefore, a mildly acidic pre-dip solution takes the copper ion into itself, saving the activator to some degree. Most activators are sensitive to copper contamination.

The pre-dip is dumped frequently enough (it is orders of magnitude less expensive than activating solution), based upon copper content, to "save" the activator from copper buildup. Usually a pre-dip will be dumped before it reaches 1000 ppm copper content.

Due to the fact that a strongly acidic pre-dip can attack the black-oxide layer on the internal copper layers of multilayer boards and promote "reverse etchback" as well as residual hydrochloric acid along the internal copper layer, the trend in recent years has been to go to reduced acid strength pre-dips (1 to 2 percent by vol. as hydrochloric acid), as well as low acidity activator solutions.

Activation

Proper activation is perhaps the *key* step in the electroless copper process, other than the electroless deposition itself. However, in order to properly activate, the preceding steps must all be in good working order.

The activating species is held primarily mechanically to both the copper surface of the laminate (in sites created by etching) and the surface of the dielectric (in sites created by piercing).

Activating solutions (or catalysts) typically contain palladium held in a reduced state by stannous ions. These solutions are typically high in chloride ion and possess some degree of acidity, typically lower than had been the case five or ten years ago (to prevent reverse etchback). Figure 13.13 depicts the type

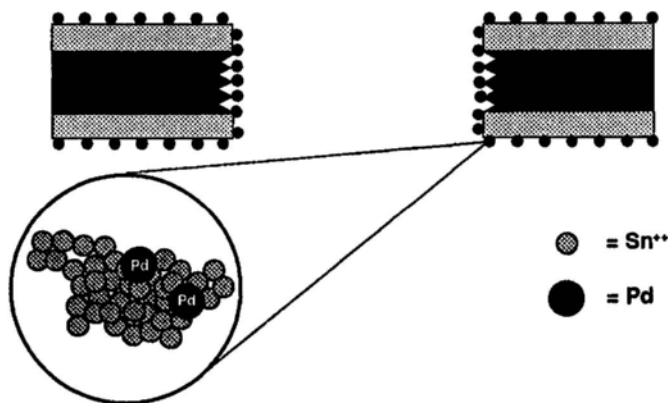


Fig. 13.13—Activation (catalyzation).

of species that is deposited all over the work, copper surfaces and dielectric alike. Typically, dielectric surfaces will take on a brownish color.

Typically, the number of tin atoms is 50 to 100 times greater than the number of palladium ions and the species is manufactured to be as small as possible. *Without* the presence of stannous tin, the palladium will readily oxidize to a non-activating form of palladium. The catalytic ability of the species is not only dependent on the palladium content, but also on the structure of the compound. Activating solutions are typically deep black-brown in color. By chemical analysis, maintenance of the solution requires monitoring the stannous tin content to insure that the activating solution has enough stannous tin to prevent the solution from becoming useless.

Activator solutions should *never* be aerated, because this will oxidize the stannous tin and make the palladium itself susceptible to oxidation—rendering it useless.

Since activator (catalyst) is a layer of material *between* the copper cladding and the subsequent electroless copper, it can prevent intimate copper-to-copper contact and interfere with adhesion. It is desirable *not* to put too much activator on the work being processed. Too *long* an immersion time is to be avoided. Palladium activator materials are such that a little goes a long way.

With improper activation, poor copper-copper bonding will probably result. Also, palladium consumption, and hence cost, will be very high (Fig. 13.14).

When withdrawing work from activating solutions, care should be taken to drain parts adequately. In most shops, more activator is dragged out of the

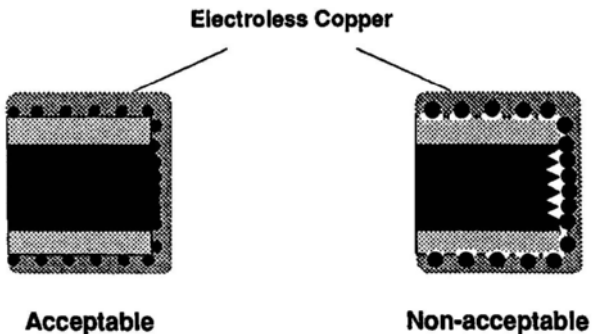


Fig. 13.14—Improper activation.

activating solution than is normally consumed by having activator mechanically adhere to the work.

Tin-palladium activating solutions are sensitive to several ions that act as contaminants, notably copper and antimony. Relatively small amounts of antimony (10 to 20 ppm) can lead to tiny voids in the electroless copper deposit. Activators tend to have different tolerances for copper contamination, based upon their formulation. The tolerance is also somewhat dependent upon what type of laminate is being processed. A difficult-to-cover multilayer laminate (due to changes effected on the dielectric by smear removal technique) may exhibit voiding problems when the copper content in the activator is around 800 ppm, while the same effect may not be observed on a standard double-sided laminate until copper concentrations of 1500 to 2000 ppm or *higher* exist in the activator.

Copper may be kept to a minimum in the activation solution by observing these precautions:

- Keep the activation time nominal, about 4-6 minutes.
- Dump the activator pre-dip frequently.
- Avoid lifting work out of the activator and re-immersing it.

Rinsing After Activation

Too long a rinse time can undermine the activator and render it useless. Long rinse times can lead to copper oxidation of surfaces.

The rinse directly following the activator usually gets cloudy due to the formation of a tin precipitate. Poor water flow usually will result in this rinse becoming very concentrated with this precipitate, which may ultimately contaminate the activated surfaces.

Aeration, while promoting beneficial rinsing, may serve to oxidize the catalytic species, making it less active or totally inactive, depending upon the severity or duration of aeration. Avoid aeration if possible, or use very low aeration.

The use of recycled water sometimes creates problems, especially in this particular rinse station and the rinse station following post-activation. Depending upon what type of recycling system is used, and which rinse waters are recycled, there arises the occasional probability that the recycled water will contain wetting agents and/or chelating agents, and/or oxidizing agents. These materials can render the activating species inactive, resulting in voiding. Once the activating species has been deposited onto the work in process, every precaution should be taken to insure its being held in its active state.

A yellow color in these rinses, or a foam development, is an indication that trouble may be on its way. Under these circumstances, it would be prudent to switch these rinses over to fresh incoming city water until the problem with the recycled water can be rectified.

Many useful rinsing habits may be obtained from an AESF Illustrated Lecture, *Rinsing, Recycle and Recovery of Plating Effluents*, by D.A. Swalheim. Suggestions made in this chapter will help in *all* rinsing considerations.

Post-Activation

The purpose of the post-activation step (or acceleration step, as it is sometimes called) is to render the activating species deposited in the activation step as "active" as possible prior to immersing the work in process into the electroless copper bath.

If the activating species is thought of as a closed flower bud, with palladium in the center of the bud, surrounded by many layers of tin, then the post-activator can be thought of as functioning to open the bud, removing some tin and perhaps some palladium in the process of doing so, and letting the inner palladium be more readily seen by the electroless copper solution.

If the post-activation step were skipped, the initiation of deposition in the electroless copper bath would be prolonged and the risk would be run of contaminating the electroless copper bath with any marginally adherent palladium-containing activating species.

Hydroxides of tin are formed in the rinses after activation, as can be seen by the cloudy nature of this rinse, and can coat the activator species on the board and mask its functionality. The hydroxides of tin are gelatinous in nature and coat the palladium metal particles. The purpose of the post-activator, then, is also to solubilize these compounds, leaving the activating species as free as possible from residual tin compounds.

Some tin is removed and small amounts of palladium are cut loose to the post-activator solution. The new activating species is "more active" and able to quickly initiate electroless deposition (Fig. 13.15).

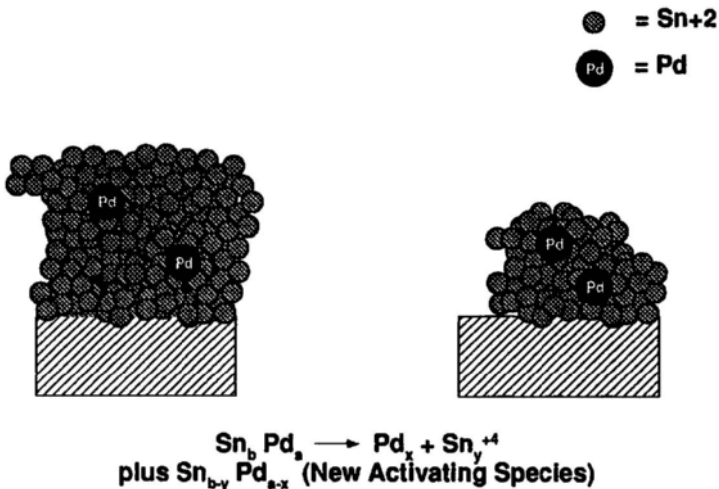


Fig. 13.15—Post-activation (acceleration).

Most post-activating solutions are acidic, and will also remove copper oxide that has formed on the copper surfaces due to the rinsing steps between activator and post-activator. Post-activators are generally considered spent when they reach a copper content of 1000 ppm.

Post-activator solutions usually contain materials that will dissolve stannous tin from the species. For this reason, care must be taken not to stay too long in these solutions. In the extreme case, enough tin can be removed to undercut the tin that is attached to the surfaces coated with activating species, and these surfaces will then be devoid of *any* activating species.

Also, the most common post-activators are based upon fluoride compounds and *some*, although minimum, amounts of fluoride ion will be ever present. The fluoride ion can attack glass fiber, which may be at the surface in a pierced hole, and thereby undercut the activator species that attached mechanically to the glass.

Some post-activators may contain reducing agents whose function it is to be dragged *into* the electroless copper solution with the activating species, to promote rapid initiation of the electroless copper deposit.

So far, a lot of time has been spent discussing everything *but* electroless copper. The reason for this is that in order to deposit electroless copper, many steps have to be carefully executed. Electroless copper is the *end* product in the electroless copper process, and as such, it takes a great deal of undeserved blame when the end result is not as anticipated.

In summary, the typical process steps are as follows:

1. Cleaning or cleaning/conditioning—3 to 5 min
2. Water rinse—30 sec to 2 min
3. Conditioning (optional)—3 to 5 min
4. Water rinse—30 sec to 2 min
5. Etch—2 to 3 min
6. Water rinse—30 sec to 1 min
7. Sulfuric acid, 10 to 15 percent by vol.—1 to 3 min
8. Water rinse—30 sec to 1 min
9. Activator pre-dip—1 to 2 min
10. Activator—4 to 7 min
11. Water rinse*—30 sec to 1 min
12. Post-activator—3 to 6 min
13. Water rinse*—20 sec to 1 min
14. Electroless copper—10 to 30 min

*Preferably a double rinse.

Steps 5 and 7 may be reversed, depending upon the type of etch used. These times are typical only, and may vary depending upon the proprietary process used.

It must be mentioned at this point that other activation chemistries have been commercially successful, although none enjoy the present widespread popularity of the tin-palladium chemistry presented in this discussion.

Basically, two other types of systems now exist:

- A neutral to alkaline pH palladium-containing activation system. This system is intended to obviate the problem of oxide attack along inner-layers in a multilayer package, thereby eliminating entrapped acid-chloride compounds and reducing the "pink ring" possibility. Also, reverse etchback, an outgrowth of inner-layer attack, should be greatly reduced with systems of this type.

- A copper-based activation system. This system provides a very cost effective activator, and utilizes a strong reducing agent type of post-activator to put the copper into a proper form to be receptive to electroless copper deposition.

Electroless Copper

Typical electroless copper bath formulations will contain the following ingredients:

- Copper salts
- Reducing agent (formaldehyde)
- Alkaline hydroxide
- Chelating agents (quadrol, EDTA, Rochelle salts, etc.)
- Stabilizers, brighteners, etc.
- Wetting agents (optional)

The formaldehyde and the hydroxide ions provide the reducing force necessary for the deposition of metallic copper. The deposition reaction must be initiated by a catalytic species on the surface of the work to be plated. This is provided through the activator step.

The main plating reaction can be postulated to be:



The reaction as written is only autocatalytic with respect to copper metal in the presence of an activated surface or when hydrogen is being generated. That is to say, if one were to place a clean piece of copper in the electroless bath, no plating would occur. Plating would only occur on this copper if the copper were catalyzed, or if another catalyzed substrate was plating near this copper and liberating hydrogen. Sitting in the bath and not plating, the copper would most likely become oxidized. Catalysis (activation) starts the reaction. A broader scope of electroless copper chemistry is provided in the Appendix to this chapter.

The choice of which bath to use is predicated upon several factors. Typical electroless copper baths are:

Slow speed baths

Room temperature

1-2 millionths in./min (plating speed)

High speed baths

Room temperature—21 to 32° C (70 to 90° F)

2-6 millionths in./min

High speed baths

Elevated temperature—38 to 60° C (100 to 140° F)

2-6 millionths in./min

If the electroless copper is to be overplated to full thickness for full panel plating, or the electroless is to be overplated with some minimal thickness (0.1 to 0.3 mil) of electrolytic copper to insure through-hole coverage before proceeding with imaging and pattern plating—as is often the case in very expensive multilayer board manufacture, then the thickness of electroless copper need only be minimal, such as 10 to 20 millionths of an inch deposit. A slow speed bath, which affords the easiest control, would be the most likely choice.

The trend in the printed circuit industry has been to get away from full panel plating and into pattern plating for economical and functional reasons, and also to get away from the additional racking and unranking steps necessary to overplate the electroless copper with electrolytic copper (flash plating) prior to imaging and pattern plating. With the proper choice of cleaning techniques, after imaging and prior to pattern plating, electroless copper alone may be satisfactory, and usually is, provided that the thickness and integrity of the deposit is suitable to withstand the cleaning technique.

If not too much cleaning is required, and cleaning can be implemented insuring that the attack of electroless copper will be minimal, then low thicknesses (20 to 40 millionths in.) of electroless copper may be adequate to the purpose, or a high speed bath may be chosen if speed of production is critical (see Fig. 13.16).

If more vigorous cleaning techniques or chemicals are required after imaging and prior to electrolytic pattern plating, then higher thicknesses of electroless copper will be needed to insure that this deposit remains intact during the cleaning. In these cases, thicknesses of 60 to 100 millionths in. are usually needed, and the use of the high speed baths is generally favored, for time considerations.

With respect to high speed baths, the elevated temperature variety seems to be increasing in popularity, since solution growth (because of needed chemical additions) is minimized due to water evaporation at the elevated temperature. Also, it is economically easier to maintain a constant temperature, which is

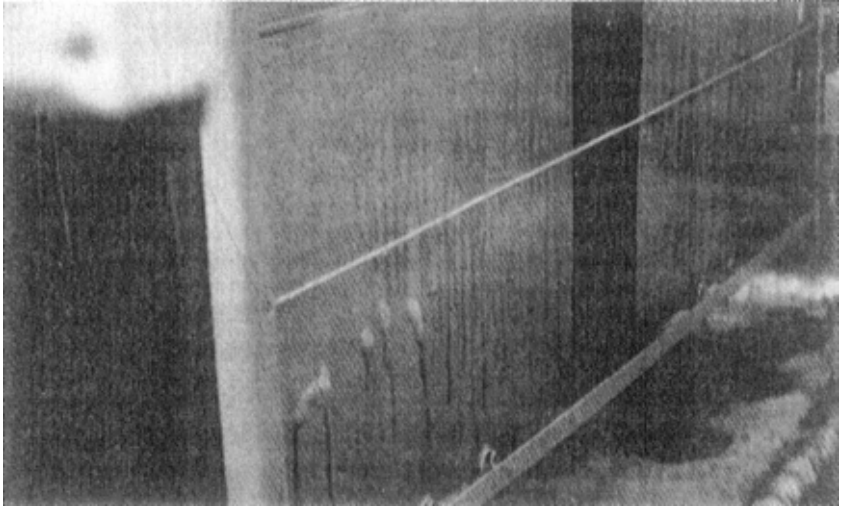


Fig. 13.16—High-speed electroless copper.

important to the rate of deposition, with an elevated temperature bath, since only heating is required. Room temperature high speed baths will require both heating and cooling facilities to keep the temperature fairly constant throughout the year in the more seasonal parts of the country.

The physical structure of the electroless copper also plays a very important part in the choice of which commercial bath should be chosen, if flash electroplating is to be eliminated. It is generally acknowledged that electroless copper is of a different physical structure than electrolytic copper. This is supported by the following facts:

- The density of electroless copper is 2 to 5 percent less than that of electrolytic copper.
- Electrolytic copper on an equal thickness basis will be less rapidly dissolving than electroless copper in any etching medium—indicating a more open structure for electroless copper.

So, if one electroless copper of 60 millionths in. thickness will withstand immersion in the cleaning process solutions for the same time as another electroless copper of 100 millionths in. thickness, the thinner copper is obviously the more economical. Rate *alone* is not the determining factor of best choice.

Another factor that can enter the picture on choice of electroless coppers is

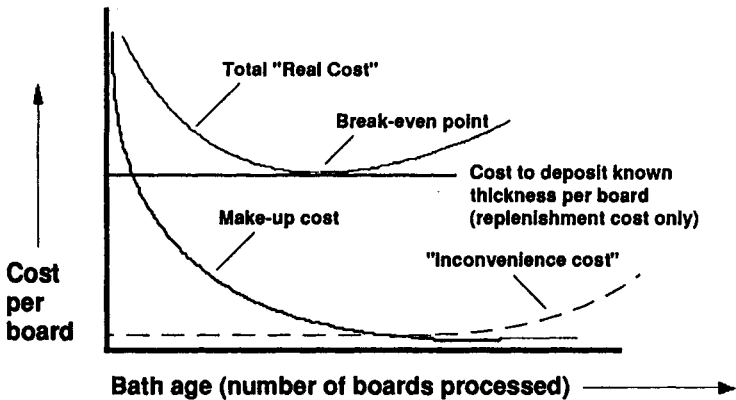


Fig. 13.17—Real electroless copper plating costs.

that of "useful economic life". All electroless copper baths build up by-products during use. All electroless copper baths require continual replenishment for copper ion, formaldehyde, sodium hydroxide and other proprietary agents during use. Depending upon the type employed, these additions will be made with concentrates, either relatively concentrated in constituents, or not so concentrated. Typically, copper ion and formaldehyde are in one component and sodium hydroxide is in the other.

Usually solution must be decanted from the bath and thrown away to make room for additions. Depending upon the concentration of the additive solutions and the bath's operating temperature, this throw away will be negligible to sizeable. If throw away is negligible, by-product accumulation in the bath will be rapid, minimizing the life of the bath. If the throw away is sizeable, by-product accumulation will be less significant and the life of the bath will be longer. Whether we throw away the whole bath frequently, or throw away *portions* of the bath frequently and the entire bath infrequently, is a choice that needs to be made, depending upon *overall* throw away over a long period of time and the nature of bath operation and deposit characteristics over a long period of time.

Every bath has a "break-even" point based upon its cost to deposit a known thickness, its make-up cost amortized over its useful life, and its "inconvenience cost" with age (more plate-out with age, more chances of voiding, more erratic operation, etc.). This overall operation is depicted in Fig. 13.17.

Keeping a bath in operation beyond the break-even point is basically not good economics.

Temperature control is perhaps one of the most important physical parameters affecting rate control and quality of deposition, and is probably the most widely abused parameter to be mentioned. Every electroless copper bath is *designed* chemically to be operated in a certain temperature range. Low temperature baths usually have the widest window of temperature operation (see Fig. 13.18).

Below a minimum temperature, all baths will fail to initiate properly, and voiding will be the most likely result. Above a certain temperature, the rate of deposition will increase beyond the point where a physically sound deposit will result, and several of the side reactions mentioned later will predominate, leading to a lessening of overall bath stability. It is therefore very important to pay close attention to electroless copper bath operating temperature.

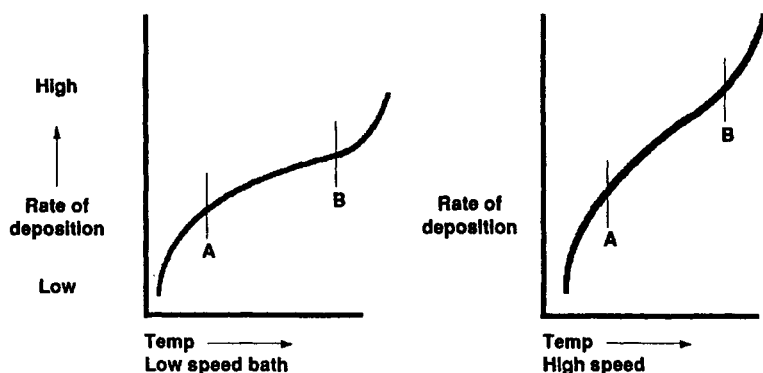
Physical Parameters of Electroless Copper

Aeration

Some electroless copper baths are somewhat dependent upon aeration for bath stability and integrity of deposit. It is thought that the mechanism involved here is the aid in removing hydrogen gas (evolved in the plating reaction), which can act as a secondary reducing medium causing localized hyperactivity.

Other electroless copper formulations are such that the introduction of air will destroy the ability of the solution to deposit upon activated surfaces.

The *amount* of aeration required depends upon the particular proprietary formulation being used.



A-B = useful operating window

Fig. 13.18—Temperature vs. rate of deposition.

Filtration

For slow speed baths, periodic batch filtration through 1-micron polypropylene filter cartridges is usually recommended on a once-a-day to once-a-week schedule, to rid the bath of extraneous copper particles. Continuous overflow filtration is better, but not critical.

For high speed baths, continuous overflow filtration through a 10- to 25-micron polypropylene filter bag is generally recommended (see Fig. 13.19).

The solution is allowed to overflow the main plating chamber, falling through a filter bag to a sump, from which it is then pumped back into the main plating chamber. High speed baths may generate a more vigorous evolution of hydrogen, and side reactions leading to the formulation of extraneous copper are more predominant than in slow speed baths, making this continuous bath filtration more desirable.

Bath loading

The concentration of replenishment concentrates is usually based upon an *average* bath loading (surface square feet of work processed per tank volume) at a certain operating temperature. Side reactions, notably the reaction of *formaldehyde* with *sodium hydroxide* to form methanol and formate, proceed at a definite rate at a given temperature and are a function of time and temperature. The formaldehyde and sodium hydroxide ratio in the concentrates to replenished copper is based upon a certain loading prediction.

If the electroless copper bath were loaded with workloads below what the manufacturer of the electroless copper concentrates recommends, the result

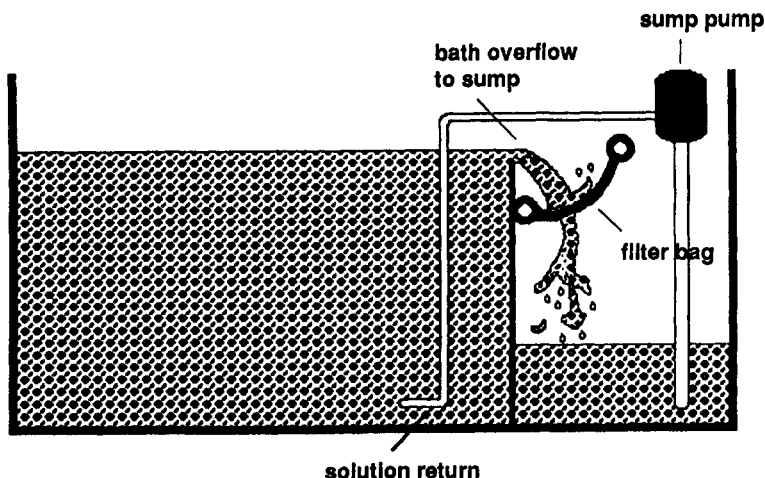


Fig. 13.19—Typical overflow filtration.

would be that the formaldehyde and sodium hydroxide content of the bath would fall off and extra additions of these components would be required. If one were to load the bath with workloads greater than those recommended, the formaldehyde and sodium hydroxide content would climb with time.

Also, with very low workloads in an elevated temperature bath, evaporation losses would exceed replenishment volumes, so that bath volume would decrease with time, making the addition of water possibly necessary.

Typically, electroless copper baths are designed to accept 1 to 1.5 ft²/gal as the *optimum* loading for the considerations described above.

Work agitation

It is generally desirable to agitate the work in the electroless copper bath with through-hole agitation, to bring fresh solution to the areas being plated, and to help remove hydrogen gas, which is generated during plating, from any recesses.

Also, care should be taken that the boards do not touch one another and that they do not come into contact with the walls of the tank, nor any solution or aeration spargers. When the boards enter the tank, they are coated with activating species, and the activator material can smear onto other surfaces—resulting in these surfaces becoming catalytic and thereby receptive to electroless copper plating.

Rack materials

Electroless copper plating racks should be constructed from 316 stainless steel. The electroless copper will plate *any* rack material. What we want is for the electroless copper plated on the rack to adhere and not flake off into the plating solution, where it will continue to plate. "Inert" racks such as plastic (PVC) or Teflon will eventually start to plate because they will hold some activator, but the plate will be loosely adherent, fostering flake-off.

Tank cleaning

Eventually, every tank will exhibit plate out on horizontal surfaces (tank bottom, overflow weir lips, etc.) due to extraneous copper particles failing to overflow and falling down through the solution. For this reason, tanks should be thoroughly cleaned and rinsed periodically by removing the electroless copper bath, preferably through a filter, doing the necessary cleaning, and returning the copper bath to the clean tank.

Tank design

Polypropylene and polyethylene are good tank construction materials since they are relatively inert, fairly resistant to impact cracking, and will not soften appreciably at the temperatures that most hot electroless copper baths are run. One should choose a thickness of material for construction that will not allow the plating tank to bow at the sides when filled with solution at intended operating temperature. PVC-lined steel tanks should be avoided, since the insides of the tanks will invariably get scratched over time, and linings tend to become cut,

allowing the electroless solution to get behind the lining. Electroless baths can become contaminated in this fashion. Also, the use of disposable PVC liner bags should not be recommended because folds will exist where solution and evolved gas will become entrapped, promoting extraneous plating in these pockets, leading to premature bath decomposition.

Tanks must be large enough in volume to handle the intended workload per immersion (1 to 1.5 ft³/gal), including the rack surface area, and also to accommodate air spargers (if used), solution return spargers if overflow filtration is employed, and a satisfactorily large external sump—again, if overflow filtration is used.

The rack immersion volume should be large enough to allow racks to be immersed and withdrawn without bumping or scraping the tank walls. Scraping will obviously put scratches in the otherwise smooth tank walls, which become sites for extraneous plating. If the scratch is created from the rack at entry, activator from the rack will be imbedded in the scratch, promoting electroless plating in the scratch. Some allowance should be made for rack (through-hole) agitation, again allowing no bumping of the walls of the tank with the rack.

A bottom drain on the plating tank is both a convenience and a nemesis. Since valves have a way of not being fully closed at times, it is practical to employ double valving for bottom drains. If an overflow sump is employed in the electroless plating tank, it too should have a bottom drain, and this drain should be the one used to control bath volume adjustments during operation, to correct for additional volume growth.

The overflow sump must be large enough so that it won't flood over when the plating rack is immersed into the plating section of the tank.

Heating, if required, is best done with hot water flowing through Teflon spaghetti coils. It is highly recommended that the coil or coils be placed in an external sump so that the rack of parts is not allowed to hit and possibly rupture a coil strand. A puncture in the coil will result in the tank of electroless copper becoming rapidly diluted with water. Coils should be periodically checked for leaks and leaking strands cut and tied off if necessary. Electric immersion heaters are difficult to use in overflow sump arrangements due to the inherent fluctuations of the liquid level in the sumps during normal operation.

The tank should also have an absolute minimum of horizontal shelf areas. Obviously a tank and sump bottom are a necessity, but other internal struts or boxes are to be avoided, since extraneous copper will settle and plate on these areas.

Rackling

In addition to preferred construction materials, several other considerations are important:

- Enough space must be provided between circuit panels to avoid their touching one another and thereby interfering with the plating, and to allow for the efficient release of gas bubbles that are generated during plating. With the release of gas from holes being plated, if panels are too close to one another, a

shadow image of an actual hole on one board can develop on the surface of an adjacent board. If panels are very long, they may have to be spot supported at a few points over their length, in addition to top and bottom, to prevent them from bowing in the plating solution and touching an adjacent board. In general, spacings of 0.3 to 0.5 inches, board center to board center, are usually adequate.

- The rack should be free of sharp edges that can either scratch parts being racked or unracked, or scratch the smooth surfaces of the plating tank itself.
- The rack should be of thin construction with respect to support rods, so as to minimize the contact area to the panel being plated—otherwise the rack can serve to mask portions of the panel being plated.
- Compromises must be made to minimize the overall surface area of the rack in general and yet have a rack that is structurally supportive, strong and sound. Rack surface area must be added to panel surface area when figuring bath loading and copper consumption during plating. The higher the rack surface area, the less efficient the plating operation.
- Racks should have no shelf or “cup” recesses that will allow them to act like ladles to carry solution from one tank to another, thereby increasing drag-out and increasing chances for contamination of process solutions or lowering the effectiveness of rinsing. Racks should be open enough in structure to allow efficient solution flow, or in the case of drying, air flow.
- The racks should be easy to load and unload with panels, so that a minimum of *handling* is required.

Handling

Panels should be handled by their edges, and gloves should be worn during racking and unracking after electroless copper. The reason for this is two-fold:

- Gloves will help protect the handler from getting glass slivers in his hand.
- Gloves will help prevent the handler leaving finger oils and skin-acid on the surface of the panels.

Panels should always be *dry* after electroless copper plating before they are handled at all. In any acid-fume environment, such as a plating area, boards will stain very easily by sitting in the environment. This staining will be accelerated if the panel is not dry. Electroless copper plated surfaces are very active chemically and *very* prone to staining.

Chemical Parameters of Electroless Copper

The chemical balance in any electroless copper formulation is very important. The bath is designed to function most optimally when the ratios of the ingredients to one another are close to the ratios existent when the bath is initially made up.

The main constituents to be monitored in any electroless copper solution are copper metal, formaldehyde and hydroxide (as sodium hydroxide, usually). Secondary to these main ingredients, but maybe requiring periodic attention would be the chelating agent (or complexor) and stabilizers.

Copper metal

Copper is consumed as the work being processed is plated, and requires frequent replenishment to keep the bath in chemical balance. The frequency and amount of replenishment required will depend upon the bath's deposition rate, as well as the workload (ft²/gal) being processed. If the deposition rate is very slow, moderate additions will only be required from every 2 to 3 hours to once or twice in an 8-hour work shift. With high speed baths, replenishments will have to be made every 30 minutes or so, since the copper content is being rapidly depleted. With high speed baths where the rate consistency is more sensitive to chemical ratios, it is generally advisable to monitor in small additions of constituents on a continual or frequent intermittent-continual basis.

Formaldehyde

As additions to the electroless copper bath are made to replenish copper that is being depleted, it is common that formaldehyde is brought into the bath along with the copper ion, and usually the two ingredients are placed in the same replenisher concentrate. If the bath were to be worked *continually at optimum* workload for the particular formulation, no further additions of formaldehyde would normally be required. However, electroless copper baths are rarely operated 24 hours a day, day after day, and workloads do vary.

The Cannizzaro reaction, or reaction of sodium hydroxide and formaldehyde to form methanol and sodium formate, goes on continually in any bath at a somewhat constant rate for that particular bath, as long as the temperature is constant. The reaction is much faster in warm solutions than in room temperature solutions. The effects of the Cannizzaro reaction (formaldehyde and caustic loss) can be corrected for by designing replenisher concentrates that will add back enough formaldehyde to account for losses due to the plating reaction *and* the Cannizzaro reaction, but once workload is lower than expected and bath downtimes enter the picture, the formaldehyde loss will be higher than can be corrected for, based upon copper consumption alone.

Therefore, corrections will have to be made for the formaldehyde level independently. The frequency of correction may be as much as 2 to 3 times per day, where elevated temperature high speed baths are concerned. A formaldehyde correction will almost always be necessary at morning bath start-up with high speed baths, particularly elevated temperature baths.

When the formaldehyde content of an electroless copper bath is too low, plating initiation may be very slow or faulty, leading to voiding. When the formaldehyde content is too high, bath hyperactivity may result, leading to the predominance of side reactions and bath instability, along with a poor physical structure to the electroless copper deposit.

Hydroxide

Due to the fact that hydroxide is consumed not only in the main plating reaction, but also in the Cannizzaro reaction previously discussed, the same replenishment comments pertain to hydroxide as pertain to formaldehyde—that

is, independent analyses will have to be made and the hydroxide levels corrected independently of corrections that are made through replenisher concentrates added to the bath at some ratio to the copper/formaldehyde replenisher concentrate(s). Carbon dioxide in the air also reacts with the sodium hydroxide in solution to form carbonate.

Hydroxide consumption increases when baths are run at elevated temperatures through the Cannizzaro reaction, and is higher for aerated baths due to the reaction with carbon dioxide in the air.

Sodium hydroxide additions to most baths are made with proprietary replenisher concentrates, which may or may not contain other ingredients that are rate-altering. Therefore, in some systems high hydroxide may produce high plating rates, while in other systems, higher hydroxide content will lessen the plating rate. No matter what system is used, it suffices to say that if the hydroxide content is not correct, problems with either bath hyperactivity and stability, or problems with plate initiation can be the result.

Chelating agents

Some electroless copper baths may require a periodic analysis and subsequent correction for chelating agent to insure keeping the copper ion soluble in the electroless copper bath, which is highly alkaline. Without enough chelator, copper ion will precipitate as copper hydroxide in alkaline solution and the bath will become extremely cloudy in appearance.

Stabilizers

Most present day electroless copper formulations contain so-called "stabilizer" materials to keep the bath from depositing copper randomly in solution. The types of materials used are such that they are thought to interfere with the side reactions promoting the formation of the cuprous ion. Cuprous ion can react to put extraneous copper into the plating bath.

Stabilizers are generally used in the 1 to 100 ppm concentration range. Too high a concentration usually will lower the plating rate and also may stop the bath from initiating deposition entirely. Typically, the types of materials used are strong chelators for palladium also, and it is thought that this is how they can interfere so dramatically with initiation.

Replenishment concentrates usually contain stabilizers. Periodic (usually once a day) additions of stabilizer are normally required, independent of other additives, to control the plating rate and provide bath stability during shutdown periods. This is particularly true with high speed plating baths.

Automatic controllers

Several very good automatic controllers (analyzers) are commercially available that will monitor electroless copper baths for copper, formaldehyde, and hydroxide content independently of one another and that will activate chemical metering addition pumps to replenish the bath for these components when additions are necessary, based upon preset low concentration points.

These devices provide for close chemical control and, consequently, optimum operation with respect to the attainment of consistent plating rates. They are

particularly useful when high speed plating baths are being used (Fig. 13.20).

Some models contain strip-chart recorders that leave the user with a record of the parameters involved.

Post-Electroless Copper Considerations

A good deal of thought should be given to how the just-electroless-plated panels are processed directly after electroless deposition. Much of what is done here will have a major impact on how easy the subsequent imaging operation will be, or how the electroplated (either flash-plated or panel-plated) deposit will look.

When panels exit the electroless copper solution, they will be coated with a highly alkaline film of solution, which must be rinsed well. Unless completely and adequately rinsed before drying, an alkaline surface on the panel will result in rapid oxidation of the copper in moist air. This heavy oxide coating will run a spectrum of colors—typically purple, blue, red, and brown. Later in processing, when the oxide is removed, the imprint of the oxide will be visible, even after electroplating, since an oxidized surface area is one that has been attacked chemically and has a different surface structure, even after oxide removal, than surrounding areas that have not developed an oxide coating.

For this reason, it is usual after the electroless copper rinse step to immerse the plated panels into a mild acid solution, typically a 1 to 5 percent sulfuric acid solution, or a mild organic acid solution such as citric acid or malic acid, or a proprietary mild organic acid solution designed to be very free rinsing.

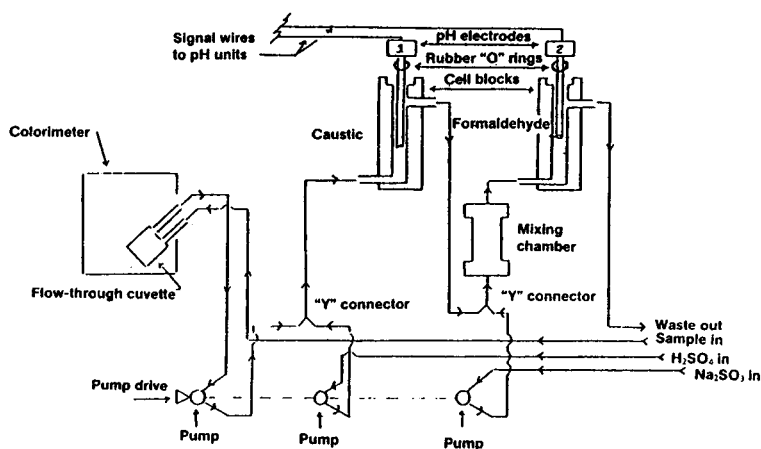


Fig. 13.20—Typical electroless copper controller plumbing.

The important consideration, if an acid dip is employed, is to *rinse* very well, so that panels do not end up with an active acid surface prior to drying. Sulfuric acid solutions are difficult to rinse satisfactorily, and therefore the popularity of the milder acid dips has gained in recent years.

If an acidic surface film is allowed to remain on the panel, the panel will oxidize over time to give a brownish oxide surface.

Once the surface has been properly neutralized, the panels should be dried quickly so that the wet or moist surface doesn't become exposed to the acid or alkaline fume-laden shop air, which defeats the purpose of the neutralization process. A dryer tank in the electroless copper line is highly recommended, where within 5 to 10 minutes, panels can be forced-hot-air dried.

A recommended practice is to immerse panels into an anti-tarnish solution prior to drying. Typically, these solutions leave a mono-molecular film on the copper surface that is somewhat water-repellent or aids in water shedding, thus allowing the panels to dry quickly and without oxidation. The residual anti-tarnish film allows panels to sit in shop air for longer periods without tarnishing, and has been shown to actually increase the adhesion of subsequently-applied inks and dry-film photoresists—in some cases eliminating the need for panel scrubbing prior to primary image plating resist application. Care must be taken to use a *very dilute* anti-tarnish solution. It is usually preferable to operate these solutions at 120 to 140° F to aid in the drying process.

Summary

Suffice it to say that there are many critical parameters to be aware of in electroless copper processing. Once routine monitoring procedures are established, however, operation of the electroless copper line becomes relatively simple, and work can be routinely processed, yielding consistent high quality.

ADDITIVE PROCESSING

The distinction between additive and subtractive processing centers about the fact that in additive processing, no *outer-layer* copper foil exists on the laminate outer surfaces prior to processing. There may be inner-layer copper, as in the case of a multilayer laminated package, but no copper on the outer surface.

One of the differences in the through-hole plating process is, then, to prepare the non-copper, or polymer, surfaces to be receptive to electroless copper deposition and adhesion. In the case of a simple double-sided package, the panel may be treated as a plating-on-plastic exercise, but in the case of multilayers, one must also contend with the hole-interfacing inner-layer copper for desmearing operations and plating pretreatment to insure good copper-to-copper bonding between this inner-layer copper and the electroless copper deposition.

The basic substrate may consist of one of the following types:

- A treatable polymer—cast, laminated, or molded—that can be prepared to accept activation and, ultimately, electroless copper.
- A polymer composite material, such as epoxy/glass, epoxy/paper, polyester/glass, etc., covered with a polymeric coating that can be pretreated prior to the through-hole plating process in order to get acceptable electroless copper coverage and adhesion.
- An epoxy/glass substrate, or epoxy/paper substrate that is “resin-rich” at the surfaces, with a layer or “butter-coat” of epoxy to insure some minimal thickness of epoxy resin on the surface before one encounters glass or paper. In this way, the epoxy itself may be treated to get adhesion promotion for complete covering and adherent electroless copper.

The concept used in preparing non-copper-clad surfaces for electroless copper deposition is *site* development. A pocketed surface must be produced on which catalyst can be anchored, or, if pre-catalyzed polymer is used, to expose catalyst. The ultimate goal in both cases is to finally anchor electroless copper to the polymer surface.

Several options are available:

- The molded polymer, the adhesive used to coat the substrate, or the entire laminated package may be pre-impregnated with electroless copper-catalytic material. The job, then, would be to open the surfaces to expose catalyst and produce adhesion pockets, and to “develop” or “activate” the catalyst prior to electroless copper immersion. Several commercial techniques are available to accomplish these prerequisites—the choice is dependent on the polymers in question—but, typically, strong oxidizers such as chromic/sulfuric acid mixtures, chromic acid alone, or potassium permanganate solutions are employed.

- In the case of laminate substrate coated with an “adhesive” or plateable coating that is non-catalyzed, the panel is simply pre-treated to promote receptive pockets for catalyst and electroless copper deposition, and then treated with activator, post-activator, and electroless copper. Here again, strong oxidizing solutions are generally used to etch the polymer coating. In most instances, these solutions will also serve to desmear the drilled hole in the case of a multilayer composite.

- In the case of epoxy-butter-coated or epoxy-rich-surface epoxy/glass laminate composites, it is usual to first “swell” the polymer with an organic solvent to make it receptive to oxidative “etching” before entering the oxidizing solution. Other polymers may be “conditioned” in this manner as well. This technique is often referred to as “swell and etch”.

- A metal foil that has been anodized or oxidized on one side may be laminated to the polymer surface prior to the start of board manufacture. The pre-treatment process prior to catalyzation, then, would involve etching away the metal from the outer surfaces, thereby leaving pockets in the underlying polymer. Aluminum has been successfully employed for this purpose.

Where oxidants are employed, a step generally follows in the production sequence *prior* to activation, to neutralize, reduce, or otherwise remove all oxidizers from the panel.

In all of these techniques, one *very* important factor is that the polymer coating where electroless deposition is to occur and adhesion is to develop, must be of *consistent* satisfactory thickness to ensure that catalyst and electroless copper come into contact with this polymer coating *only*, and not with other materials, such as glass-fiber, paper, or underlying nontreatable polymer—otherwise, adhesion will be lost at these points of contact, eventually resulting in blistered plating. The coated polymer integrity must be such to ensure that the polymer pretreatment does not take away too much of it, either. These concerns relate primarily to surfaces, and not usually to holes in the panel, since adhesion in the holes is governed by the same mechanism that is involved in subtractive processes. Usually the holes are rough already, and the plating is somewhat “locked” into the hole because it is completely plated through, with no edge to be undercut, as in the case of circuitry lines on board surfaces.

In almost every method employed, at some step in the manufacturing process *after* electroless copper deposition, the panel will be heated or baked to lock in the electroless copper to the polymer. This is generally how “ultimate” adhesion is obtained.

Additive processing may be grouped into two general categories: semi-additive and fully additive.

Semi-Additive Processing

In this mode of processing, the panel is prepared to create surface polymer adhesion sites, neutralized or washed free of any oxidizing agents used, then activated (if the composite is not pre-activated), and immersed in electroless copper solution, so that the entire panel becomes covered with electroless copper. Usual thicknesses in semi-additive processing are 20 to 100 millionths of an inch of electroless copper. Panels may be flash-electroplated at this point if desired. Otherwise, the panel may now be treated as though it were copper-clad to begin with, and a plated-through-hole operation has simply been performed. Very little change in the overall mode of operation is required for a production facility to change from standard subtractive processing to semi-additive processing.

The benefit of processing in this fashion is that after final pattern plating, very little final etching is required to produce final circuitry. In fact, a solder overplate to circuitry as a final etch resist may not be necessary, since only 20 to 100 millionths in. of electroless has to be etched away as background copper, and this thickness can usually be sacrificed on the circuitry traces. This feature becomes most attractive when one is producing all copper circuits for solder-mask-over-bare-copper applications, whether or not hot air leveling or hot-oil leveling will be used.

Another feature of not having to use tin or tin-lead as a final etch resist overplate is that one is free to choose a wider range of final etchant chemistries, notably, cupric chloride or ferric chloride—these choices not possible when tin or tin-lead is used as a final etch resist.

An obvious advantage to eliminating tin-lead plating in particular is the elimination of the tin-lead stripping operation for SMOBC or for finger plating with nickel/gold. Also eliminated is a hazardous waste (lead) that would otherwise have to be dealt with from spent tin-lead stripping solutions.

The types of electroless copper plating solutions used in semi-additive processing are very similar to those used for standard subtractive processing, with one exception—the initiation of plating speed is generally inhibited to prevent too *rapid* a start of plating. This is done to ensure a low-porosity deposit. If the initiation is too rapid, spongy, high-porosity deposits will be obtained. A standard subtractive-processing electroless copper bath will usually initiate much faster on a polymeric coating because the polymer usually has a much higher density of palladium present, due to its surface structure being more highly “pocketed” than an etched copper-clad surface.

Fully-Additive Processing

Fully-additive processing differs from semi-additive processing in the fact that only circuit traces and holes will receive electroless copper—not the entire panel. Thus, all the plating must be done electrolessly, since there will be no underlying conductive path to allow electrolytic plating.

The process steps through activation are the same as for semi-additive processing. *Prior* to electroless copper immersion, however, those areas of the surface where copper is not wanted are masked with a plating resist.

The plating resist must be of a special type, since in fully-additive electroless copper plating, immersion times are very long (8 to 14 hours for 1 mil deposition) to achieve desired circuit thicknesses, and panels are immersed in a highly alkaline medium (the electroless copper) at elevated temperatures (usually 120 to 140° F). The resist must be very tenacious, and thus, will be hard to strip off after use. As a matter of fact, there is no reason to strip it off the panel at all, since no later processing step requires its removal. In most cases, then, the resist becomes an integral part of the final board. Because of this, however, the resist should possess electrical insulation characteristics and flammability requirements that the final product is intended to meet.

Once the resist is applied, it is usual to post-activate the panel to be plated, prior to electroless copper deposition.

The electroless copper formulations used for fully-additive processing are usually quite different from those formulations used in standard subtractive processing. The entire physical properties of the copper circuitry are now dependent on those of the electroless copper alone. Much research has been done to develop electroless coppers that will have physical properties adequate to meet the standards set by the printed circuit industry. Electroless coppers are available commercially that are adequate to this task.

Table 13.2 shows the minimum physical property values of electroless copper deposition that an electroless copper bath of this type is required to produce.

Generally, electroless copper densities are slightly lower than those of electrolytically deposited copper. This is probably a result of the slightly more

Table 13.2
Minimum Physical Properties
Of Fully-Additive Electroless Copper Deposits

Property	Units	Electroless copper*	Electrolytic copper**
Purity	%	99.2% minimum	99.9%
Density	g/cm ³	8.8 ±0.1	8.92
Resistivity (volume)	μOhm-cm at 20° C	1.90 maximum	1.72
Tensile strength	lb/in. ²	30,000 maximum	44,000
Percent elongation	%	3.0 minimum	10'

*According to IPC specification IPC-AM-372.

**Typical high-throw copper sulfate with brighteners.

open structure of the electroless deposit. In general, electroless copper deposits will etch somewhat faster than electrolytically deposited copper on an equal thickness basis.

Fully-additive processing is satisfactory to produce boards of many types, but there are some drawbacks when certain auxiliary electroplating operations are desired.

Table 13.3 serves to illustrate some of the differences between what is achievable through standard subtractive processing, semi-additive processing, and fully-additive processing.

A big advantage of using fully-additive processing is that *no* final etching is required, making this process ideally suited for fine line and close spacing board production. Also, since no electroplating is required, one need not worry about the skewness of a circuit pattern on the panel to be plated; therefore, circuitry of uniform height will be produced with fully-additive processing. This uniformity is not easily attainable through *pattern* electroplating if there is any degree of skewness in the board. One must electrolytically panel-plate to full thickness if one is to have any chance of obtaining uniform-height circuitry when skewed patterns are involved, usually as a result of uneven current density distribution across the panel.

The more important processing step differences between standard subtractive, semi-additive and fully-additive processes in the manufacture of a bare copper board (for solder mask over bare copper) are illustrated in Table 13.4.

Finally, control of the electroless copper bath is critically important in fully-additive processing. It is important to monitor the consumption of all the critical bath ingredients and to keep the plating rate steady throughout the long immersion times. This control is needed to insure that the correct physical properties are obtained. While physical properties are important with the thin electroless deposits used for standard subtractive and semi-additive processing, these deposits contribute only to a minor extent to the *overall* physical properties of the circuitry produced, since more than 90 percent of the circuitry thickness in these instances is produced with electrolytic copper, which is the major physical property contributor. In the case of fully-additive processing, if the electroless copper goes out of control in any way, the results can be disastrous. Automatic controllers are *highly* recommended in any additive circuitry processing for electroless copper maintenance.

Table 13.3
Comparison of Subtractive, Semi-Additive,
And Fully-Additive Electroless Copper Processes

Desired operation, achievement or feature	Subtractive	Fully-additive	Semi-additive
Solder/tin circuitry	Standard	Thin only (immersion)	Standard
Nickel/gold on tabs	Standard	Extremely difficult (bussing required)	Standard
Physical properties (thermal shock)	Standard	High degree of electroless copper control necessary	Close to standard
Plating resist	Standard	Special	Standard
Laminate	Standard	Special	Special
Process control	Standard	Critical	Close to standard
All copper circuits	Much etching and stripping required	Easy	Relatively easy
Etching costs	25 to 100% depending on foil thickness	0%	5 to 10% depending on electroless thickness
Drill life	Standard	Increased	Increased

Table 13.4
Comparison of Process Steps

Step	Subtractive	Semi-Additive	Fully-Additive*
1.	Cut panels	Cut panels	Cut panels
2.	Drill holes	Drill holes	Drill holes
3.	Deburr	Adhesion promote	Adhesion promote
4.	Clean	Water rinse	Water rinse
5.	Water rinse	Neutralize	Neutralize
6.	Microetch	Water rinse	Water rinse
7.	Water rinse	Pre-activate	Pre-activate
8.	Acid dip	Activate	Activate
9.	Water rinse	Water rinse	Water rinse
10.	Pre-activate	Post-activate	Dry
11.	Activate	Water rinse	Apply electroless resist
12.	Water rinse	Electroless copper	Post-activate
13.	Post-activate	Rinse, neutralize	Water rinse
14.	Water rinse	Dry	Electroless copper
15.	Electroless copper	Apply electroplating resist	Rinse, neutralize
16.	Rinse, neutralize	Clean	Dry
17.	Dry	Water rinse	Apply solder mask
18.	Apply electroplating resist	Microetch	
19.	Clean	Water rinse	
20.	Water rinse	Acid dip	
21.	Microetch	Electrolytic copper	
22.	Water rinse	Water rinse	
23.	Acid dip	Dry	
24.	Electrolytic copper	Strip resist	
25.	Water rinse	Water rinse	
26.	Acid dip	Final etch (FAST)	
27.	Water rinse	Rinse	
28.	Tin-lead or tin plate	Dry	
29.	Water rinse	Apply solder mask	
30.	Dry		
31.	Strip resist		
32.	Water rinse		
33.	Final etch		
34.	Rinse		
35.	Dry		
36.	Solder or tin strip		
37.	Apply solder mask		

ALTERNATIVE PROCESSES

Electroless copper is used in many other processes that have commercial viability in the production of printed wiring boards, using substrates in some instances that deviate from the typical laminates discussed so far in this chapter.

Processes exist for bonding electroless copper to ceramic substrates, thermoplastic materials (permitting the molding and circuitizing of boards *molded* into any three-dimensional shape), and for metallizing holes only, using print-and-etch or other schemes to produce discrete wiring patterns on board surfaces.

Generally speaking, the alternative processes use electroless copper solutions that operate similarly to the types of electroless copper discussed in this chapter. The differences in processing relate to surface preparation of the substrate involved and the imaging/activation techniques employed. With the trend toward finer lines and spacings on printed wiring boards, several processes have been developed that employ no classical *resist* materials to define circuitry for plating, but rather utilize *printing* (photoimaging) of an activated substrate to either activate or deactivate selected areas prior to electroless plating. In this fashion, the line definitions obtainable in the process are not subject to any limitations inherent to the plating resist itself.

Many interesting alternative processes, either using resist or photoactivation (resistless) techniques, have been developed, and references are given in the bibliography of this chapter for further investigation by the reader.

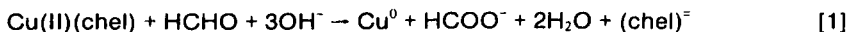
Much research has been done in recent years, and is continuing, on the use of activation systems for electroless copper that obviate the use of classical palladium activation, or for that matter, the use of any metallic-type activation at all.

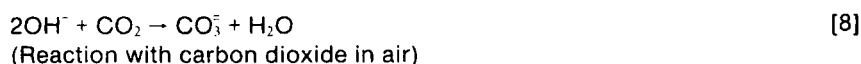
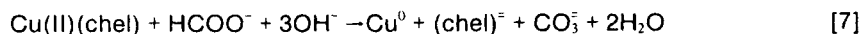
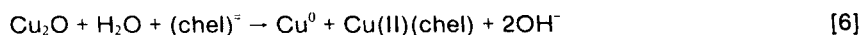
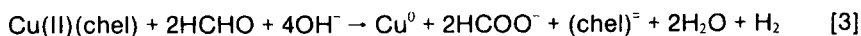
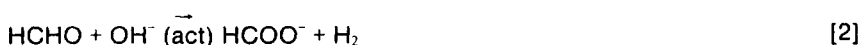
SUMMARY

The purpose of this chapter has been to acquaint the reader with general considerations about the use of electroless copper deposition in the manufacture of printed wiring boards. For further reading, the Bibliography references many texts and articles that have appeared in the literature, which the author feels will help to provide the reader with further depth into topics that may be of interest and could only be briefly mentioned in this chapter.

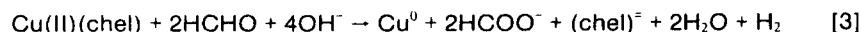
APPENDIX

The reactions pertinent to electroless copper deposition are as follows:





Combining Eqs. 1 and 2, the overall reaction is expressed in Eq. 3:

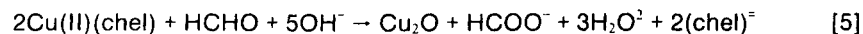


After the reaction is initiated with catalyst, the reaction becomes autocatalytic as a result of the presence of hydrogen gas in solution. As long as H₂ gas is being produced, reduction of more copper on freshly deposited copper surfaces continues. Reaction 3 can be made more efficient with respect to Reaction 1 by the inclusion of suitable additives to the electroless bath. This will result in less hydrogen evolution per unit of copper metal deposited and, in general, leads to better deposit characteristics.

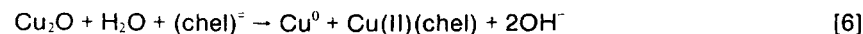
Some notable side reactions that occur are as follows:



This reaction tendency increases with the alkalinity of the bath. While it can be retarded to some degree, it is difficult to stop entirely.

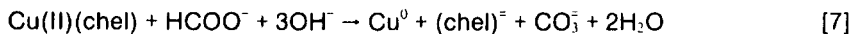


Particular attention has been paid to this reaction, since Cu₂O is only sparingly soluble, and early formulations contained no specific complexing agent (or "stabilizer") for Cu in the +1 valance state. Any Cu⁺¹ in the bath will not be as readily reduced to Cu⁰ via the catalytic reduction mechanism (Reaction 3) as will Cu⁺², but has a marked tendency to undergo spontaneous disproportionation to Cu⁰ and Cu⁺², to produce random copper particle formulation throughout the solution. This tendency is shown in Reaction 6:



A sizeable volume of research has been done to find ways of mitigating the effects of Cu(I) in electroless copper baths by either prevention of Cu₂O formation, inactivation of the Cu⁺¹ so formed, or retarding the disproportionation reaction.

The formate ion formed in many of the reactions presented thus far is, in itself, a good reducing agent in alkaline media, because of its aldehyde "character" and may react as such in the electroless copper bath.



Formate will not, however, catalytically or spontaneously reduce Cu(II) to Cu⁰, unless some formaldehyde is also present. When formate is present in considerable amount, the tendency is to promote the occurrence of Reaction 5, with resultant loss in solution stability.



This reaction occurs as a result of bath aeration and is most noticeable when baths are not utilized for long periods of time, yet continue to be aerated and replenished for sodium hydroxide. High carbonate levels will ultimately yield the electroless copper bath totally inactive. As the carbonate level rises, the alkalinity level of the bath by analysis will be progressively erroneous, because some contribution to the alkalinity reading will be made by the Na₂CO₃. The value obtained, then, is not all NaOH.

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