Chapter 2
Profile of the Making Holes Conductive Use Cluster

This section of the Cleaner Technologies Substitute Assessment (CTSA) describes the technologies that comprise the making holes conductive (MHC) use cluster. A use cluster is a set of chemical products, technologies, or processes that can substitute for one another to perform a particular function. In this case, the function is "making holes conductive" and the set of technologies includes electroless copper, carbon, conductive polymer, graphite, non-formaldehyde electroless copper, organic-palladium, and tin-palladium. Information is also provided for a conductive ink technology, which can be used to perform the MHC function on double-sided boards, but not multi-layer boards.

Section 2.1 presents process descriptions for each of the MHC technologies and describes the chemical composition of MHC chemical products that were evaluated in the CTSA. Section 2.2 briefly describes additional technologies that may be used to perform the MHC function, but were not evaluated. Section 2.3 summarizes the market for MHC technologies, including information on the total market value of MHC chemicals, and the market shares of electroless copper processes as compared to the technologies.

2.1 CHEMISTRY AND PROCESS DESCRIPTION OF MHC TECHNOLOGIES

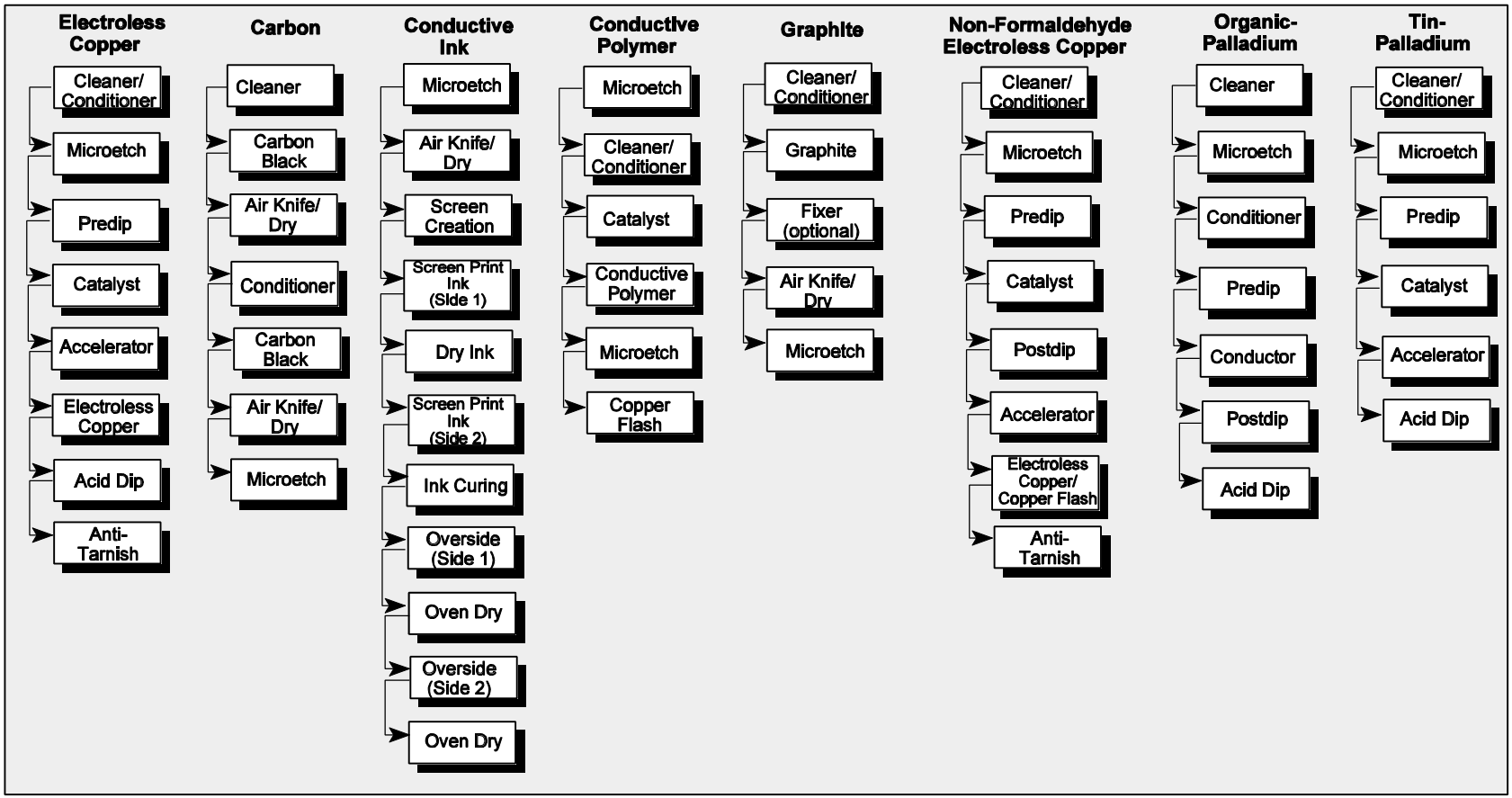
This section introduces the MHC technologies evaluated in the CTSA and details the MHC process sequences, including descriptions of individual process baths in each of the technologies. Typical operating conditions and operating and maintenance procedures are described in an overview of the MHC manufacturing process. The chemical processes occurring in each bath are detailed along with additional process information specific to each technology. Finally, this section describes the sources of bath chemistry information, methods used for summarizing that information, and use of publicly-available bath chemistry data.

2.1.1 Substitutes Tree of MHC Technologies

Figure 2.1 depicts the eight MHC technologies evaluated in the CTSA. Because the function of MHC can be performed using any of these technologies, these technologies may "substitute" for each other in PWB manufacturing. Except for the conductive ink technology, which is a screen printing technology, each of the MHC technologies is a wet chemistry process, consisting of a series of chemical process baths, often followed by rinse steps, through which a rack of panels is passed to apply the conductive coating or seed layer.

For each of the wet chemistry technologies, the process baths depicted in the figure represent an integration of the various commercial products offered within a category. For example, chemical suppliers to the PWB industry submitted product data for six different electroless copper processes for evaluation in the CTSA, and these and other suppliers offer additional variations to the electroless copper processes that may have slightly different bath

Figure 2.1 Substitutes Tree of MHC Technologies[a]



[a] The conductive ink technology can substitute for MHC technologies used to manufacture double-sided PWBs, but not multi-layer PWBs.

chemistries or bath sequences. Figure 2.1 lists the types of baths in a typical, or generic, electroless copper line, but the types of baths in an actual line may vary.

2.1.2 Overview of MHC Technologies

MHC technologies typically consist of a series of sequential chemical processing tanks separated by water rinse stages. The process can either be operated in a vertical, non-conveyorized immersion-type mode or in a horizontal, conveyorized mode. In either mode, selected baths may be operated at elevated temperatures to facilitate required chemical reactions, or agitated to improve contact between the panels and the bath chemistry. Agitation methods employed by PWB manufacturers include panel agitation, air sparging, and fluid circulation pumps.

Most process baths are followed by a water rinse tank to remove drag-out, the clinging film of process solution covering the rack and boards when they are removed from a tank. Rinsing is necessary to provide a clean panel surface for further chemical activity, while preventing chemical drag-out which may contaminate subsequent process baths. PWB manufacturers employ a variety of rinse water minimization methods to reduce rinse water usage and consequent wastewater generation rates. The nature and quantity of wastewater generated from MHC process lines are discussed in Section 3.1, Source Release Assessment, while rinse water reduction techniques are discussed in Section 6.1, Pollution Prevention.

In non-conveyorized mode, drilled multi-layered panels are desmeared, loaded onto a rack, and run through the MHC process line. Racks may be manually moved from tank to tank, moved by a manually or automatically controlled hoist, or moved by other means. Process tanks are usually open to the atmosphere. To reduce volatilization of chemicals from the bath or worker exposure to volatilized chemicals, process baths may be equipped with a local ventilation system, such as a push-pull system, bath covers for periods of inoperation, or floating plastic balls. Conveyorized systems are typically fully enclosed, with air emissions vented to a control technology or to the atmosphere outside the plant.

Regardless of the mode of operation, process baths are periodically replenished to either replace solution lost through drag-out or volatilization, or to return the concentration of constituents in the bath to within acceptable limits. During the course of normal operations, bath chemistry can be altered by chemical reactions occurring within the bath, or by contamination from drag-out. Bath solution may be discarded and replaced with new solution, depending on analytical sampling results, the number of panel surface square feet (ssf) processed, or the amount of time elapsed since the last change-out. Process line operators may also clean the tank or conveyorized equipment during bath change-out operations.

Some process baths are equipped with filters to remove particulate matter, such as copper particles plated out of solution due to the autocatalytic nature of the electroless copper process (discussed in the following section). Process line operators or other personnel periodically replace the bath filters based on criteria such as analytical sampling results from the process baths, elapsed time, or volume of product produced.

2.1.3 Chemistry and Process Descriptions of MHC Technologies

This section describes in detail the processes for adding a conductive coating to the substrate surfaces of PWB drilled through-holes. A brief description of the chemical mechanisms or processes occurring in each of the process steps along with other pertinent process data such as substrate compatibilities and modes of operation (e.g., non-conveyorized or conveyorized) are presented for each technology. For technologies with more than one chemical supplier (e.g., electroless copper, graphite, and tin-palladium), a process description for each chemical product line was developed in consultation with the chemical supplier, and then combined to form a generic process description for that technology. Notable differences in the chemical mechanisms or processes employed in a single product line from that of the generic process are detailed.

Electroless Copper

Electroless copper has been the standard MHC method used in the manufacture of double-sided and multi-layered boards. A palladium/tin colloid is adsorbed onto the through-hole walls, which then acts as the catalyst for the electroless plating of copper. The autocatalytic copper bath uses formaldehyde as a reducing agent in the principle chemical reaction that applies a thin, conductive layer of copper to the nonconducting barrels of PWB through-holes. Electroless copper processes are typically operated in a non-conveyorized mode and are compatible with all types of substrates and desmear processes.

Figure 2.2 is a flow diagram of the process baths in a generic electroless copper process. The following is a brief description of each of the process steps provided by technology suppliers (Wood, 1995a; Bayes, 1995a; Thorn, 1995a) shown in the flow diagram.

Step 1: Grease and contaminants are removed from the through-hole walls in a cleaning/conditioning solution. The solution prepares the through-hole surfaces for plating and facilitates the adhesion of the palladium catalyst.

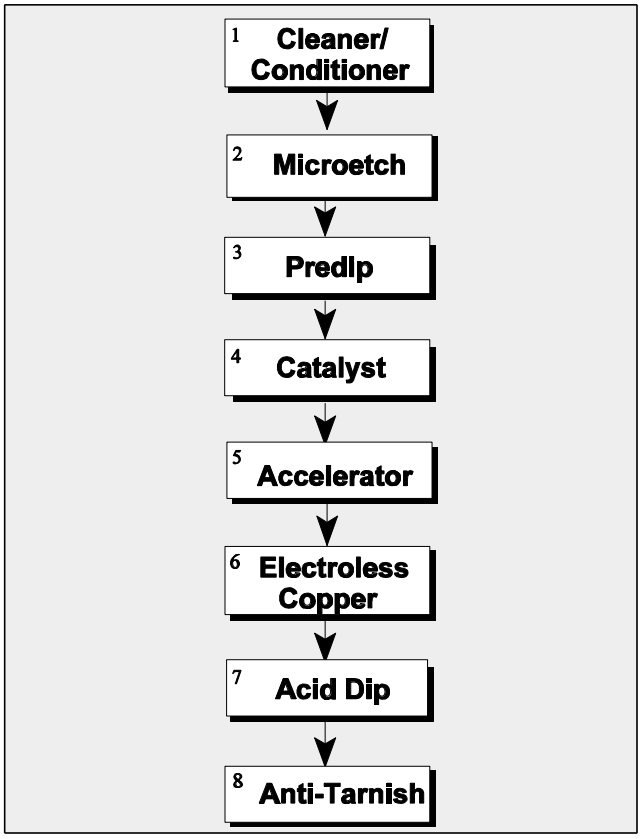
Step 2: A microetch solution, which typically consists of dilute hydrochloric or sulfuric acid, etches the existing copper surfaces to remove any contaminants or oxides to ensure good copper-to-copper adhesion at all of the copper interconnect points.

Step 3: Etched panels are processed through a predip solution which is chemically similar to that of the palladium catalyst and is used to protect the catalyst bath from harmful drag-in.

Step 4: The catalyst, consisting of a colloidal suspension of palladium/tin in solution, serves as the source of palladium particles. The palladium particles adsorb onto the glass and epoxy surfaces of the substrate from the colloidal solution, forming a catalytic layer for copper plating.

Step 5: An accelerator solution prepares the surface for copper plating by chemically removing, or accelerating, the protective tin coating from the palladium particles, exposing the reactive surface of the catalyst.

Figure 2.2 Generic Process Steps for the Electroless Copper Technology



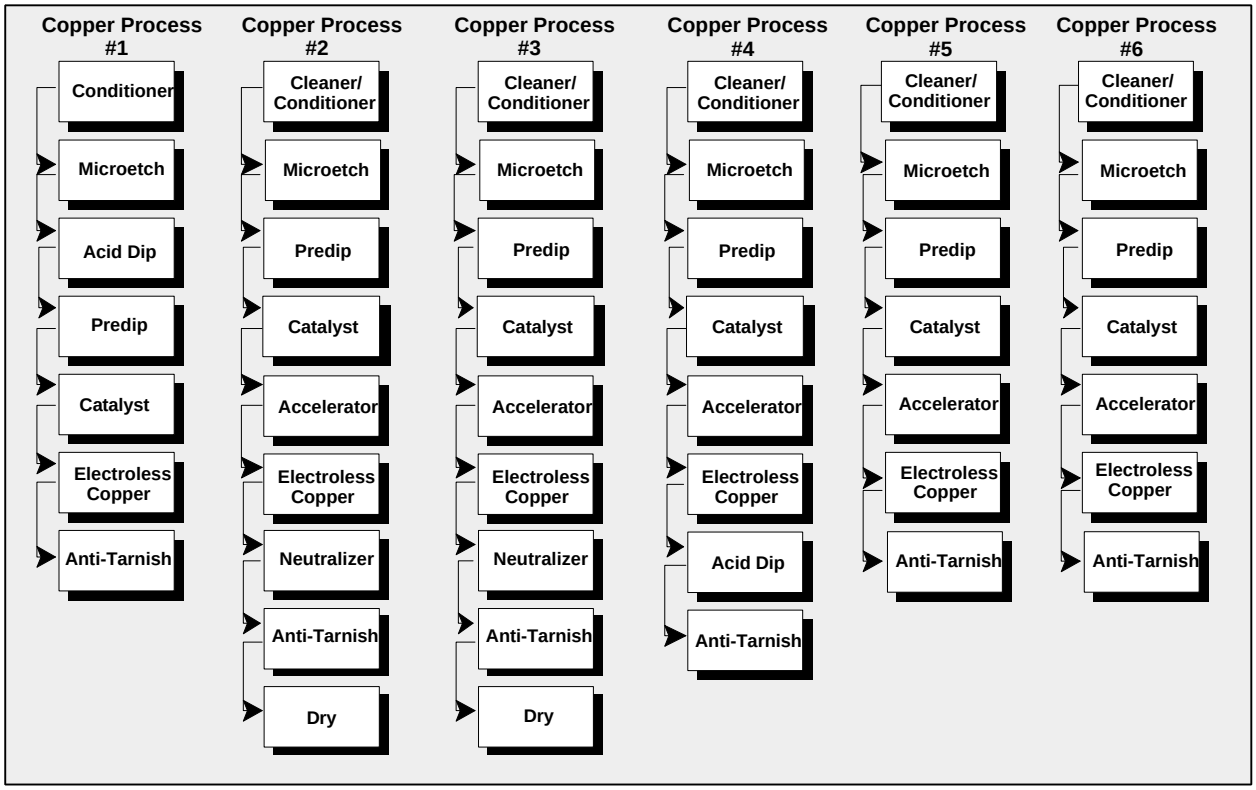
Step 6: An electroless copper solution plates a layer of copper onto the surface of the palladium catalyst. The electroless copper bath is an alkaline solution containing a source of copper ions, a chelator to keep the copper ions solubilized, a stabilizer to prevent the copper solution from plating out, and a formaldehyde reducing agent. Several chelating agents are currently used in electroless copper baths, including ethylenediaminetetraacedic acid (EDTA), quadrol, and tartrate. The formaldehyde reducing agent promotes the reduction of copper ions onto the surface of the exposed palladium seeds. Because the bath is autocatalytic, it will continue plating copper until the panel is removed.

Step 7: A weak acidic solution neutralizes residual copper solution from the board and prepares the surface for dry film application.

Step 8: The copper surfaces are treated with an anti-tarnish solution to prevent oxidation and further prepare the panel surfaces for dry film lamination. This process step may not be needed with some processes; it is required primarily in cases where long delays in panel processing are encountered.

Several chemical manufacturers market electroless copper processes for use in MHC applications. Figure 2.3 lists the process baths for each of the electroless copper processes provided by chemical suppliers for evaluation in the CTSA. The processes differ slightly in types of chelating agents or stabilizing compounds used, but all are similar to the electroless copper process described above.

Figure 2.3 Electroless Copper Processes Submitted by Chemical Suppliers



Carbon

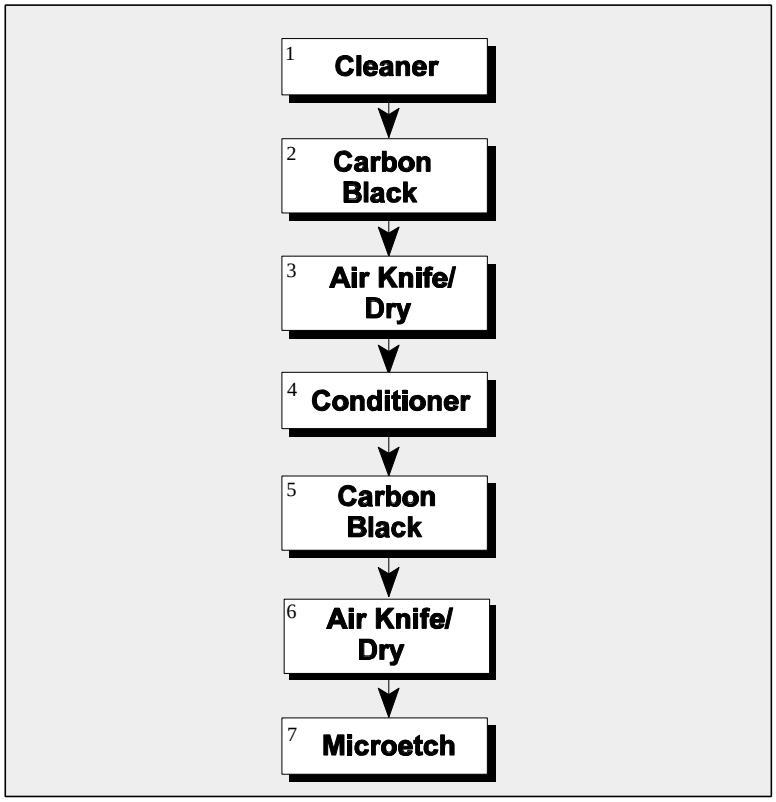
Carbon processes utilize a suspension of carbon black particles to deposit a conductive layer of carbon onto the substrate surface. The spherical carbon black particles form an amorphous, or noncrystalline, structure of randomly scattered crystallites, which create a conductive layer. The process is typically operated in a conveyorized fashion, but can be modified to be run in a non-conveyorized mode. It is compatible with all common substrates and, in the conveyorized mode, can be fed directly into a cut-sheet dry-film laminator (Wood, 1995b).

Figure 2.4 is a flow diagram of the process baths in a generic carbon process. The following is a brief description of each of the process steps provided by technology suppliers (Retalick, 1995; Wood, 1995b; Gobhardt, 1993) shown in the flow diagram.

Step 1: A cleaner solution containing a cationic wetting agent removes oil and debris from the panel while creating a positive charge on the glass and epoxy surfaces of the drilled through-hole.

Step 2: Carbon black particles are adsorbed onto the positively charged substrate surface from the alkaline carbon black dispersion. The adsorbed particles form an amorphous layer of carbon that coats the entire panel including the through-hole surfaces.

Figure 2.4 Generic Process Steps for the Carbon Technology



Step 3: An air knife removes the excess carbon dispersion before a hot air oven dries the carbon layer.

Step 4: A conditioner bath cleans and conditions the panel surface and prepares the panel for a second layer of carbon black.

Steps 5-6: Steps 2-3 are repeated using a similar carbon bath which deposits a second layer of carbon black particles onto the exposed surfaces of the panel. After the second drying step, a porous layer of carbon black covers the entire panel, including the outside copper surfaces and the inner-layer interconnects. This carbon layer must be removed from the copper surfaces before the panel is electroplated or laminated with dry film in subsequent process steps.

Step 7: A copper microetch penetrates the porous layer of carbon and attacks the copper layer underneath, lifting the unwanted carbon off the copper surfaces while cleaning the copper surface for plating. Because the microetch does not attack the glass and epoxy surfaces, it leaves the carbon-coated glass and epoxy surfaces intact. The etched copper surfaces can also be directly laminated with a dry-film photoresist without any additional processing.

The non-conveyorized version of carbon is operated in an identical fashion to the process described above. The carbon direct-plate process may be operated in a single or double pass configuration depending on the complexity of the product. The double-pass system described above ensures a high level of reliability for high multi-layer, high aspect ratio hole applications.

A single-pass, conveyorized system has also been developed and is now being utilized in less rigorous process applications.

Conductive Ink

Conductive ink MHC processes are effective with double-sided, surface mount applications. This type of process utilizes a mechanical screen printing process to deposit a special conductive ink into the through-holes of a PWB. Possible screen materials include stainless steel or polyester, with the former being preferred for high volume or fine registration applications. Several types of inks have been developed, each with unique properties (e.g., solderability, conductivity, cost, etc.), to meet the demands of each specific application. This process is compatible with most common types of laminate including epoxy glass and phenolic paper boards.

Figure 2.5 is a process flow diagram of the process steps in a generic conductive ink process. The following is a brief description of each of the process steps provided by technology suppliers (Peard, 1995; Holmquest, 1995) shown in the flow diagram.

Step 1: A microetch solution etches the surface of the copper laminate, removing oil and other contaminants, providing a good copper-to-ink connection.

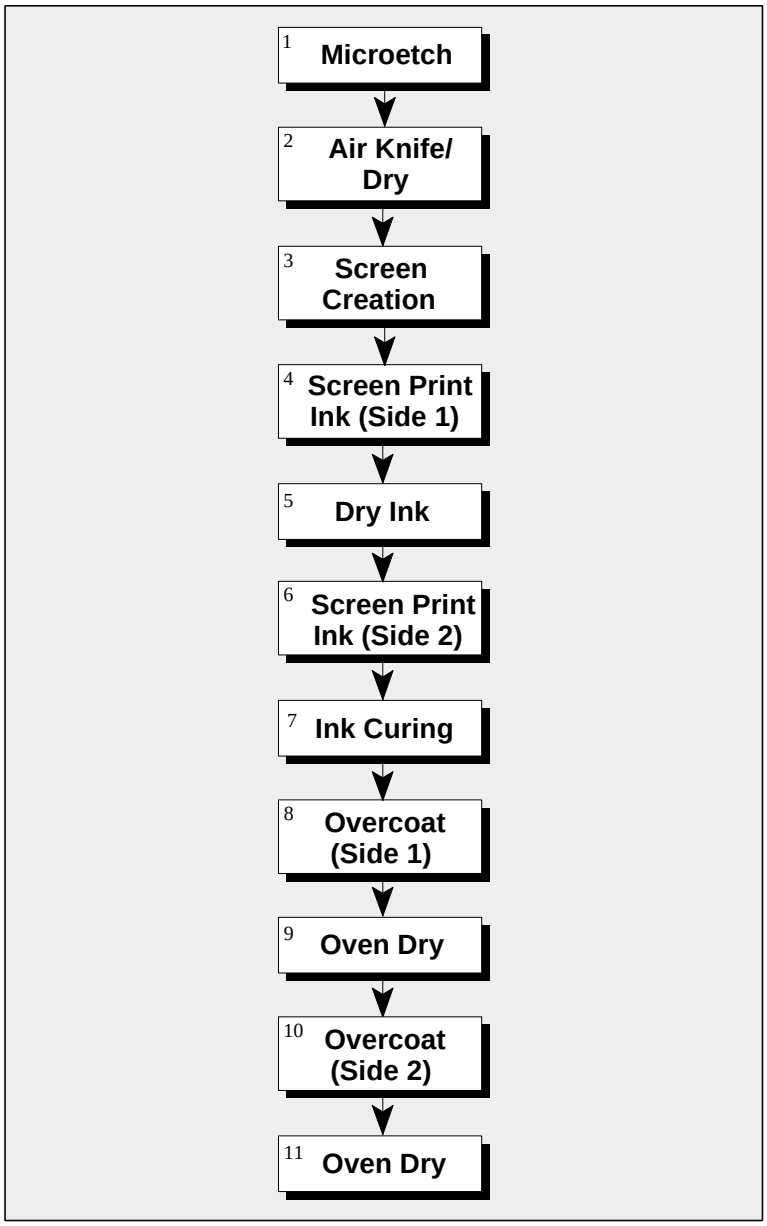
Step 2: An air knife removes any residual chemistry from the PWB panels before the panels are dried in a oven. The panels must be dried completely to remove any moisture from the substrate before screening.

Step 3: The screen with the image of the panel to be processed is created for each side of the panel. Screen material, mesh size, and screen tension are all factors that must be considered. After the type of screen is selected, the printing image is transferred to the screen, using a combination of direct and indirect emulsions, to achieve an emulsion thickness sufficient for ink deposition. A platen, with holes slightly larger than the drilled holes, is created to both support the panels while screening, and to allow uniform ink flow through each hole. Other parameters such as ink viscosity, screen off-contact distance, and squeegee speed and hardness are all interdependent and must be optimized.

Step 4: A squeegee is passed over the surface of the ink-flooded screen, effectively forcing the ink through the screen and into the drilled holes of one side of the panel. Squeegee angle and speed, ink viscosity, and through-hole size as well as other factors all contribute to the amount of ink forced into the through-hole. After processing, the screen may be reclaimed for reuse with another image. For more information on screen reclamation refer to the *Cleaner Technologies Substitutes Assessment, Industry: Screen Printing* (EPA, 1994).

Step 5: Hot air drying removes solvent from the ink deposit, partially curing the ink. Solvent must be completely removed from the ink prior to curing in order to prevent voiding and bubbles which develop as residual solvent tries to escape.

Figure 2.5 Generic Process Steps for the Conductive Ink Technology



Step 6: The screened panel is flipped over and the screening step described in Step 4 is repeated. Ink should completely fill the hole, without the presence of voids, and should overlap the copper on both top and bottom surfaces to promote good conductivity. The second screening step is typically needed to get the required amount of ink into the through-hole, but may not be necessary. The second screening step may be eliminated through the use of a vacuum while screening which allows the use of a higher-viscosity ink that improves ink coverage of the through-hole.

Step 7: Hot air or infrared methods are used to first dry and then cure the conductive ink, leaving the ink solvent-free while cross-linking the thermoset resins that form the final polymer.

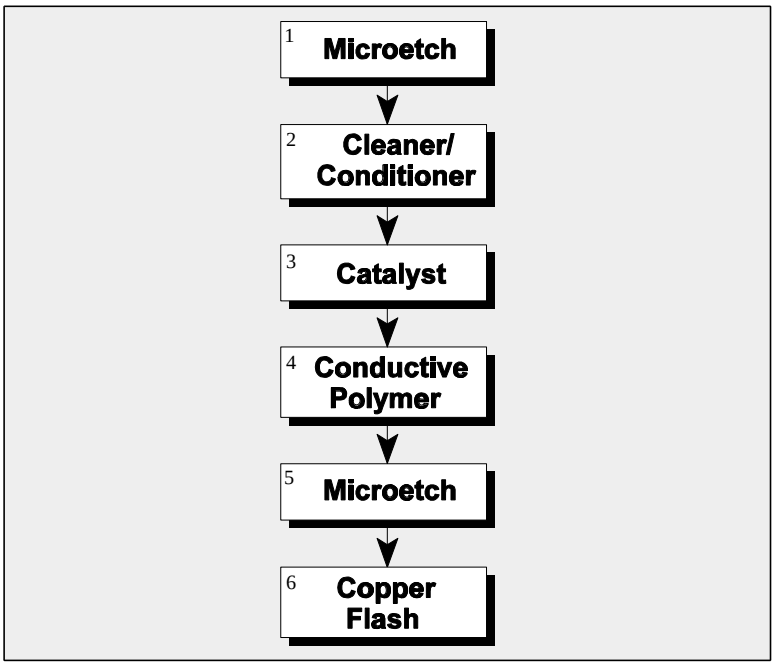
Steps 8-11: A final coating of soldermask is applied to cover the printed through-holes on both sides of the PWB, protecting them against oxidation and potential physical or chemical damage. The solder mask is typically applied using a screen printing and drying sequence similar to that described in Steps 4-5. The process is then repeated for the reverse side.

Conductive Polymer

This MHC process forms a conductive polymer layer, polypyrolle, on the substrate surfaces of PWB through-holes. The polymer is formed through a surface reaction during which an immobilized oxidant reacts with an organic compound in solution. The conductive polymer process can be operated horizontally and is compatible with most common substrates as well as traditional etch-back and desmear processes. Because of the relative instability of the polymer layer, the process may be operated with a flash-plating step, but this step was not evaluated in the risk characterization (Boyle, 1995c; Boyle, 1995d).

The process steps for the conductive polymer process are shown in Figure 2.6. The following is a brief description of each of the process steps provided by technology suppliers (Boyle, 1995c; Boyle, 1995d; Meyer et al., 1994) shown in the flow diagram.

Figure 2.6 Generic Process Steps for the Conductive Polymer Technology



Step 1: The microetch solution lightly etches the exposed copper surfaces of the panel, including the inner layer copper interconnects, to remove any chemical contamination and metal oxides present.

Step 2: A cleaner/conditioner step removes any oil or debris from the hole and coats the glass and epoxy surfaces of the substrate with a water-soluble organic film. The organic film is designed to both adhere to the substrate surfaces of the hole barrel and be readily oxidized by permanganate.

Step 3: The film is then exposed to a permanganate catalyst solution, which deposits manganese dioxide (MnO_2) through the oxidation of the organic film. The MnO_2 deposition is selective, only reacting with the film-coated surfaces of the substrate. This is important, since the final formation of the polymer occurs only on the glass and epoxy surfaces where MnO_2 is present, not on the copper surfaces where interconnect defects could occur.

Step 4: Polymerization occurs when a weakly acidic conductive polymer solution containing a pyrolle monomer is applied to the substrate coated with MnO_2. The polymerization of pyrolle, which forms the conductive polymer polypyrolle, continues until all of the MnO_2 oxidant is consumed. The resulting layer of conductive polymer on the substrate is thin and relatively unstable, especially in alkaline solutions.

Step 5: A microetch solution removes oxides and chemical contamination from all exposed copper surfaces, preparing them for flash-plating.

Step 6: The conductive polymer-covered through-holes are flash plated with copper in an acid copper electroplating bath. A thin layer of copper plating is sufficient to prepare the panel for lamination with dry film photoresist and subsequent pattern-plating, or the panel can be fully panel plated. Flash plating may not be required in instances where minimal hold times are experienced between the formation of the polymer and the pattern plating step.

The conductive polymer process has been successfully operated in Europe, and has been recently adopted in the U.S.

Graphite

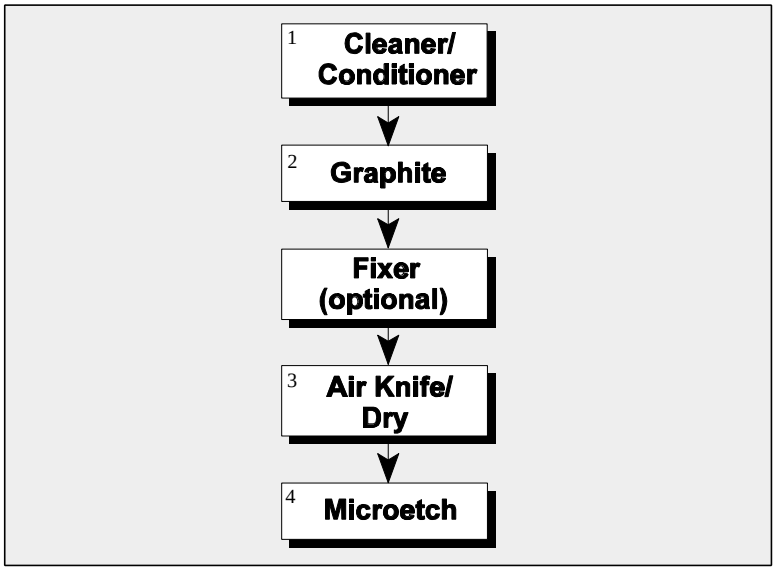
Graphite processes provide for the deposition of another form of carbon—graphite—onto the substrate surfaces of the through-holes, in a process similar to the carbon process described above. Graphite has a three-dimensional, crystalline structure as opposed to the amorphous, randomly arranged structure found in carbon black (Carano, 1995). One notable difference between the carbon and graphite processes is that the graphite system requires only one pass of the panel through the graphite bath to achieve sufficient coverage of the through-hole walls prior to electroplating.

Figure 2.7 is a flow diagram of the process baths in a generic graphite process. The following is a brief description of each of the process steps provided by technology suppliers (Thorn, 1995b; Carano, 1995; Bayes, 1995c) shown in the flow diagram.

Step 1: A cleaner/conditioner solution removes oil and debris from the panel and creates a slight positive charge on the exposed surfaces of the through-hole.

Step 2: Graphite particles are flocculated onto the substrate surfaces of the through-hole. The conductive graphite layer coats the entire panel, including the nonconductive substrate surfaces, the copper surfaces of the outside layers, and the interconnects.

Figure 2.7 Generic Process Steps for the Graphite Technology



Step 3: An air knife removes the excess graphite dispersion from the through-holes before a hot air oven dries the conductive graphite layer, causing it to polymerize. After drying, a porous layer of graphite coats both the copper surfaces and the substrate surfaces of the through-hole. The graphite must be removed from the copper surfaces before they are plated with copper or the panels are laminated with dry film.

Step 4: A copper microetch undercuts the porous layer of graphite, removing a thin layer of copper underneath, lifting the unwanted graphite off the copper surfaces while cleaning the copper surface for plating. Because the microetch does not attack the glass and epoxy surfaces, it leaves the graphite-coated glass and epoxy surfaces intact. The etched copper surfaces can also be directly laminated with a dry-film photoresist without any additional processing.

The graphite process typically is operated in a conveyorized mode but can also be modified for non-conveyorized applications. When operated in non-conveyorized mode, a fixer step (the optional step shown in Figure 2.7) is employed directly after the graphite bath and before the hot air drying. The fixer step promotes the uniform coating of the hole walls by causing the graphite coating to polymerize and adhere to the substrate. This is necessary to counteract gravity, which will cause the carbon to deposit more heavily along the lower, bottom side of the holes.

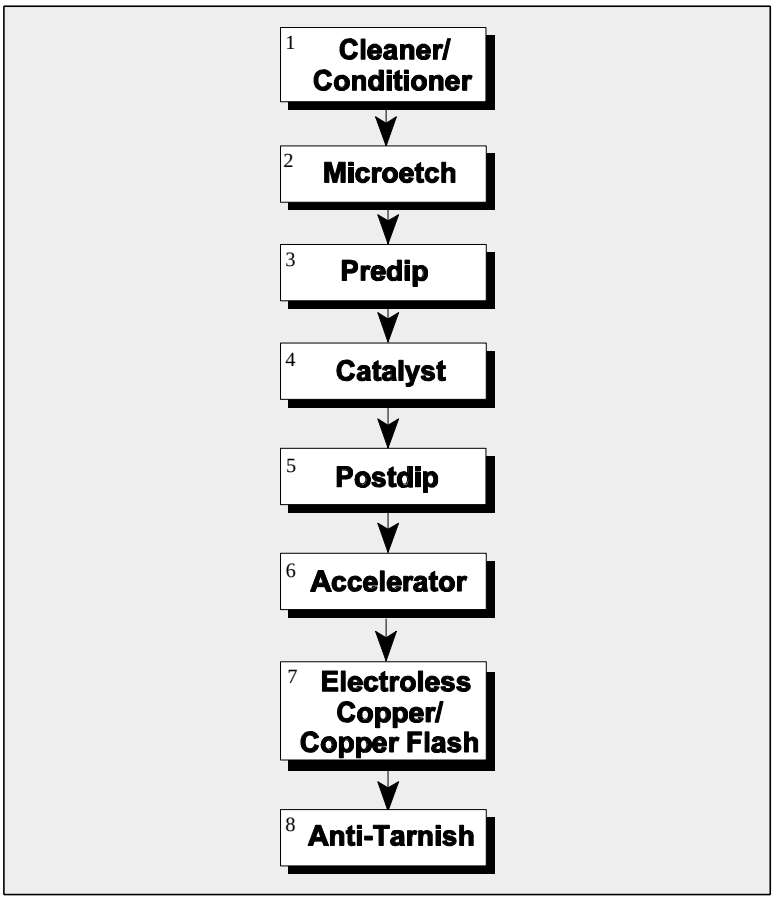
A fixer step can also be useful in conveyorized process modes where high aspect ratio holes (small diameter holes in thick panels) are being manufactured. The fixer causes the graphite to cover the entire hole barrel evenly and prevents the solution from accumulating at one end.

Non-Formaldehyde Electroless Copper

This process is a vertical, non-conveyorized immersion process that allows the electroless deposition of copper onto the substrate surfaces of a PWB without the use of formaldehyde. The process uses hypophosphite in place of the standard formaldehyde as a reducing agent in the electroless copper bath. The hypophosphite electroless bath is not autocatalytic, which reduces plate-out concerns, and is self-limiting once the palladium catalyst sites have been plated. Once a thin layer of copper is applied, the panel is placed under an electrical potential and electroplated while still in the bath, to increase the copper deposition thickness.

Figure 2.8 is a flow diagram for a typical non-formaldehyde electroless copper process. The following is a brief description of each of the process steps provided by the technology suppliers (Retalick, 1995; Wood, 1995a; Wood, 1995b) shown in the flow diagram.

Figure 2.8 Generic Process Steps for the Non-Formaldehyde Electroless Copper Technology



Steps 1-3: Panels are cleaned, conditioned, microetched, and predipped in a chemical process similar to the one described previously for electroless copper.

Step 4: The catalyst solution contains a palladium/tin colloidal dispersion that seeds the nonconductive surfaces of the drilled through-holes. Because the electroless

copper bath is not autocatalytic, the catalyst process is designed to maximize the adsorption of palladium/tin, which ensures that adequate copper plating of the substrate will occur.

Step 5: A hydrochloric acid postdip solution partially removes the residual tin, exposing the palladium seeds.

Step 6: The accelerator oxidizes the remaining tin to a more conductive state, enhancing the catalytic properties of the palladium layer, before the panel enters the electroless plating bath.

Step 7: The electroless plating bath uses hypophosphite, instead of formaldehyde, to promote the reduction of copper onto the palladium catalyzed surfaces. The nonautocatalytic bath plates copper only in the presence of the palladium seeds. Copper plating continues until all palladium surfaces have been covered, resulting in a thin layer (10 to 15 micro inches) of copper covering the hole walls.

Additional copper is added to the thin initial deposit, creating a thicker copper layer, by a flash-plating step. The flash-plating is typically performed directly in the electroless copper bath by placing copper anodes into the bath and applying an electrical potential. Copper electroplating continues until a total of 80 to 100 micro inches of copper is present on the through-hole surfaces. The panels may also be flash-plated in an acid copper plating bath, if desired.

Step 8: The copper surfaces are treated with an anti-tarnish solution to prevent oxidation and further prepare the panel surfaces for dry film lamination. This process step may not be needed with some processes; it is required primarily in cases where long delays in panel processing are encountered.

This non-conveyorized immersion process is compatible with all substrate types but requires a permanganate etchback process prior to desmear.

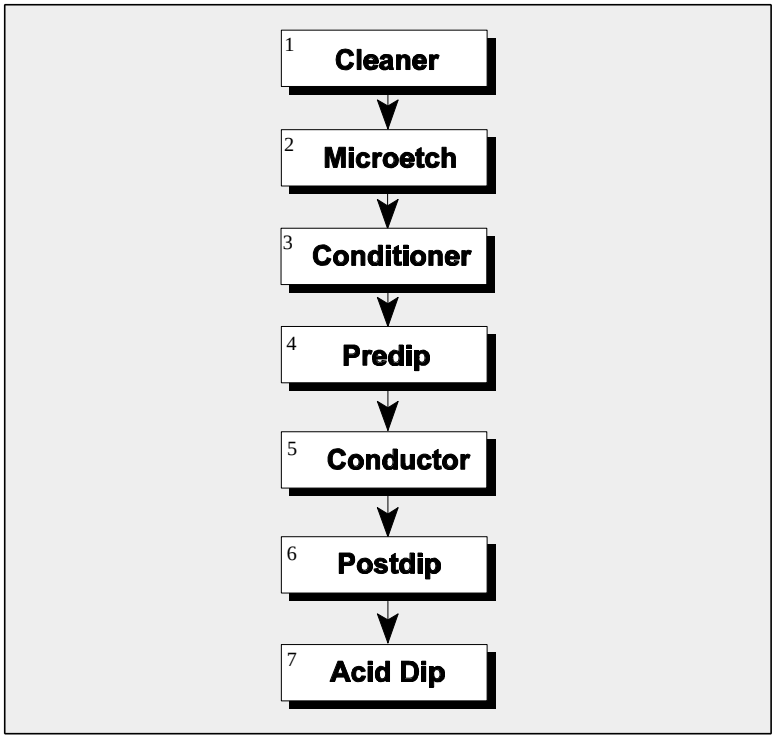
Organic-Palladium

Two types of alternatives use dispersed palladium particles to catalyze nonconducting surfaces of PWB through-holes: organic-palladium and tin-palladium. In both of these processes, the palladium particles are adsorbed from solution directly onto the nonconducting substrate, creating a conductive layer that can be electroplated with copper. Palladium particles dispersed in solution tend to agglomerate unless they are stabilized through the formation of a protective layer, or colloid, which surrounds the individual palladium particles. The organic-palladium process uses a water-soluble organic polymer to form a protective layer, or colloid, around the palladium particles. The protective colloid surrounds the individual palladium particles, preventing them from agglomerating while in solution. The organic-palladium colloidal suspension is formed when the organic polymer complex and the palladium particles are combined with a reducing agent. The resulting colloidal suspension must be kept under reduction conditions to ensure colloidal stability. After the particles have been deposited onto

the board, the protective colloid is removed, making the layer of palladium particles conductive (Boyles, 1995b; Boyles, 1995d).

Figure 2.9 is a flow diagram of the process baths in a generic organic-palladium process. The following is a brief description of each of the process steps provided by technology suppliers (Boyle, 1995a; Boyle, 1995b; Boyle, 1995d) shown in the flow diagram.

Figure 2.9 Generic Process Steps for the Organic-Palladium Technology



Step 1: A cleaner bath containing a cationic wetting agent removes oil and debris from the panel while creating a positive charge on the glass and epoxy surfaces of the drilled through-hole.

Step 2: The microetch solution lightly etches the exposed copper surfaces of the panel, including the inner layer copper interconnects, to remove any chemical contamination and metal oxides present.

Step 3: Upon entering the conditioner bath, the substrate surfaces of the PWB are conditioned with a polymer film designed to bond effectively with both the palladium-tin colloid and the palladium particles themselves. The film adsorbs from an aqueous solution onto surfaces of the through-holes where it acts as an adhesion promoter for the tin-palladium colloid, binding strongly to its surface. The polymer film has no affinity for the copper surfaces, leaving them film-free.

Step 4: Conditioned panels are processed through a predip solution that is chemically similar to the following conductor bath. The predip wets the substrate surfaces with a mild acidic solution and protects the conductor bath from harmful drag-in chemicals.

Step 5: During the conductor step, organic-palladium colloids adsorb onto the film-covered glass and epoxy surfaces from a colloidal suspension. The adsorbed colloidal particles form a nonconductive organic-palladium layer across the substrate surfaces of the through-hole.

Step 6: A postdip solution removes the stabilizing organic sheath from the surface deposition, uncovering the remaining palladium particles and making them conductive. The polymer film layer bonds with the conductive palladium particles, keeping them from returning to solution.

Step 7: A weak acid dip stabilizes the active palladium surface and prepares the palladium-covered surface for electroplating.

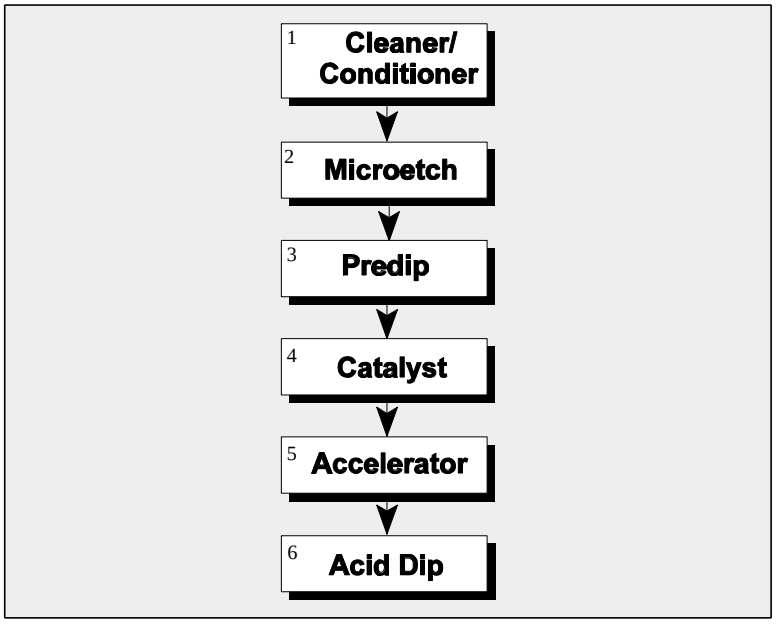
Organic-palladium can be operated successfully in either conveyorized or non-conveyorized modes. The process is compatible with all common substrates, including Teflon.

Tin-Palladium

Tin-palladium processes also make use of a palladium activation step. These processes use tin to form the colloid with palladium. After the adsorption of the tin-stabilized palladium colloid, the tin is removed, creating a layer of conductive palladium particles on the surface of the substrate.

Figure 2.10 depicts the process baths in a generic tin-palladium process. The following is a brief description of each of the process steps provided by technology suppliers (Thrasher, 1995; Harnden, 1995a; Harnden, 1995b; Bayes, 1995a; Bayes, 1995b; Bayes, 1995c; Marks, 1996) shown in the flow diagram.

Figure 2.10 Generic Process Steps for the Tin-Palladium Technology



Steps 1-2: Panels are cleaned, conditioned, and microetched by a chemical process that is similar to the process described in Steps 1-2 of the organic-palladium method described previously.

Step 3: Etched panels are processed through a predip solution which is chemically similar to that of the palladium catalyst and is used to protect the catalyst bath from harmful drag-in.

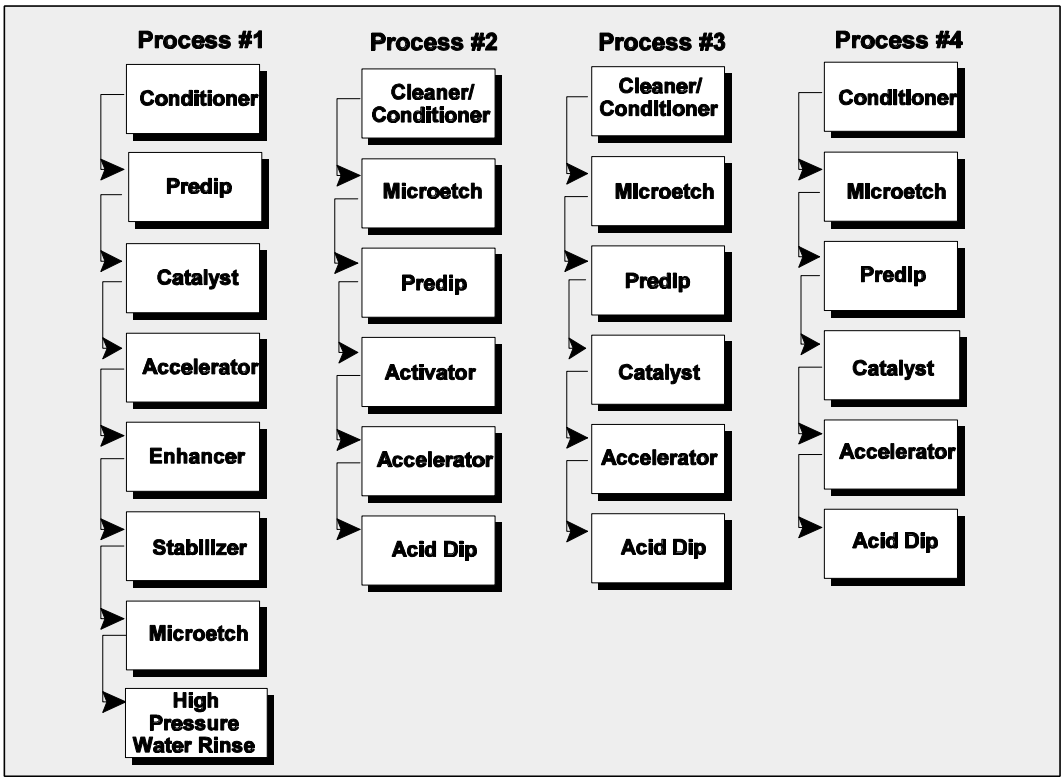
Step 4: Tin-palladium colloids adsorb from the colloidal suspension of the catalyst solution onto the slightly charged through-hole surfaces. The adsorbed palladium colloids form a relatively nonconductive coating on the substrate surfaces of the through-hole.

Step 5: An accelerator solution typically removes the protective tin coating from the tin/palladium layer, exposing the catalytic surface of the palladium particles, making the layer conductive.

Step 6: A weak acid dip stabilizes the active palladium surface and prepares the palladium-covered surface for dry film application and electroplating.

Many tin-palladium processes are similar up through Step 4, but use different methods to optimize the conductivity of the palladium deposit. Figure 2.11 illustrates the process steps in each tin-palladium product line submitted by chemical suppliers for evaluation in the CTSA. Methods used to optimize the conductivity of the palladium layer are discussed below.

Figure 2.11 Tin-Palladium Processes Submitted by Chemical Suppliers



One method accelerates, or removes, the protective tin colloid from the palladium, leaving a coating of fine palladium particles on the surface of the substrate. Sulfide is then reacted with palladium to form a more stable chemical layer. Sulfidation of the palladium sites is not selective to the substrate surfaces only, and will adsorb onto the exposed copper of the inner layers. To prevent plating defects from occurring, a microetch step removes the adsorbed sulfide from the exposed copper surfaces of the interconnects (Bayes, 1995b; Bayes, 1995c).

A second method converts the positively charged tin colloid to metallic tin, while simultaneously reducing copper onto the surface of the new tin-palladium layer. Both reductions are a result of a disproportionation reaction occurring under alkaline conditions and in the presence of copper ions. The reduction of copper onto the tin-palladium layer creates an electrically conductive palladium/tin/copper metallic coating that can be subsequently electroplated to the desired specifications (Nargi-Toth, 1996).

A third method uses a chemical called vanillin in the formation of the tin-palladium colloid. Vanillin will attach to most other molecules, except another vanillin molecule. As a consequence, the vanillin on the surface of the palladium/tin colloid prevents the colloidal suspension from agglomerating while also facilitating the deposition of the colloid onto the substrate surface. The water-soluble vanillin is then removed along with the tin in the following water rinse step. Copper ions are complexed with the palladium in an accelerator step, to form a palladium/copper layer which is then chemically stabilized by a mild acid setter step (Harnden, 1995a; Harnden, 1995b).

2.1.4 Chemical Characterization of MHC Technologies

This section describes the sources of bath chemistry information, methods used for summarizing that information, and use of publicly-available bath chemistry data. Publicly-available information alone is used to assess exposure and risk because MHC chemical suppliers have not fully provided proprietary bath chemistry data.[1] This section does not identify any proprietary ingredients.

<u>Use of Publicly-Available Chemical Formulation Data</u>

Assessment of releases, potential exposure, and characterizing risk for the MHC process alternatives requires chemical-specific data, including concentrations for each chemical in the various baths. Although some bath chemistry data were collected in the IPC Workplace Practices Questionnaire, the decision was made not to use these data because of inconsistencies in responses to the questions pertaining to bath chemistry. Instead, the suppliers participating in the Performance Demonstration each submitted publicly-available data on their respective product lines. This information includes:

[1] Three suppliers, Electrochemicals, LeaRonal, and Solution Technology Systems, have provided information on proprietary chemical ingredients to the project. W.R. Grace had been preparing to provide information on proprietary chemical ingredients in the conductive ink technology when it was determined that this information was no longer necessary because risk from the conductive ink technology could not be characterized. The other suppliers participating in the project (Atotech, Enthone-OMI, MacDermid, and Shipley) have declined to provide proprietary information.

- Material Safety Data Sheets (MSDSs).
- Product Data Sheets.
- Patent data, in some cases.

MSDSs identify the chemicals in a supplier's product and Product Data Sheets describe how those products are mixed together to make up the individual baths. The available patents for the product lines were consulted to identify unlisted ingredients.

Table 2.1 presents all chemicals identified in MHC process lines and the MHC technologies in which they are used. Methods for summarizing the publicly-available and other supplier information and calculation of concentrations are described below.

Table 2.1 Non-Proprietary Chemicals and Associated MHC Technologies

Chemical List	Electroless Copper	Carbon	Conductive Ink	Conductive Polymer	Graphite	Non-Formaldehyde Electroless Copper	Organic-Palladium	Tin-Palladium
2-Ethoxyethanol	✔							
1,3-Benzenediol								✔
1H-Pyrrole				✔				
2-Butoxyethanol Acetate; Butylcellusolve Acetate			✔					
Ammonia					✔			
Ammonium Chloride	✔							
Benzotriazole	✔							
Boric Acid	✔							
Carbon Black		✔	✔					
Copper (I) Chloride; Copper	✔							✔
Copper Sulfate; or Cupric Sulfate	✔	✔			✔	✔		✔
Diethylene Glycol n-Butyl Ether			✔					
Diethylene Glycol Ethyl Ether			✔					
Diethylene Glycol Methyl Ether			✔					
Dimethylaminoborane	✔							
Dimethylformamide	✔							
Ethanolamine; Monoethanolamine; 2-Aminoethanol	✔	✔			✔			✔
Ethylene Glycol	✔	✔						
Ethylenediaminetetraacetic Acid (EDTA)	✔							
Fluoroboric Acid; Sodium Bifluoride	✔							✔
Formaldehyde	✔							
Formic Acid	✔							
Graphite			✔		✔			
Hydrochloric Acid	✔					✔	✔	✔
Hydrogen Peroxide	✔					✔		✔
Hydroxyacetic Acid	✔							
Isophorone			✔					

Chemical List	Electroless Copper	Carbon	Conductive Ink	Conductive Polymer	Graphite	Non-Formaldehyde Electroless Copper	Organic-Palladium	Tin-Palladium
Isopropyl Alcohol; 2-Propanol	✔					✔		✔
Lithium Hydroxide								✔
m-Nitrobenzene Sulfonic Acid; Sodium m-Nitrobenzenesulfonate	✔							
Magnesium Carbonate	✔							
Methanol	✔		✔					
p-Toluene Sulfonic Acid; Tosic Acid	✔							
Palladium	✔							✔
Palladium Chloride								✔
Peroxymonosulfuric Acid; Potassium Peroxymonosulfate	✔			✔	✔			
Phenol-Formaldehyde Copolymer			✔					
Phosphoric Acid				✔				✔
Potassium Bisulfate	✔							
Potassium Carbonate		✔			✔			✔
Potassium Cyanide	✔							
Potassium Hydroxide	✔	✔				✔		
Potassium Persulfate	✔					✔		
Potassium Sulfate	✔							
Potassium-Sodium Tartrate	✔							
Silver			✔					
Sodium Bisulfate	✔						✔	✔
Sodium Carbonate	✔			✔			✔	
Sodium Chloride								✔
Sodium Chlorite	✔					✔		
Sodium Cyanide	✔							
Sodium Hydroxide	✔			✔		✔		✔
Sodium Hypophosphite	✔						✔	
Sodium Persulfate		✔			✔		✔	✔
Sodium Sulfate	✔							
Stannous Chloride; Tin (II) Chloride	✔					✔		✔
Sulfuric Acid	✔	✔		✔	✔	✔		✔
Tartaric Acid	✔							
Triethanolamine; or 2,2',2"-Nitrilotris Ethanol	✔							✔
Trisodium Citrate 5.5-Hydrate; Sodium Citrate							✔	
Vanillin								✔

Determining Chemical Formulations

The first step in determining chemical formulations was to divide each supplier's product lines into the basic bath steps identified in Section 2.1.3, Chemistry and Process Descriptions of MHC Technologies, for each MHC technology. This was accomplished by consulting with suppliers to determine the MHC technology in which each product is used, as well as the step(s)

in the process in which the product is used (i.e., in which bath). Then, the non-proprietary chemicals in each bath were identified for each MHC process.

The individual chemical concentrations in the baths were calculated by:

$$C_b = (C_{CHEM})\,(C_{FORM})\,(D)\,(1000\ cm^3/L)$$

where:

C_b = concentration of constituent in bath (g/L)
C_{CHEM} = the chemical concentration, by weight, in the product, from MSDSs (%)
C_{FORM} = proportion of the product formulation volume to the total bath volume, from Product Data Sheets (%)
D = density of the product (g/cm^3)

An example calculation for the triethanolamine concentration in the conditioner/cleaner bath is shown below for one supplier's tin-palladium process. Each product's MSDS lists the chemicals that are contained in that product on a weight percentage basis. For triethanolamine, this is ten percent, or ten grams triethanolamine per 100 grams of product. The supplier's Product Data Sheet then lists how much of that package is used in the total bath makeup on a volume percentage basis: in this case, 25 percent, or 25 liters of product per 100 liters of the total bath. The remaining volume in the bath is made up of deionized water. The MSDSs also include the specific gravity or density of the product, which was multiplied by the weight and volume percentages above to obtain the bath concentration for that constituent. (In some cases, the Product Data Sheets list chemicals or product packages on a mass per volume basis. This was multiplied by the weight percentage from the MSDS for that product package to obtain a concentration in the bath.) The example calculation is shown here:

$$\frac{10g}{100g}\left(\frac{25L}{100L}\right)\left(\frac{1.015g}{cm^3}\right)\left(\frac{1000cm^3}{L}\right) = 25.4\frac{g}{L}$$

After the MSDS and Product Data Sheet data were combined in the above manner for each supplier's product line, a list of non-proprietary chemicals in each MHC technology category (electroless copper, tin-palladium, etc.) was compiled. This list shows all chemicals that might be in each bath, by technology, as well as the concentration range for each chemical. However, some of the alternatives (e.g., electroless copper, graphite, and tin-palladium) have more than one chemical supplier using different bath chemistries. It was decided to include all of the identified chemicals in the formulations rather than selecting a typical or "generic" subset of chemicals.

Estimated concentration ranges (low, high, and average) were determined based on the publicly-available information and are presented in Appendix B. Concentrations are for each bath in each MHC process alternative.

Data Limitations

Limitations and uncertainties in the chemical characterization data arise primarily from the use of publicly-available data which do not account for side reactions in the baths, and which do not always contain a full disclosure of chemical ingredients or concentrations. Side reactions in the baths may result in changing concentrations over time and/or formation of additional chemicals in the baths. This information is not reflected in MSDSs or Product Data Sheets but would affect bath concentrations over time.

MSDSs are required of industry by OSHA (29 CFR 1910.1200). This includes reporting any hazardous chemicals (as defined in the regulation) making up at least one percent of a products formulation, or at least 0.1 percent for carcinogens.[2] Any other chemical must be reported if its release poses a hazard, even if <1 percent (or <0.1 percent). There are two basic limitations to using this data: 1) chemical identity may be withheld from an MSDS if claimed to be a trade secret; and 2) because the MSDS is focused on human health concerns, chemicals posing ecological hazards may not be included. Table 2.2 summarizes the available information on hazardous and carcinogenic trade secret chemicals as provided on the supplier's MSDSs.

Table 2.2 Material Safety Data Sheet Trade Secret Information

MHC Technology	No. of Trade Secret Chemicals Listed as Hazardous	No. of Trade Secret Chemicals Listed as Carcinogenic	No. of MSDSs Reviewed
Electroless Copper (BASELINE)	3[a]	0	50
Carbon	0	0	12
Conductive Polymer	0	0	7
Graphite	1[b]	0	17
Non-Formaldehyde Electroless Copper	0	0	21
Organic-Palladium	3[c]	1[d]	5
Tin-Palladium	1[e]	1[f]	40

[a] Confidential ingredient 1: Cationic emulsifier - <10%. Confidential ingredient 2: 1-5%; oral 7460 mg/kg LD_{50} rat, skin 16 g/kg LD_{Lo} rabbit. Confidential ingredient 3: 1-5%, oral 350 mg/kg LD_{50} mouse.
[b] Confidential ingredient: surfactant - < 2% by weight.
[c] Confidential ingredient 1: 5-15%; considered to be "relatively non-hazardous"; toxicity data: oral > 6400 mg/kg LD_{50} rabbit. Confidential ingredient 2: 1-5%; toxicity data: oral 100 g/kg LD_{50} rat, oral 1040 mg/kg LD_{50} rabbit. Confidential ingredient 3: 10-20%; toxicity data: IPR 5600 mg/kg LD_{50} MUS, INV 2350 mg/kg LD_{50} MUS.
[d] Confidential ingredient 2: listed as a Class 3 carcinogen by IARC. A Class 3 carcinogen, as defined by IARC, is "not classifiable as to human carcinogenicity," which means that there is "inadequate or no evidence."
[e] Confidential ingredient: Non-ionic surfactant - <3%.
[f] An MSDS for one of the tin-palladium technologies states, "This product may contain small amounts of chemicals listed as being known to the State of California to cause cancer or birth defects or other reproductive harm, under the California Safe Drinking Water and Toxic Enforcement Act of 1986. It does not contain sufficient amounts of such chemicals to make it subject to federal rules on hazard communication for carcinogens administered by OSHA [29 CFR 1910.1200 (d), Reference (1)]." The reference to federal rules on hazardous communication for carcinogens means that it is present at <0.1%.

[2] OSHA requirements apply to a chemical product as sold by a product manufacturer or supplier. Thus, as referred to here, "product formulation" refers to the concentration of chemical ingredients in an MHC chemical product prior to being mixed with other products or water in a chemical bath.

Many of the weight percent data on the MSDSs were reported as a "<" or ">" value. In these cases the reported value is assumed in estimating bath concentrations. For example, if "< 50 percent" was reported for a constituent on an MSDS, it is assumed that product contained 50 percent by weight of that constituent. Also, some data were reported as ranges. In these cases, mid-points for the ranges are used to estimate bath concentrations (e.g., if 20 to 30 percent by weight was reported on the MSDS, 25 percent by weight is assumed).

Some manufacturers did not account for the total mass in each product formulation on their MSDS report, or the remaining mass was identified simply as "non-hazardous" material. In these cases, the suppliers were contacted directly for further information on the constituents. As noted previously, some suppliers have provided additional information on chemical ingredients to the project, but others have not.

Finally, it should be noted that the bath concentrations are estimated and the actual chemical constituents and concentrations will vary by supplier and facility. As part of the risk characterization, two chemicals are assessed further in terms of sensitivity of the risk results to the possible range of bath concentrations.

Chemical Properties

Appendix C contains chemical properties data for each of the non-proprietary chemicals identified in MHC baths. For example, properties listed include molecular weight, vapor pressure, solubility, Henry's Law Constant, and octanol-water partition coefficient. Basic chemical properties information for each chemical is followed by a summary description of fate and transport mechanisms for that chemical.

2.2 ADDITIONAL MHC TECHNOLOGIES

The MHC technologies described in Section 2.1 represent the technologies that were evaluated in this CTSA. However, additional MHC technologies exist which were not evaluated in the CTSA for one or more of the following reasons:

- A product line was not submitted for the technology by any chemical supplier.
- The technology was not available to be tested in the Performance Demonstration.
- The technology has only recently been commercialized since the evaluation began or was submitted too late to be included in the evaluation.

Despite not being evaluated, these technologies are important because they are alternative methods for MHC that accomplish the removal of formaldehyde from PWB manufacturing, which is a goal of members of the PWB industry. A brief description of two MHC technologies not evaluated in this CTSA is presented below. Other technologies may exist, but they have not been identified by the project.

2.2.1 Lomerson Process

The lomerson process utilizes the drilling operation itself as the mechanism to apply a conductive layer of material to the substrate surface of drilled through-holes. The panels can then be cleaned and etched as with other MHC processes before undergoing subsequent manufacturing processes. Completed panels can be assembled and soldered using typical PWB manufacturing methods.

In this process a drill bit is forced through the substrate and into a block of soft conductor material, usually indium or an indium-alloy. While the bit is turning, conductive cuttings from the block are carried up through the hole and smeared throughout the barrel of the drilled hole by the turning drill bit. The smeared material forms the conductive coating required to connect the different layers of the PWB. The lomerson process was described several years ago, but is still in development. However, the process continues to generate interest due to its obvious efficiencies (EPA, 1995).

2.2.2 Non-Formaldehyde Electroless Nickel

The electroless nickel process uses a non-formaldehyde reducing agent to deposit a conductive coating of nickel into the barrels of drilled through-holes. The process is similar to the other wet processes presented earlier in this chapter. It consists of a sequence of chemical baths separated by water rinse steps through which previously drilled and desmeared PWB panels are processed. The supplier recommended sequence of process steps are as follows:

- Conditioner.
- Microetch.
- Sensitizer.
- Activator.
- Dry.

- Cleaner.
- Electroless nickel.

The non-formaldehyde electroless nickel process may be operated in either conveyorized or non-conveyorized modes and is compatible with most types of substrates. While the electroless nickel process is a mature technology (EPA, 1995) very few PWB facilities currently use this technology. No suppliers submitted this technology at the beginning of the CTSA, although one supplier came forward after the Performance Demonstration.

2.3 MARKET PROFILE OF MHC TECHNOLOGIES

The market for MHC chemicals is characterized as being very competitive with slim profit margins, similar to the PWB manufacturing industry (Nargi-Toth, 1997). The industry trade association, the Institute for Interconnecting and Packaging Electronic Circuits (IPC), has a Technology Market Research Council (TMRC) that tracks market, management and technology trends for the electronic interconnection industry. The TMRC publishes annually information on the total value of chemicals used in producing PWBs and the total value of chemicals used in specific applications, such as plating, solder mask, etching, and imaging. Information on plating chemicals is further broken down to include additive/full build copper, electroless copper, electrolytic, etch back/desmear, and oxide process chemicals. Table 2.3 presents TMRC chemical market data for 1985, 1990, and 1995, including the total value of PWB chemicals and the value of electroless copper chemicals. TMRC does not list market values for the alternative MHC chemical products separately.

Table 2.3 Market Value of PWB and Electroless Copper Chemicals[a]

	1985	1990	1995
Total Value of Chemicals Used to Produce PWBs	$336 million	$495 million	$580 million
Value of Chemicals Used in Electroless Copper Process (excluding basic chemicals)	$48 million	$60 million	$52 million
Percent of Total Chemicals Market Held by Electroless Copper Chemicals	14 %	12 %	9 %

[a] Source: IPC Assembly Market Research Council Meeting and IPC Technology Market Research Council Meeting materials provided by Christopher Rhodes/IPC.

For the three years shown in Table 2.3, the market value of PWB chemicals increased between 1985 and 1995, but the market value of electroless copper chemicals peaked in 1990 prior to a decline in 1995. Part of the decline may be due to the increased use of the MHC alternatives in this decade.

Until the latter half of the 1980s, all PWB shops were using an electroless copper process to perform the MHC function (EPA, 1995). Circuit Center in Dayton, Ohio was one of the first U.S. PWB facilities to use an MHC alternative for full-scale production. Circuit Center began beta testing a carbon technology in the mid-to-late 1980s, went to full scale use of the technology in 1989, and has since implemented a graphite technology (Kerr, 1997). By 1995, one supplier estimates 80 percent of shops were using electroless copper, with the rest using mainly carbon, graphite, or tin-palladium (Nargi-Toth, 1997). Another supplier estimates the current market value of the MHC alternatives at about $7 to $8 million, with carbon and graphite technologies accounting for about $5 to $5.5 million of that market (Carano, 1997). Currently, the first full-scale conductive polymer line in the U.S. is being installed by H-R Industries in Richardson, Texas.

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