Electroless Copper Plating
A Review: Part I

By Cheryl A. Deckert

Electroless, or autocatalytic, metal plating is a non-electrolytic method of deposition from solution. The minimum necessary components of an electroless plating solution are a metal salt and an appropriate reducing agent. An additional requirement is that the solution, although thermodynamically unstable, is stable in practice until a suitable catalyzed surface is introduced. Plating is then initiated upon the catalyzed surface, and the plating reaction is sustained by the catalytic nature of the plated metal surface itself. This definition of electroless plating eliminates both those solutions that spontaneously plate on all surfaces (“homogeneous chemical reduction”), such as silver mirroring solutions; also “immersion” plating solutions, which deposit by displacement a very thin film of a relatively noble metal onto the surface of a sacrificial, less noble metal.

The history of electroless plating began with the serendipitous discovery, by Brenner and Riddell, of electroless nickel-phosphorus, during a series of nickel electroplating experiments in 1946. Electroless copper chemistry was first reported in the following year by Narcus. The first commercial application of electroless copper was reported in the mid-1950s with the development of plating solutions for plated-through-hole (PTH) printed wiring boards. Electroless copper solutions resembling today’s technology were first reported in 1957 by Cahill with the report of alkaline copper tartrate baths utilizing formaldehyde as reducing agent. Copper baths of the 1950s were difficult to control and very susceptible to spontaneous decomposition. Over the years, continual advances in control and capabilities have taken place and continue to be recorded in a variety of reviews. At present, not only are formulations extremely stable and predictable in behavior over long periods and under a wide variety of operating conditions, they also provide copper deposits having excellent physical and metallurgical properties comparable with electrolytic deposits.

Electroless copper plates much more slowly, and is a much more expensive process, than electrolytic copper plating. Electroless copper plating, however, offers advantages over electrolytic plating that make it the method of choice in certain cases. Electroless copper plates uniformly over all surfaces, regardless of size and shape, demonstrating 100 percent throwing power; it may be plated onto non-conductive, or conductive surfaces that do not share electrical continuity. The ability to plate large racks of substrates simultaneously is also an advantage in certain instances. These advantages have contributed to the choice of electroless copper in the applications to be discussed.

Bath Chemistry
The theoretical basis of the electroless copper deposition process has been studied on numerous occasions and has recently been reviewed. As stated earlier, the minimum necessary components of an electroless plating solution are the metal salt and a reducing agent. The source of copper is a simple cupric salt, such as copper sulfate, chloride or nitrate.

Various common reducing agents have been suggested for use in electroless copper baths, namely formaldehyde, dimethylamine borane, borohydride, hypophosphite, hydrazine, sugars (sucrose, glucose, etc.), and dithionite. In practice, however, virtually all commercial electroless copper plating solutions have utilized formaldehyde as reducing agent. This is a result of the combination of cost, effectiveness, and ease of control of formaldehyde systems, and is particularly remarkable in view of the considerable and continual pressures exerted on the plating industry by environmental and regulatory agencies because of health concerns regarding formaldehyde exposure. In view of their predominant commercial importance, the discussion will be confined to formaldehyde-based systems.

For copper(II), the relevant half-cell reaction for electroless deposition is:

\[ \text{Cu}^{2+} + 2e^- \leftrightarrow \text{Cu}^{0} \quad E^\circ = +0.340 \text{ V} \]

For formaldehyde, \( E^\circ \) depends on the pH of the solution:

\[ \text{HCOOH} + 2H^+ + 2e^- \leftrightarrow \text{HCHO} + H_2O \ (pH = 0, E^\circ = +0.056) \]

\[ \text{HCOO}^- + 2H_2 + 2e^- \leftrightarrow \text{HCHO} + 3OH^- \ (pH = 14, E^\circ = -1.070) \]

Therefore, electroless copper solutions, utilizing formaldehyde as reducing agent, employ high pH, above 12 (typical NaOH concentration is \( > 0.1 \text{ N} \); theoretically 0.1 N = pH 13).

Because simple copper salts are insoluble at pH above about 4, the use of alkaline plating media necessitates use of a complexing, or chelating, component. Historically, complexing agents for electroless copper baths have almost always fallen into one of the following groups of compounds:

1. Tartrate salts
2. Alkanol amines, such as quadrol (N,N,N',N'tetakis(2-hydroxypropyl)ethylenediamine) or related compounds
3. EDTA (ethylenediamine tetraacetic acid) or related compounds

Glycolic acids and other amines have also been reported.
Tartrates were used in the earliest baths, and continue to be used, particularly for low plating rate (≥0.5 µm/20 min), low-temperature (near ambient) applications. Tartrates are more easily waste-treatable than the other two classes of chelates, but have not readily lent themselves to formulation of faster plating systems.

Alkanol amines came into wide use in electroless Cu baths in the late 1960s, with the advent of faster plating systems. This type of chelate made it possible to achieve “high build” (≥22 µm/20 min) electroless copper solutions, and continues to have wide use even today. Since quadrol and its analogs are liquids, totally miscible with water, they are not easily removed from the waste solution; accordingly, they are resistant to many conventional waste treatment procedures.

EDTA salts are also widely used for complexing electroless copper solutions. EDTA has certain desirable characteristics vs. quadrol, based on waste treatability; specifically, EDTA can be more easily separated (precipitated) from waste solutions by pH adjustment. Starting in the late 1970s, bath additives for EDTA systems were developed that allowed excellent control of plating rate, grain structure, and other important factors. Because of the very high affinity of EDTA for any metal ions, even small residual amounts of dissolved EDTA can draw potentially toxic metals into the waste stream. This has led to increased legislative efforts (notably in Germany and Japan) against use of this chelate and its derivatives. At present, however, the most commonly used plating baths are based on EDTA.

In addition to the copper salt, reducing agent, source of alkalinity, and chelate, other important components are present in commercial electroless copper solutions. These components are generally considered the proprietary portion of the formulation, and control such parameters as initiation and plating rate, stability (vs. dragged-in catalyst; vs. excessively high bath activity; vs. long shutdown periods; vs. Cu(I) oxide), deposit stress, color, ductility, etc. Prior to development of well-characterized and controlled trace additives, electroless copper baths were prone to “triggering” (spontaneous decomposition of the bath), “plate-out” (decomposition over a prolonged standing period), “second-day startup” (inability to induce a controlled plating reaction when first stored after make-up), dark deposit color, rough deposit, coarse grain structure, and other undesirable characteristics. Literally hundreds of papers and patents have been published relating to these additives. Useful summaries of these data are available.9,10

Additives that stabilize the bath against various manifestations of undesired plate-out are referred to as stabilizers; understanding their composition, mechanism, and optimal replenishment rate is key to successful operation of a bath. They are usually employed at low concentrations, typically one to 100 ppm. Principal among the materials reported are compounds such as mercaptobenzothiazole, thiourea, other sulfur compounds, cyanide or ferrocyanide salts, mercury compounds, molybdenum and tungsten, heterocyclic nitrogen compounds, methyl butynol, propionitrile, etc. Pressure from environmental and regulatory groups over the years has led to near elimination of cyanide and mercury types of additives. It is noteworthy that perhaps the most common stabilizer for electroless copper baths is a steady stream of air (i.e., oxygen) bubbled through the solution.

Additives that increase the plating rate of the solution are variously referred to as rate promoters, rate enhancers, exaltants, or accelerators. This last term is particularly unfortunate and confusing in view of the use of the term “accelerator” as a key process step in electroless copper processes. Materials that have been reported to function as rate promoters include ammonium salts, nitrates, chlorides, chlorates,

### Table 1

<table>
<thead>
<tr>
<th></th>
<th>Low Build</th>
<th>High Build</th>
<th>High Build</th>
<th>Full Build</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Tartrate)</td>
<td>(Quadrol)</td>
<td>(EDTA)</td>
<td>(EDTA)</td>
</tr>
<tr>
<td>Copper salt as Cu(II)</td>
<td>1.8 g/L 0.028 M</td>
<td>2.2 g/L 0.035 M</td>
<td>2.0 g/L 0.031 M</td>
<td>3.0 g/L 0.047 M</td>
</tr>
<tr>
<td>Chelate Rochelle salt</td>
<td>25 g/L 0.089 M</td>
<td>Quadrol</td>
<td>13 g/L 0.044 M</td>
<td>Disodium EDTA dihydrate 30 g/L 0.080 M</td>
</tr>
<tr>
<td>Formaldehyde as HCHO</td>
<td>10 g/L</td>
<td>3 g/L</td>
<td>3 g/L</td>
<td>1.5 g/L</td>
</tr>
<tr>
<td>Alkalinity as NaOH</td>
<td>5 g/L</td>
<td>8 g/L</td>
<td>7 g/L</td>
<td>3 g/L</td>
</tr>
<tr>
<td>Additives*</td>
<td>&lt;2 g/L</td>
<td>&lt;2 g/L</td>
<td>&lt;2 g/L</td>
<td>&lt;2 g/L</td>
</tr>
<tr>
<td>Temperature ºC</td>
<td>20</td>
<td>43</td>
<td>45</td>
<td>70</td>
</tr>
<tr>
<td>Plating rate µm/20 min</td>
<td>0.2</td>
<td>2.5</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

*Examples of additives: 2-mercaptobenzothiazole, diethylthiocarbamate, 2,2'-dipyridyl, potassium ferrocyanide, vanadium pentoxide, nickel chloride, polyethylene glycol

![Figure 2](image.png)

Fig. 2—Examples of commercially produced molded interconnect devices. (Courtesy of J. Rychwalski, Shipley Co.)
perchlorates, molybdates and tungstates. Rate promoters may be present in the electroless formulation at concentrations of 0.1 M or higher.

Other additives may also be incorporated in certain cases. For example, surfactants may be used to improve deposit characteristics; incorporation of excess halide ion into the formulation permits elimination of the normal accelerator step. Typical examples of freshly made-up electroless copper baths are given in Table 1.

The overall electroless copper plating reaction is theoretically given as:

$$\text{Cu}^{2+} + 2\text{HCHO} + 4\text{OH}^- \rightarrow \text{Cu}^0 + \text{H}_2 + 2\text{H}_2\text{O} + 2\text{HCO}_2^-$$

This equation calls for consumption of four hydroxyl ions and two molecules of formaldehyde for each atom of copper deposited. Certain side reactions may also take place, however, the most common being the Cannizzaro reaction, which consumes additional caustic and formaldehyde:

$$2\text{HCHO} + \text{OH}^- \leftrightarrow \text{CH}_3\text{OH} + \text{HCOO}^-$$

In addition, other side reactions also occur, consuming formaldehyde and producing unwanted byproducts, such as cuprous oxide, which can lead to bath decomposition unless suitable stabilizers are present.

Once use of the bath begins, copper, caustic and formaldehyde are consumed and must be replenished. This is typically carried out by routine analysis, either manually or electronically, with back addition of appropriate replenishment chemicals. Ordinarily, some bailing of the plating solution must be done at this point, to allow for the volume of new chemicals to be added. Because the anion of the copper salt (usually sulfate or chloride), and the cation of the caustic component (usually sodium) are not consumed, a build-up of sodium sulfate or chloride occurs, which can cause deleterious effects, such as “voiding” or high deposit stress over prolonged bath life, particularly when bailed volumes are very low. In addition, formate ion builds up as a by-product of the plating reaction itself. The extent to which the Cannizzaro reaction takes place also contributes to the quantity of by-product build-up. By-product build-up can cause deterioration of bath and deposit properties, and is now typically accounted for during bath formulation. Steady-state performance is achieved after a specified number of bath turnovers (or “cycles”), depending on the recommended bailed volume, and is typically controlled through specific gravity.

**Deposit Properties**

**Plating Rate/Deposit Thickness**

Not strictly a deposit property, plating rate is a key characteristic of an electroless copper plating bath. Plating rate and useful range of deposit thickness dictate the specific applicability of a formulation. Plating baths are typically categorized as one of the following:

**Low Build:** Deposits about one-half µm (or less) in about 20 min, and typically operates at ambient temperature. This was typical of the earliest stable bath formulations developed in the 1960s. These baths are traditionally tartrate-based; in fact, it has proven difficult to formulate stable, faster plating baths using a tartrate-chelate system. These deposits are typically fine-grained and exhibit good deposit integrity.

**High (Heavy) Build:** Deposits two to three µm in about 20 min; typically operates at elevated temperature (35 to 55 °C), but room temperature formulations are also available. These baths are usually based on EDTA or quadrol chemistry. Acceptable formulations of this type were first developed near the early 1970s. Earlier baths tended to give coarse-grained deposits and produced somewhat highly stressed deposits; however, these formulations have been greatly refined and are readily controlled to give excellent deposit properties. A major application for this type of bath is in situations where intervening process steps may occur prior to subsequent plate-up, such as with pattern plate printed wiring boards.

**Full Build:** Typically deposits 25 µm, or more, of copper over a more prolonged plating cycle of as many as 15 hr. (By comparison, a typical electroplating process would deposit 25 µm of copper in 35 to 50 min.) Typical temperature of operation is 55 to 80 °C. A fundamental requirement in developing this type of bath has been the realization and maintenance of deposit characteristics, such as high ductility and tensile strength, fine grain structure, low intrinsic stress, etc., throughout the thick deposit. This type of bath was first reported in 1964, and has been employed primarily in the additive type of printed wiring board application. EDTA has been the main chelate used. This deposit typically represents the full metal thickness required for the application, and so eliminates the need for electroplating altogether (Fig. 1). The very high expense of building a thick copper deposit using an electroless vs. electroplating process is warranted (and required) for certain applications, such as the case when absolutely uniform thickness is needed, when electrically discontinuous surfaces are to be plated, or when very high aspect-
ratio holes are to be plated. Processes for fabricating multichip modules (MCMs), for example, require a full-build electroless copper; in this application, the copper thickness requirement may be substantially less than 25 µm. A number of advances in the area of full-build copper plating have occurred over the past five or more years. The most critical deposit characteristics are ductility and tensile strength, particularly at the elevated temperatures (260 to 288 °C) employed in printed wiring board assembly processes. Current development activities in this area have the goal of substantially higher plating rates without loss of deposit properties.

Other: Of course, intermediate thicknesses of copper are attainable by appropriate manipulation of the bath’s operating parameters. Very Slow and Medium Build formulations are also utilized in some of the applications to be discussed.

Purity, Density and Electrical Properties
Deposit purity of electroless copper films is somewhat lower than that of electrolytic films, because of codeposition of traces of electroless bath components. This alters several physical properties, including percent purity, density, and resistivity. Typical acid-copper electrolytic baths produce films of 99.9 percent purity, 8.92 g/cm³ density, and 1.72 µΩ-cm volume resistivity (at 20 °C), whereas the printed wiring board industry standard for full-build electroless copper is 99.2 percent purity (min.), 8.8 ±0.1 g/cm³ density, and 1.90 µΩ-cm (at 20 °C) resistivity (max.).

Grain Structure
Because electroless copper deposition is initiated on the randomly distributed catalytic particles on the substrate, initial grain structure is largely determined by the morphology of that surface. Bath formulation is, of course, a strongly determining factor as well, and will control the grain structure as the deposit thickness increases. It is thought that fine-grained deposits, initiating at close proximity on the catalytic sites, and coalescing to form a film early in the deposition process, offer superior copper quality in the early stages of film growth. Recently, full-build electroless copper grain structure was studied, correlated with etching rate in a variety of common copper foil etching solutions and compared with typical electrolytic copper grain structure.

Tensile Strength and Ductility
Advances in electroless copper formulations, particularly for full-build applications with printed wiring boards, have centered on obtaining desirable mechanical properties, specifically tensile strength and ductility, which ensure the needed film reliability. Tensile strength of up to 70 kpsi (50 kg/mm²), and elongation of as much as 15 percent can now be achieved, although these properties are not derived from the same formulation. Improvement in the as-plated elongation values may be obtained with heat aging, at the expense of tensile strength. It has also been reported that ductility at thermal shock temperature (e.g., 260-288 °C) may be significantly higher than as measured at ambient temperature. Some discussion is still in progress, regarding the relative importance of these two properties in defining an ideal plated deposit. Other deposit properties, such as hydrogen inclusion, are also of interest.

Applications
Printed Wiring Boards (PWBs)
By far the most important commercial application of electroless copper plating has been the PTH process for fabricating printed wiring boards. Prior to the mid-1950s, mounting components on PWBs relied on mechanical interlocking, using inserted eyelets. The through-holes could not be electroplated directly because the base material of the circuit board (paper-phenolic, epoxy-glass, or other dielectric) did not provide the needed electrical conductivity. Development of electroless copper plating solutions, made practical by concurrent development of suitable selectively-adsorbing catalytic materials, led to a dramatic improvement in the reliability of printed circuit boards, and prompted the rapid growth of the PWB market during the 1960s through 1980s.

The vast majority of printed wiring boards is made by a subtractive process, using base material, typically epoxy-glass laminate, clad with electrolytic copper foil. The substrate is drilled, after which electroless copper is plated through the holes (and incidentally over the foil surface). Then, electrolytic copper build-up and surface copper imaging (using dry film) take place; the order of these processes defines the fabrication process as either panel plating or pattern plating. In pattern plating, the plated areas are next overplated with a dissimilar metal (typically Sn/Pb), the dry film is removed, and all exposed copper is etched. In panel plating, no dissimilar metal plating is required; etching takes places immediately after imaging. The term subtractive processing arises from the fact that the circuitry is ultimately formed by removing base copper from the circuit board.

Although the basic overall process flow for fabricating a PWB has remained essentially constant for decades, the technology associated with every subprocess has undergone great improvement over that time, and the electroless copper pro-
cess is no exception. Improvements in electroless copper formulations, as discussed earlier, have greatly improved control of PWB processing and end product reliability. Developments in PTH pretreatment, however, have probably contributed even more greatly to end board reliability over that period. New hole preparation methods for multilayer boards were found to provide substantial benefit in terms of key criteria, such as copper coverage, adhesion (to laminate) and solderability,\textsuperscript{23} to the extent that two-sided boards are also frequently processed through these additional steps. Careful integration of the steps immediately preceding catalysis has also ensured that the optimal uniform, yet minimal, catalyst film is deposited in preparation for plating; this has provided the key to gaining interconnector bonds sufficiently strong to withstand multiple thermal shocks,\textsuperscript{24} assuring very high end product reliability. At present, the PWB market is under considerable environmental and cost pressure to replace electroless copper with a direct metallization process. Recent quality improvements, such as those described, represent a significant opportunity for replacement technologies.

Additive processes for PWBs rely, as the name implies, on the build-up of the circuit copper over bare laminate. Variations on the fully-additive process include semi-additive and partly additive processes. Description of these is documented in many published reports, which have been recently reviewed.\textsuperscript{25} Fully-additive processes have been in use since 1964, and offer a number of advantages over conventional subtractive processing. Despite this, growth in the additive market has been slow; worldwide production in 1992 has been estimated at two to five percent of the world PWB production.\textsuperscript{26,27} This slow growth is partly a result of the more difficult adhesion and selectivity requirements, and partly because of the lack of adequate physical properties in the full-build electroless copper, which is an integral component of the process. However, in recent years the quality of full-build electroless has become satisfactory; this, coupled with improved process control and new automatic bath controllers, provide support for future growth of the additive PWB market.

Decorative Plating-on-Plastics (POP)\textsuperscript{28} Since the 1950s, plastics have been substituted for metals in a multitude of applications, and for a variety of reasons, including weight and cost advantages, as well as the relative ease of creating complex-shaped substrates through molding. These factors prompted the development of suitable decorative finishing processes, specifically plating processes, starting in the early 1960s. Electroless metal deposition as a base for a thicker, decorative electrolytic deposit, has proven extremely reliable and commercially successful. For lower performance applications, electroless nickel is a suitable choice; however, since the demonstration in the 1970’s,\textsuperscript{29,30} that electroless copper provides better resistance to environmental exposure, Cu has become the material of choice in the majority of higher performance applications, especially automotive. The molded substrate is chemically treated to improve adhesion of the copper film, then about 0.5 to 0.75 \( \mu \text{m} \) of electroless copper is applied. Typically an electrolytic copper or Watts nickel strike follows, then a thicker (12 to 25 \( \mu \text{m} \)) electrolytic bright acid copper deposit. Finishing coats of electrolytic nickel and/or chromium plating are then applied.

Substrate materials\textsuperscript{28} for decorative plating-on-plastic include ABS (acrylonitrile-butadiene-styrene), ABS/polycarbonate, polyethylene-oxide, polycarbonate, polysulfone, polyester, nylon, etc. There are many grades of a given plastic, which may differ considerably in platability. Certain grades of foamed plastics may also be used. For decorative POP, ABS is by far the most commonly used plastic. ABS is a thermoplastic alloy with an acrylonitrile-styrene matrix that has butadiene rubber dispersed throughout. The butadiene is selectively etched by the pretreatment chemistry, creating a uniformly roughened surface suitable for plating.

In all plating-on-plastics applications, control of the molding process is critical. Care must be taken to avoid introducing stresses or strains, to avoid troublesome mold-release agents, to limit use of “regrind” resin, to ensure a resin-rich surface (in cases where fillers are used), etc. The use of complex-shaped parts necessitates close attention to such details as mold design and maintenance, melt and mold temperatures, fill speed, and many other parameters. It is critical, in designing or troubleshooting a plating-on-plastic process, to use molded parts from the actual application, as there is high interdependence between molding and plating processes.

Functional Plating-on-Plastic (EMI Shielding) Another commercially important application for electroless copper is in electromagnetic interference (EMI) shielding of electronic components. The need to reduce (attenuate) electromagnetic signals,\textsuperscript{31} generated either internally or externally, for a packaged component necessitates EMI shielding. Shielding capability is directly related to conductivity of the component; accordingly, metal cases are highly effective in attenuating EMI. The same factors (cost, weight), however, that led to use of plastics as base materials for decorative applications have also led to their implementation in electronic cabinetry. Because plastic enclosures are poor at attenuating EMI signals, a variety of coating methods has been developed to address this need. These methods include electroless copper plating, as well as various types of metal-filled paints, zinc arc/flux spray, sputtered or evaporated metals, and conductive foils/tapes. Table 2 summarizes and updates published data,\textsuperscript{32,33} on the most common methods of shielding. Key in choosing a method is the attenuation (measured in decibels) over a desired frequency range.\textsuperscript{34} Note that decibels of shielding is a logarithmic term, so a difference of 20 dB equals 100 times the shielding effectiveness.

Clearly, electroless copper is a very effective method of EMI shielding over a wide range of radio frequencies, having been first suggested in 1966\textsuperscript{35} and subsequently developed in the early 1980s.\textsuperscript{36} Considerable commercial development has taken place, as several large computer manufacturers anticipated that higher clock speeds of electronic devices would require rapid conversion to the most effective methods of EMI shielding, such as electroless copper. Up to this time, however, development of electroless copper for EMI shielding applications has lagged vs. the rate previously anticipated. It is believed that sustained growth in the use of electroless copper for EMI shielding is probable in the future, because of increased “clock speed” of the device emitting the signal, which accentuates the need for more effective shielding.

In employing electroless copper for EMI shielding, the conductive film used typically consists of electroless copper plating to about 0.7 to 2 \( \mu \text{m} \) thickness, overplated with a thin film (0.25 to 0.5 \( \mu \text{m} \)) of electroless nickel. The parameter used to specify copper thickness is surface resistivity,\textsuperscript{37} normally less than 0.05 \( \Omega/\text{square} \) is readily achievable using
electroless copper. The nickel contributes virtually nothing to the shielding effectiveness, but provides durability and corrosion resistance.

Specific substrate resins used in electronic enclosures include solid and/or foamed forms of ABS, polycarbonate, ABS/polycarbonate alloys, polyphenylene oxide, poly styrene, and polysulfone. A newly emerging, and potentially very large, market involves electroless copper for shielding fabric used in cable, military and wall covering applications.

Electroless copper plating for EMI shielding may employ either a two-sided or single-sided process. In the two-sided process, the entire cabinet is treated and plated; this approach generally requires a finish coat of paint. The single-sided process involves plating of the interior surface only and the molded plastic surface represents the final surface finish. These two processes involve totally different pretreatments, to be discussed in a later section.

**Hybrid and Advanced Applications**

**Molded Interconnect Devices**

Following on advances in control and capability of imaging and plating technologies, and on commercialization of high-performance injection molded plastics, a natural development was the molded circuit board or molded interconnect

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**Table 2**

**Methods of EMI Shielding**

<table>
<thead>
<tr>
<th>Material/Method</th>
<th>Shielding Capability*</th>
<th>Process Cost*</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc arc spray</td>
<td>H</td>
<td>H</td>
<td>Good conductivity</td>
<td>Special equipment needed</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hard, dense coat</td>
<td>Prone to flaking</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Very effective</td>
<td>May distort housing</td>
</tr>
<tr>
<td>Conductive paints</td>
<td>VH</td>
<td>VH</td>
<td>Good conductivity</td>
<td>Expensive</td>
</tr>
<tr>
<td>Silver</td>
<td></td>
<td></td>
<td>Conventional equipment</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Resist flaking</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Easy to apply</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>L</td>
<td>M</td>
<td>Conventional equipment</td>
<td>Multiple coats needed</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Effectiveness not high</td>
<td>Thickness causes problems</td>
</tr>
<tr>
<td>Copper</td>
<td>M–H</td>
<td>M</td>
<td>Conventional equipment</td>
<td>Multiple coats needed</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Thickness causes problems</td>
<td></td>
</tr>
<tr>
<td>Evaporated metal</td>
<td>M</td>
<td>H</td>
<td>Familiar technology</td>
<td>Size limited by vacuum chamber</td>
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<tr>
<td>Sputtered metal</td>
<td>M</td>
<td>M</td>
<td>Good conductivity</td>
<td>Expensive equipment</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Expensive equipment</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>May distort housing</td>
<td></td>
</tr>
<tr>
<td>Conductive foils/tapes</td>
<td>H</td>
<td>VH</td>
<td>Good conductivity</td>
<td>Complex parts are difficult</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Good for experimentation</td>
<td>Labor-intensive</td>
</tr>
<tr>
<td>Conductive plastics</td>
<td>L</td>
<td>L</td>
<td>No secondary process</td>
<td>Material expensive</td>
</tr>
<tr>
<td>Electroless plating</td>
<td>VH</td>
<td>M</td>
<td>Uniform thickness</td>
<td>Limited to certain plastics</td>
</tr>
<tr>
<td>Copper (2-sided)</td>
<td></td>
<td></td>
<td>Good for all shape parts</td>
<td>2-sided process usually requires paint finish</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Resists chipping</td>
<td>Prone to oxidation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Good conductivity</td>
<td></td>
</tr>
<tr>
<td>Nickel (2-sided)</td>
<td>M</td>
<td>H</td>
<td>Same as above, except conductivity</td>
<td>High thickness required for effective shielding</td>
</tr>
<tr>
<td>Copper/Nickel (2-sided)</td>
<td>VH</td>
<td>M</td>
<td>Same as copper only, plus corrosion resistant</td>
<td>Same as copper only, except no oxidation</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Copper/Nickel (1-sided)</td>
<td>H</td>
<td>M</td>
<td>Same as Cu/Ni 2-sided</td>
<td>Same as Cu/Ni 2-sided, except no finish coat</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fewer chemical steps</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Allows molded-in-color</td>
<td></td>
</tr>
</tbody>
</table>

*Table based on data in Ref. 32 and 33.

<table>
<thead>
<tr>
<th>Attenuation</th>
<th>Cost, $/ft²</th>
</tr>
</thead>
<tbody>
<tr>
<td>VH = very high</td>
<td>90-120 dB+</td>
</tr>
<tr>
<td>H = high</td>
<td>60-90 dB</td>
</tr>
<tr>
<td>M = moderate</td>
<td>30-60 dB</td>
</tr>
<tr>
<td>L = low</td>
<td>10-30 dB</td>
</tr>
<tr>
<td>VL = very low</td>
<td>0-10 dB</td>
</tr>
</tbody>
</table>
device (MID). Adhesion promotion principles developed for the decorative POP industry have been applied to adhesion promotion processes for a variety of engineering thermoplastics, permitting deposition of adherent electroless copper coatings that could be built up in thickness and imaged similarly to conventional printed wiring boards.

In certain cases, conventional plastics (such as ABS) have been used as MID substrates; however, in order to survive board assembly temperatures, more advanced plastics are often required; these include polyetherimide, polyethersulfone, polyarylsulfone, liquid crystal polymers, etc. Molding requirements are even more critical than for decorative POP because of the need for higher levels of adhesion (typically $\geq 1.1$ kN/m (6 lb/in.) peel strength vs. approx. $0.7$ kN/m for decorative POP), and to the stresses induced by plate-up, imaging and assembly processes. Certain of the plastics mentioned have proven more amenable than others to development of suitable adhesion promotion processes. Polyetherimide, in particular, has proved compatible with surface chemistry-altering pretreatments that produce very strongly adherent electroless copper, while not roughening the substrate surface excessively. The latter characteristic is particularly important when fine-line imaging processes are to be employed later in the operations.

Depending on the MID design and process chosen, plate-up of the initial electroless copper strike plate may employ either electrolytic copper or full-build additive copper (20 to 35 $\mu$m). Imaging of three-dimensional substrates has necessitated development of inventive materials and processes. Electrodeposited photoresists, as well as novel methods of exposure and related equipment, have proven key in this effort.

At present, the molded interconnect device market has proven feasibility and has achieved commercial success in several dedicated facilities. Many ingenious and cost-saving devices have been designed and are currently in production. Figure 2 demonstrates a number of commercially produced MIDs. This market has not achieved the level of acceptance predicted in the late 1980’s, however, as a consequence of several factors, including the need for high volumes of a given design to amortize mold costs, failure of material costs to come down to required levels, and tendency of electronic designers to employ more familiar methods, such as conventional PWBs, whenever possible.

**Composite Connectors**

The composite connector application is a hybrid of two-sided EMI shielding with molded interconnects. These parts are currently made of aluminum, and for all the usual reasons, considerable interest lies in replacing the aluminum with a lighter material, such as plastic. The physical requirements of the connector are such that only advanced engineering plastics, such as those used in the MID market, are suitable. The parts must be plated, not to form circuitry, but to provide EMI shielding. Fabrication of these devices employs the plastics and pretreatments for electroless plating employed for molded interconnects. Because of the durability, lubricity and hardness requirements of the finished parts, the electroless nickel overcoat is built up to a noticeably higher thickness (~5 $\mu$m) than for EMI shielding of electronic cabinetry. Examples of some plastic composite connectors, processed through electroless copper and nickel, are shown in Fig. 3.

**Multichip Modules**

Progress in semiconductor technology continues to place increasing demands on interconnection and assembly technology. In the 1980s, the response to this demand on the PWB side was increasing numbers of layers and finer circuitry. This trend cannot be sustained at the needed rate, leading to the requirement for an intermediate level of interconnection onto which bare chips may be mounted. These devices, known as multichip modules (MCMs), may be fabricated using several approaches; however, a common feature is the use of full-build electroless copper to build up the conductive traces.

An example of a fabrication process for an MCM is given in Fig. 4. The electroless copper subprocess generally follows the procedures of the PTH and POP processes to be discussed in more detail later. Adhesion promotion for the metallization layer to the unique dielectric materials employed in MCMs can be a challenge in itself. Conventional “swell and etch” approaches are normally used; other approaches are also in development.

**Silicon Devices**

Recently some interest has arisen in employing electroless copper for integrated circuit manufacture. It is felt that aluminum, used in providing the conductive path on chips, may not be sufficiently conductive at the very high resolutions required in future devices. Very thin films of electroless copper (~0.1 to 0.2 $\mu$m), deposited additively in channels between a photodefined temporary film, have been used.
Acknowledgment

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About the Author

Dr. Cheryl A. Deckert is currently manager of Product Engineering and Manufacturing Development at Shipley Company, 500 Nickerson Rd., Marlborough, MA 01752. She was principal inventor and developer of Shipley’s permanganate desmear processes for multilayer printed wiring boards, of self-accelerating electroless copper formulations, and of high-reliability desmear-PTH processes. She has also managed various R&D programs in interconnect imaging. She has served as Shipley’s European technical manager and as business development technical marketing manager, in addition to numerous R&D roles, prior to assuming her current position. Dr. Deckert is author of co-author of more than 30 papers, inventor or co-inventor of five patents, and has presented papers at numerous scientific and trade gatherings.
Electroless copper deposition. The first step in the plating process is the chemical deposition of a very thin layer of copper on the hole walls. The operator clamps the production panels into the jigs. The line is fully computer controlled and the panels are carried through a series of chemical and rinsing baths by the overhead crane. Almost all PCBs with 2 or more copper layers use plated through holes to connect the conductors between the layers. A good connection needs about 25 microns of copper on the walls of the holes. This thickness must be electroplated, but the walls of the holes are Electroless plating, also known as chemical or auto-catalytic plating, is a non-galvanic plating method that involves several simultaneous reactions in an aqueous solution, which occur without the use of external electrical power. It is mainly different from electroplating by not using external electrical power. In the manufacture of printed circuit boards, electroless plating is used to form the conductive part of plated through holes. The non-conductive part is treated with palladium catalyst and Electroless copper plating for defense, aerospace, biomedical, communications, medical, military and other applications. Various processes include electroless nickel, gold, rhodium and high phosphorus electroless nickel plating. Capable of plating parts up to 5.5 ft. dia. Prototype to specialty and low volume production can be done. Emergency and rush services available. Electroless copper plating services for parts and components manufactured from engineered plastics or metal alloys. Acid, pyrophosphate and diffused plating services are also offered. Electroforming can be done on copper in excess of 0.060 in.