Chapter 2
Profile of the Surface Finishing Use Cluster

This section of the Cleaner Technologies Substitutes Assessment (CTSA) describes the technologies that comprise the surface finishes 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 the application of a final surface finish to the printed wiring board (PWB). The set of technologies includes hot air solder leveling (HASL), which was selected as the baseline, and the alternative surface finishes, including electroless nickel/immersion gold (nickel/gold), electroless nickel/electroless palladium/immersion gold (nickel/palladium/gold), organic solderability preservative (OSP), immersion silver, and immersion tin.

Section 2.1 presents process descriptions for each of the surface finishing technologies and describes the chemical composition of products that were evaluated in the CTSA. Section 2.2 briefly describes additional technologies that may be used to perform the surface finishing function, but were not evaluated.

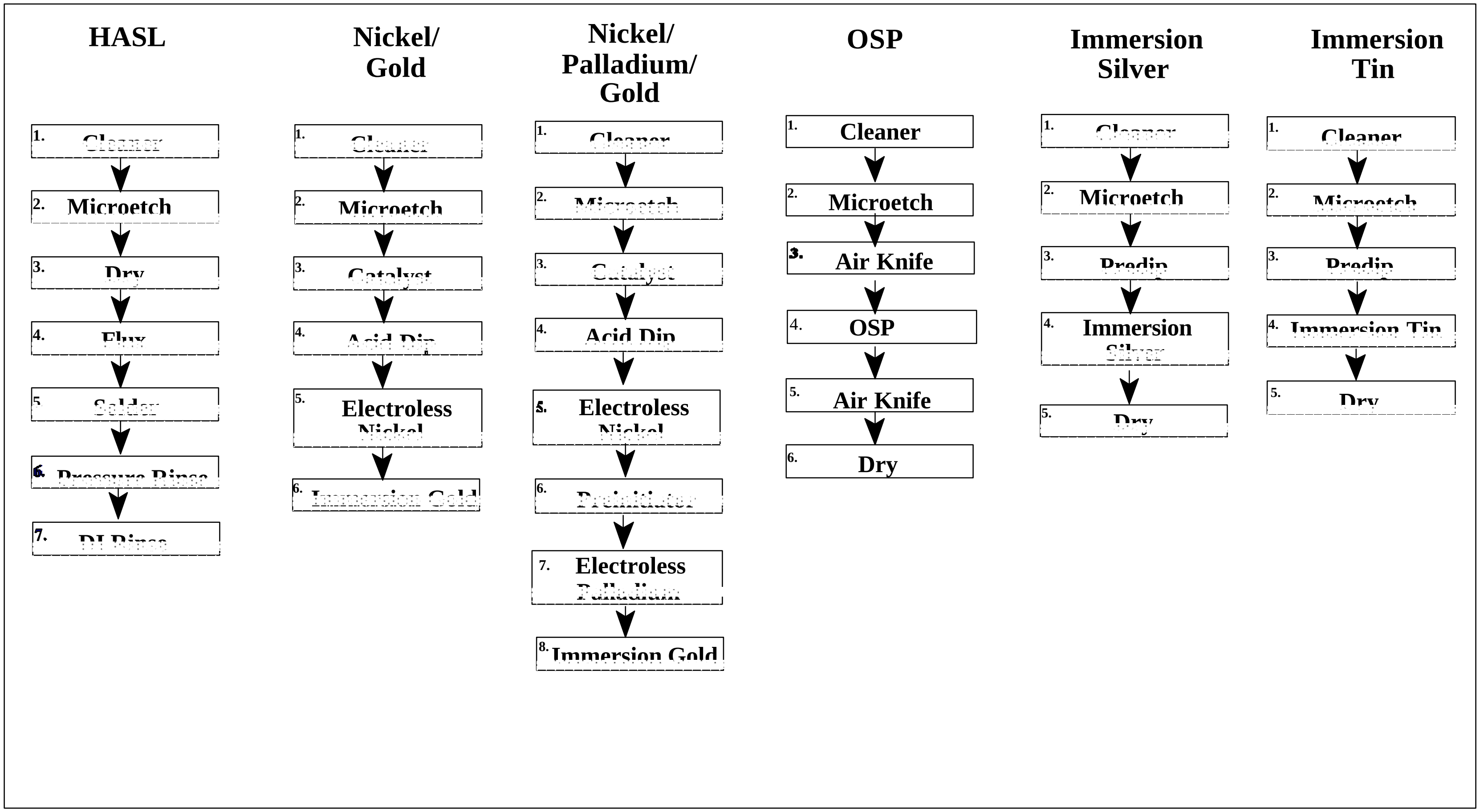
2.1 CHEMISTRY AND PROCESS DESCRIPTION OF SURFACE FINISHING TECHNOLOGIES

This section introduces the surface finishing technologies evaluated in the CTSA and details the process sequences. Typical operating conditions and operating and maintenance procedures are described in an overview of the surface finishing manufacturing process. Then the chemical processes occurring in each bath are detailed, along with additional process information specific to each technology.

2.1.1 Process Sequences of Surface Finishing Technologies

Figure 2-1 depicts the six surface finishing technologies evaluated in the CTSA. Because the function of applying a final surface finish can be performed using any of these technologies, these technologies may be substituted for each other in PWB manufacturing. The surface finishing technologies are all wet chemistry processes consisting of a series of chemical process baths, often followed by rinse steps, through which the PWB panels are passed to apply the final surface finish. The exception is the HASL process, which combines the typical cleaning and etching chemical processes with a mechanical process of dipping a board into molten solder followed by rinsing (described in Section 2.1.3).

For each of the surface finishes evaluated, the process steps depicted in the figure represent an integration of the various commercial products within the technology category. For example, chemical suppliers to the PWB industry submitted product data for two different OSP processes. The chemical suppliers offer additional variations to the OSP process that may have slightly different bath chemistries or process sequences, than the processes submitted. Figure 2-1 lists the process steps in a typical, or generic, OSP surface finishing line. The process steps in an actual line may vary.



Note: One or more intermediate rinse steps typically separate the process steps listed above. For simplicity, these intermediate rinse steps have not been included in the diagram.

Figure 2-1. Typical Process Steps for Surface Finishing Technologies

2.1.2 Overview of the Surface Finishing Manufacturing Process

Surface finishing technologies typically consist of a series of sequential chemical processing tanks (baths) separated by water rinse stages. The process can either be operated in a vertical, non-conveyorized submersive-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 baths may be agitated to improve contact between the panels and the bath chemistry. Agitation methods employed by PWB manufacturers include panel agitation, ultrasonic vibration, 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 and to prevent 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 quantities of wastewater generated from surface finishing lines are discussed in Section 5.1, Resource Conservation, while the composition of the wastewater is modeled and presented in Section 3.2, Exposure Assessment. Rinse water reduction techniques are discussed in Section 6.1, Pollution Prevention.

After the application, imaging, and development of the solder mask, panels are loaded into racks (vertical, non-conveyorized mode) or onto a conveyor (horizontal, conveyorized mode) for processing by the surface finishing 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, or covered during extended periods of latency. Horizontal, conveyorized systems are typically fully enclosed, with air emissions vented to a control technology or to the atmosphere outside the plant.

The HASL process differs from the other alternatives in that it does not rely on a chemical process to apply the final surface finish. Instead, the process combines the chemical processes of board preparation and cleaning with a mechanical step to apply the finish.

Regardless of the mode of operation or type of alternative, process chemical 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-in. Bath solution may be discarded and replaced with new solution as required, with the frequency of replacement 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 also may clean the tank or conveyorized equipment during bath change-out operations.

Some process baths are equipped with filters to remove particulate matter that may be introduced to the bath or formed as a precipitate through a chemical reaction. 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 Surface Finishing Technologies

This section describes in detail the processes for applying a solderable and protective coating, or surface finish, to the outside surfaces of a PWB. A brief description of the chemical mechanisms or processes occurring in each of the process steps, along with other pertinent process data such as flux compatibilities, storage limitations, assembly methods required, 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., nickel/gold, OSP, immersion tin), 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.

Each alternative surface finishing process evaluated in the CTSA uses one of the following mechanisms to apply the final finish.

- <u>Electroless process</u>: This chemical process promotes continuous deposition of a metal onto the PWB surface through an oxidation-reduction chemical reaction, without the use of an external electrical potential. A reducing agent, such as sodium hypophosphite, donates electrons to the positively charged metal ions in solution, thereby reducing the metal and promoting its deposition onto the catalyzed metal surfaces of the PWB. This reaction is considered auto-catalytic because it will continue to plate in the presence of source metal ions and a reducing agent until the board is removed from the plating bath. The thickness of plated deposits vary according to the amount of time spent in the plating bath, but are typically in the 3 to 5 micron range.
- <u>Immersion process</u>: This chemical process uses a chemical displacement reaction to deposit a metal layer onto the exposed metal surface of the PWB. In this reaction, the base metal donates the electrons that reduce the positively charged metal ions in the solution. Driven by the electrochemical potential difference, the metal ions in solution (e.g., gold ions in the immersion gold portion of the nickel/palladium/gold process) are deposited onto the surface of the board, simultaneously displacing ions of the surface metal (e.g., nickel ions for the example above) back into solution. This reaction is considered self-limiting, because once the surface metal is plated, there is no longer a source of electrons and the reaction stops. Surface finish deposits of up to 0.2 microns are considered typical for immersion processes.
- <u>Coating</u>: A protective coating is applied by submerging the PWB into a chemical bath. Although a coating does not require an exchange of electrons to facilitate deposition of the protective layer, some coatings may be formulated to adhere selectively to exposed metal surfaces. Typical coating thicknesses range from 0.1 to 0.5 microns.

Hot Air Solder Leveling (HASL)

HASL has long been the standard surface finishing method used in the manufacture of double-sided and multi-layered boards, because its excellent solderability during assembly. However, due to its technological limitations, environmental concerns, and process safety issues, assemblers and manufacturers have begun to seriously consider other surface finishes as viable alternatives to HASL. During the HASL process, soldermask-coated boards are first cleaned and etched to prepare the contact surfaces for the solder. Following the application of flux to a board, a layer of solder is applied to the copper surfaces by submersing the panel in molten solder. The excess solder is then blown from the board by an air knife, leaving a thin, protective layer of solder on the exposed circuitry.

Any of these three process segments - board preparation, solder application, or cleaning - may be automated or manual, or any combination thereof. These segments may also be integrated into one entire conveyorized process, combining the chemical pretreatment and cleaning steps with the solder application. Flux formulations are altered depending on the mode of operation and the desired flux characteristics. HASL finishes are compatible with surface mount technology (SMT) and typical through hole components; however, the lack of planarity, or flatness, of the finish makes assembly with fine pitch, small components difficult to control. In addition, the HASL finish cannot be wirebonded. Extended shelf life on a typical SMT pad or plated through hole (PTH) annular ring is not a concern with HASL finished boards, because of the durability of the finish. However, large flat surfaces can exhibit solderability problems after storage due to removal of all but a very thin coating of solder by the HASL process. This thin coating allows exposure of intermetallic surfaces that can create solderability problems (Carroll, 1999). Typically HASL finished PWBs have a shelf life of up to a year (Kerr, 1999).

A flow diagram of the process steps in a typical HASL process is presented in Figure 2-2. A brief description of each of the process steps is also given.

Step 1: Cleaner: An acid-based cleaner removes surface oils, oxides, and any organic residues left after the solder mask application. The cleaner provides a clean, consistent copper surface to ensure uniform etching.

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

Step 3: Dry: The etched panels are then air-dried using a non-heated blower to minimize the formation of oxides on the cleaned and etched copper surfaces.

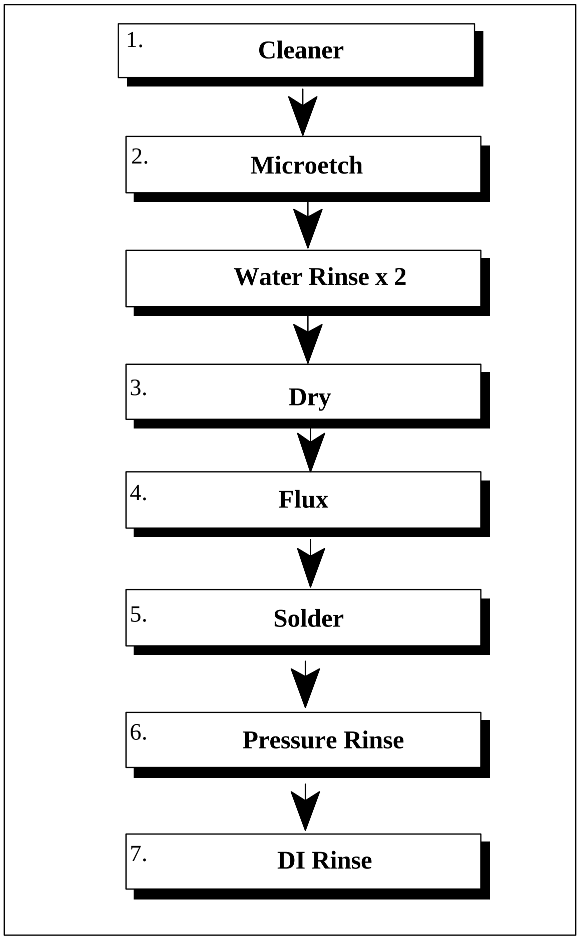


Figure 2-2. HASL Process Flow Diagram

Step 4: Flux: A chemical flux is applied to the panel to reduce the surface tension of the copper pads, thereby maximizing the wetting of the copper surfaces. The flux is composed of a heat transfer fluid, stabilizers, inhibitors, and activating agents. Flux formulations may vary considerably depending on the characteristics desired. Horizontal HASL system fluxes tend to be lower in viscosity and more highly activated than fluxes for vertical, non-conveyorized systems.

Step 5: Solder: Solder is selectively applied to the copper surfaces of the panel by submerging the preheated, fluxed panels in a bath of molten solder. The excess solder is then removed from the board by an air knife when the panel is withdrawn from the solder bath.

Step 6-7: Pressure Rinse: A high-pressure water rinse is used to dislodge any solder balls or excess solder flash that may be present on the PWB. The water rinse also removes any remaining flux residue that was not vaporized in the solder bath. This rinse stage may consist of several rinse tanks and include heated rinses or rinses combined with mechanical scrubbing. A post-solder chemical cleaner may also be used as a rinse aid if desired, or if water rinsing is insufficient. The final step in the post-clean process is rinsing in de-ionized water to reduce ionic contaminants on the surface finish.

Flux selection is critical to the sound operation of the HASL process. The flux is responsible for creating the copper surface conditions required to achieve a high quality solder deposit on the PWB. Fluxes are available in a variety of formulations with differing characteristics such as viscosity, foam level, acidity, volatile content, and type of activator. The type of HASL flux ultimately selected will depend on the type of chemicals and processes used in previous manufacturing stages, type of solder mask, and the solder deposit characteristics required.

The cleaning steps after the application of the solder can vary quite a bit, depending on several factors including the type of flux, type of solder mask, and the cleanliness standards to be met. The most commonly reported post-clean sequence by survey respondents utilized a series of water rinse baths combined with either high pressure rinsing, scrubbing, or a mild detergent. The post-clean system described above was selected to represent the HASL baseline.

Nickel/Gold

The nickel/gold process promotes the deposition of an initial, thick layer of nickel followed by a thin, protective layer of gold onto the exposed copper surfaces of the PWB. Nickel characteristics such as hardness, wear resistance, solderability, and uniformity of the deposit make this process a durable alternative PWB surface finish. The thin layer of immersion gold preserves the solderability of the finish by preventing oxidation of the highly active nickel surface. Nickel/gold finishes can typically withstand as many as six or more thermal excursions (heating cycles) during assembly without losing solderability.

This process can be operated in either a horizontal, conveyorized or vertical, non-conveyorized mode. A nickel/gold finish is compatible with SMT, flip chip, and ball grid array (BGA) technologies, as well as with typical through hole components. The thin layer of gold makes the surface aluminum wire-bondable, with thicker gold deposits also allowing gold wire-bonding. The high plating temperatures and low pH of the nickel/gold plating process can be incompatible with solder masks with high acrylic content, although solder masks high in epoxy content are unaffected by the plating solution. Nickel/gold plated boards have a shelf life of up to two years or more.

A flow diagram of the process baths in a typical nickel/gold process is presented in Figure 2-3, followed by a brief description of each of the process steps.

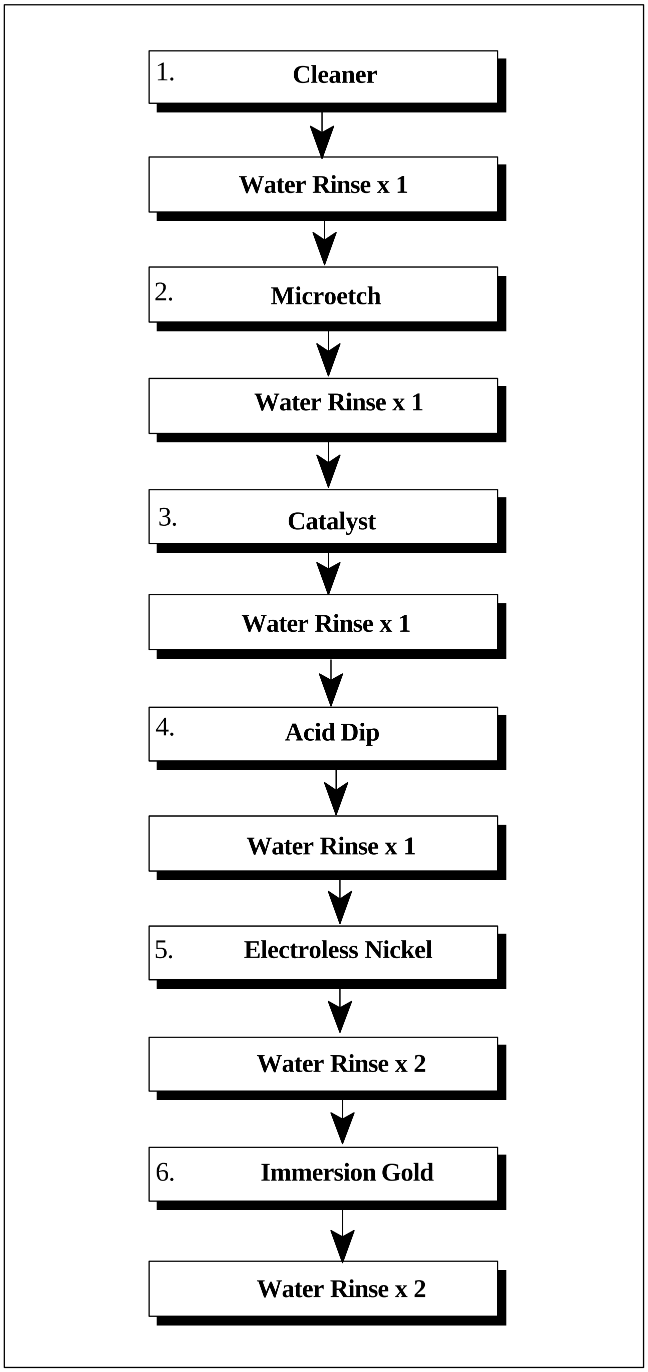


Figure 2-3. Nickel/Gold Process Flow Diagram

Step 1: Cleaner: Grease, contaminants, and any organic solder mask residues are removed from the PWB surface in an acidic cleaner solution. The cleaner provides a clean, consistent copper surface to ensure uniform etching and prepares the board for application of the palladium catalyst.

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

Step 3: Catalyst: The catalyst consists of a palladium salt in an acidic solution. Palladium ions are deposited onto the surface of a PWB in a displacement reaction, effectively exchanging the surface copper layer for palladium, thus forming a catalytic layer for subsequent nickel plating.

Step 4: Acid Dip: The acid dip, usually a weak sulfuric or hydrochloric acid, removes any residual catalyst from the non-copper surfaces of the PWB, to prohibit plating on the solder mask or other unwanted areas of the board.

Step 5: Electroless Nickel: An electroless nickel solution is used to plate a layer of nickel onto the surface of the palladium-covered areas in a high temperature, acidic bath. The electroless nickel solution contains a source of nickel ions, phosphorous, and a reducing agent, which is typically either sodium hypophosphite or dimethylamine borane. In the presence of the palladium, the reducing agent provides electrons to the positively charged nickel ions, causing reduction of the nickel and the deposition of elemental nickel onto the exposed palladium catalyst (Parquet and Sedacca, 1996). Phosphorous is co-deposited with the nickel, and the resulting nickel-phosphorous alloy forms a corrosion-resistant layer protecting the underlying copper. Because the bath is autocatalytic, it will continue plating until the panel is removed from the nickel bath. Nickel layer thicknesses for PWBs are typically 3 to 5 microns (120 to 200 microinches).

Step 6: Immersion Gold: A very thin, protective layer of pure gold is deposited onto the surface of the nickel in the immersion gold plating bath. A chemical displacement reaction occurs, depositing the thin layer of gold onto the metal surface while displacing nickel ions into the solution. Because the reaction is driven by the electrochemical potential difference between the two metals, the reaction ceases when all of the surface nickel has been replaced with gold. Gold layer thicknesses are typically 0.2 microns (8 microinches), but can be increased to allow gold wire-bonding of the final surface.

Although electroless nickel plating processes all require the presence of a catalyst to plate nickel onto a copper surface, the catalyst can at times be too aggressive and catalyze areas where plating is undesirable, such as areas of fine pitch circuitry, causing unintended short-circuiting. This problem is handled successfully (with typically less than a 5 percent failure rate) by introducing the panel to an acid dip after the catalyst bath, as described above (Kerr, 1999). The acid dip removes the unintended palladium salt deposits, without harming the elemental palladium deposited onto the copper surfaces.

A second method employed by some manufacturers is to use a less active catalyst, which tends not to bridge fine pitch circuitry or adhere onto solder mask-covered PWB surfaces. A ruthenium-based catalyst is used to deposit a ruthenium seed layer, in place of the more typical palladium-based catalysts. A nickel surface is then plated to the ruthenium seed layer using a sodium-hypophosphite-reduced nickel plating chemistry, until the desired nickel thickness is obtained. The gold is then applied as described above.

Nickel/Palladium/Gold

The nickel/palladium/gold process is similar to the nickel/gold process described above, except it uses a palladium metal layer that is deposited after the nickel layer, but prior to depositing the final gold layer. The palladium layer is much harder than gold, providing added strength to the surface finish for wirebonding and connector attachment, while protecting the underlying nickel from oxidation.

The process can be operated in either a horizontal, conveyorized, or a vertical, non-conveyorized mode. A nickel/palladium/gold finish is compatible with SMT, flip chip, and BGA technologies, as well as with typical through hole components. The finish is also both gold and aluminum wire-bondable. The high plating temperatures and low pH of the nickel/palladium/gold plating process can be incompatible with solder masks with high acrylic content, although solder masks high in epoxy content are unaffected by the plating solution. Nickel/palladium/gold-plated boards can withstand as many as six thermal excursions during assembly, and have a shelf life of up to two years or more.

A flow diagram of the process steps in a typical HASL process is presented in Figure 2-4. A brief description of each of the process steps is also given.

Steps 1- 4: Cleaner/Microetch/Catalyst/Acid Dip: PWBs are cleaned, microetched, and a palladium catalyst is applied to the exposed copper surfaces in a chemical process similar to the one described previously for nickel/gold. An acid dip is then used to remove the catalyst from areas of the board where plating is undesirable.

Step 5: Electroless Nickel: An electroless nickel solution plates a layer of nickel onto the surface of the thin, initial nickel deposit. The electroless nickel bath is a slightly alkaline solution containing a source of nickel ions, and a sodium hypophosphite reducing agent. The reducing agent provides electrons to the positively charged nickel ions, causing the reduction of the nickel and the plating of elemental nickel onto the exposed nickel-boron layer. Phosphorous is co-deposited with the nickel, causing the formation of a corrosion resistant layer of nickel-phosphorous alloy that protects the underlying copper. Because the bath is autocatalytic, it will continue plating until the panel is removed from the nickel bath. Nickel layer thicknesses are typically 3 to 5 microns (120 to 200 microinches).

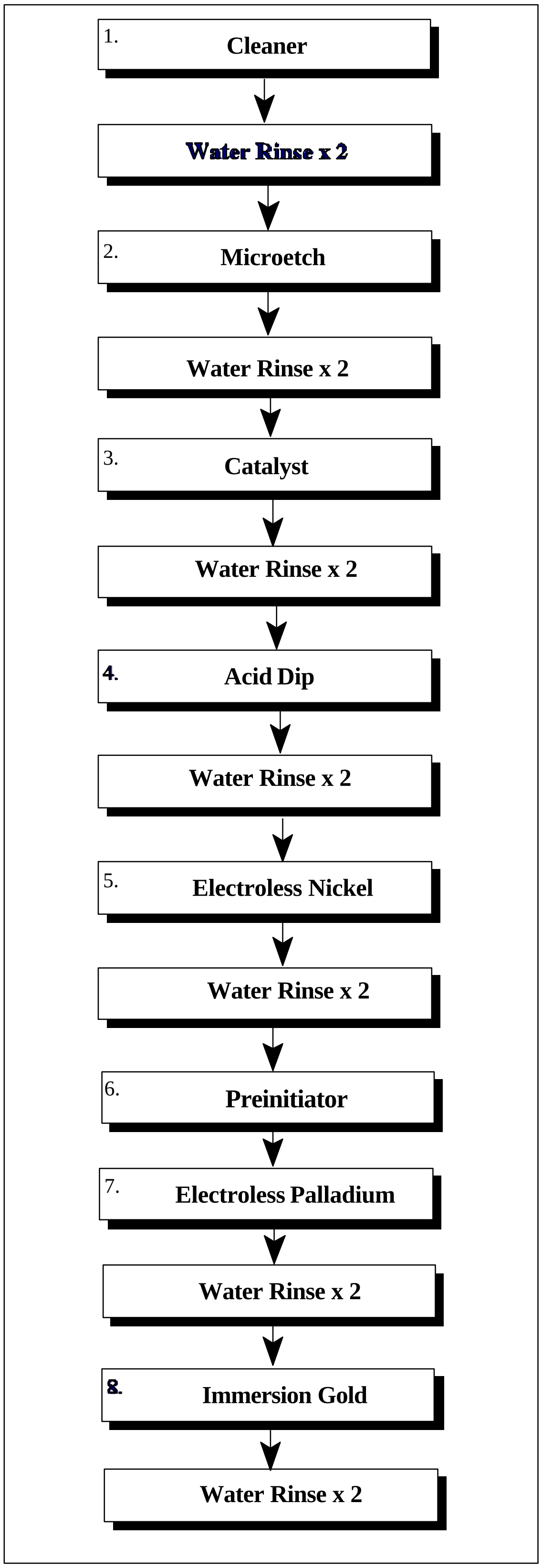


Figure 2-4. Nickel/Palladium/Gold Process Flow Diagram

Step 6: Preinitiator: The preinitiator reactivates the nickel surfaces by using a mineral acid to remove oxide from the surface of the nickel. In addition, the preinitiator deposits trace quantities of a catalytic metal that promotes homogeneous palladium deposition, ensuring that all nickel surfaces begin plating quickly and at the same time.

Step 7: Electroless Palladium: The electroless palladium bath deposits a thin layer of palladium onto the nickel-covered circuitry through an oxidation-reduction reaction. Hypophosphite or formate is used as the reducing agent, providing electrons to the positively charged palladium ions, resulting in the plating of palladium onto the nickel surfaces of the PWB. Palladium layer thicknesses are typically 0.3 to 0.8 microns (12 to 32 microinches).

Step 8: Immersion Gold: A very thin, protective layer of pure gold is deposited onto the surface of the palladium in the immersion gold plating bath. A chemical displacement reaction occurs, depositing the thin layer of gold onto the metal surface while displacing palladium ions into the solution. Because the reaction is driven by the potential difference of the two metals, the reaction ceases when all of the surface palladium has been replaced with gold. Gold layer thickness is typically 0.2 microns (8 microinches).

Organic Solderability Preservative (OSP)

The OSP process selectively applies a flat, anti-oxidation film onto the exposed copper surfaces of the PWB to preserve the solderability of the copper. This coating reacts with the copper in an acid and water mixture to form the nearly invisible protective organic coating. OSP processes can be based on benzimidazole chemistries that deposit thicker coatings, or on benzotriazoles and imidazoles chemistries which deposit thinner coatings. The thicker OSP coatings, which are evaluated in this CTSA, can withstand a minimum of three and up to as many as five thermal excursions while still maintaining coating integrity. Coating thicknesses of 0.1 to 0.5 microns (4 to 20 microinches) are typical for the thicker coatings, as opposed to the monomolecular layer formed by the thinner OSPs.

The process is typically operated in a horizontal, conveyorized mode but can be modified to run in a vertical, non-conveyorized mode. OSP processes are compatible with SMT, flip chip, and BGA technologies, as well as with typical through hole components. The OSP surface finish cannot be wirebonded. OSP surfaces are compatible with all solder masks, can withstand 3 to 4 thermal excursions during assembly, and have a shelf life of up to one year; extended shelf life times may result in a degradation of the coating.

A flow diagram of the process baths in a typical OSP process is presented in Figure 2-5, followed by a brief description of each of the process steps.

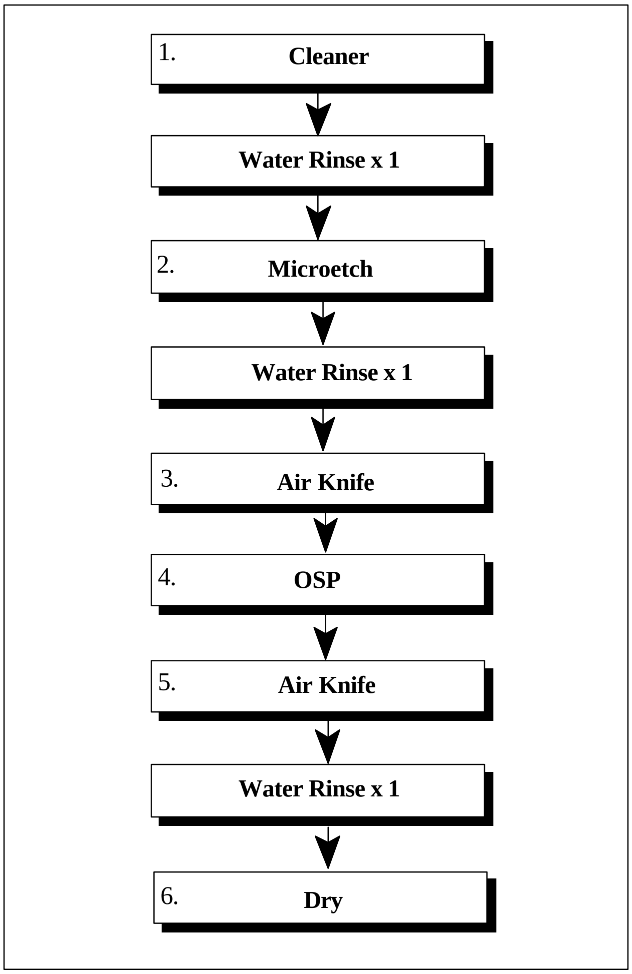


Figure 2-5. OSP Process Flow Diagram

Step 1: Cleaner: Surface oils and solder mask residues are removed from the exposed copper surfaces in a cleaner solution. The acidic solution prepares the surface to ensure the controlled, uniform etching in subsequent steps.

Step 2: Microetch: The microetch solution, typically consisting of dilute hydrochloric or sulfuric acid, etches the existing copper surfaces to further remove any remaining contaminants and to chemically roughen the surface of the copper to promote coating adhesion.

Step 3: Air Knife: An air knife removes excess water from the panel to limit oxidation formation on the copper surfaces prior to coating application. This step also minimizes drag-in of sulfates, which are harmful to the OSP bath.

Step 4: OSP: A protective layer is formed selectively on the exposed copper surfaces by the OSP in an acidic aqueous bath. The deposited protective layer chemically bonds to the copper, forming an organometallic layer that preserves the solderability of the copper surface for future assembly (Mouton, 1997).

Step 5: Air Knife: An air knife removes excess OSP from the panel and promotes even coating across the entire PWB surface. The air knife also minimizes the chemical losses through drag-out from the OSP bath.

Step 6: Dry: A warm-air drying stage cures the OSP coating and helps to remove any residual moisture from the board.

Immersion Silver

The immersion silver process promotes the selective deposition of silver onto the exposed copper surfaces of the PWB through a chemical displacement reaction. Silver surfaces are protected from tarnishing by a co-deposited organic inhibitor that forms a hydrophobic layer on top of the silver, thus preserving the coating's solderability. The final silver finish thickness is typically 0.1 microns (3 to 4 microinches). The silver process submitted for evaluation is operated exclusively as a horizontal, conveyorized process, however the process may be operated in either vertical or horizontal mode. Immersion silver finishes are compatible with SMT, flip chip, and BGA technologies, as well as with typical through hole components. They are also both gold and aluminum wire-bondable. Silver finishes are compatible with all types solder masks, can withstand up to five thermal excursions during assembly, and have a shelf life of at least six months.

A flow diagram of the process steps in a typical HASL process is presented in Figure 2-6. A brief description of each of the process steps is also given.

Step 1: Cleaner: An acid-based cleaner removes surface oils, oxides, and any organic residues left after the solder mask application. The cleaner provides a clean, consistent copper surface to ensure uniform etching.

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

Step 3: Predip: Etched panels are processed through a predip solution prior to silver deposition to remove any surface oxidation that may have occurred in the previous rinse stage. The predip, which is chemically similar to that of the silver deposition bath, is also used to protect the bath from any harmful drag-in chemicals that may be detrimental to the deposition bath.

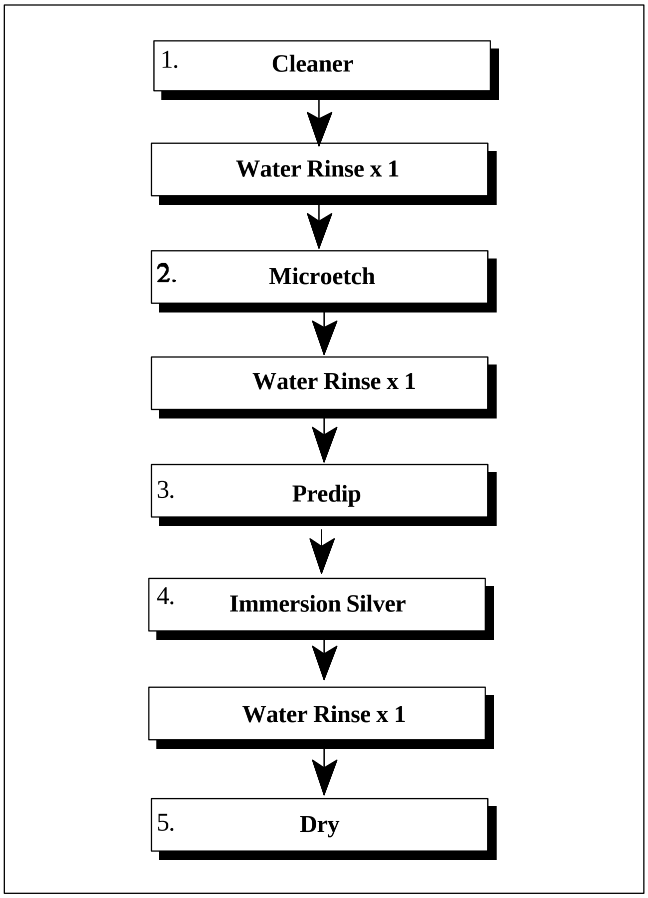


Figure 2-6. Immersion Silver Process Flow Diagram

Step 4: Immersion Silver: The immersion silver bath is a pH-neutral solution that selectively deposits a 0.1 micron (3 to 4 microinch) layer of silver onto all of the exposed copper surfaces of the PWB. Coating proceeds by a simple displacement reaction, with silver ions displacing copper ions from the surface. The liberated copper ions are benign to the bath chemistry and thus do not inhibit the bath effectiveness as copper concentrations increase. Because the bath is an immersion process, plating is self-limiting and will cease when the entire copper surface has been coated.

Step 5: Dry: A drying stage removes any residual moisture from the board to prevent staining and to ensure metal quality in the through holes.

Immersion Tin

The immersion tin process utilizes a thiorea-based reducing agent to create an electrochemical potential between the surface and stannous ions in solution, causing the reduction of a layer of tin onto the copper surfaces of the PWB. An organo-metallic compound, which is co-deposited along with the tin, acts to retard the formation of a tin-copper intermetallic layer, preserving the solderability of the finish. The organo-metallic compound also inhibits the formation of tin whiskers (i.e., dendritic growth). The process is typically operated in a conveyorized fashion, but can be modified to run in a vertical, non-conveyorized mode. Immersion tin surfaces are compatible with SMT, flip chip, BGA technologies, and typical through hole components. The immersion tin surface cannot be wirebonded. Tin surfaces are compatible with all solder masks, have a reported shelf life of one year and can typically withstand a minimum of five thermal excursions during assembly.

A flow diagram of the process steps in a typical immersion tin process is presented in Figure 2-7. A brief description of each of the process steps is given.

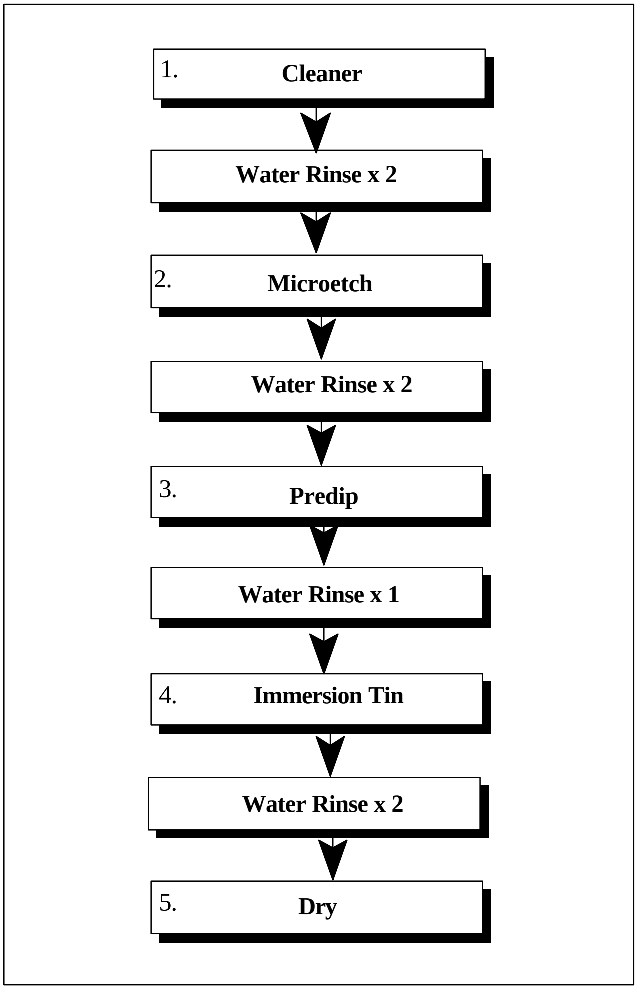


Figure 2-7. Immersion Tin Process Flow Diagram

Step 1: Cleaner: Surface oils and solder mask residues are removed from the exposed copper surfaces in a cleaner solution. The acidic solution prepares the surface to ensure controlled, uniform etching.

Step 2: Microetch: A microetch solution, typically consisting of dilute hydrochloric or sulfuric acid, removes any remaining contaminants from the copper surface. The etching also chemically roughens the copper surface to promote good tin-to-copper adhesion.

Step 3: Predip: Etched panels are processed through a predip solution that is chemically similar to that of the tin bath, thus protecting the plating bath from harmful drag-in chemicals.

Step 4: Immersion Tin: A tin plating bath deposits a thin layer of tin onto the exposed copper circuitry through a chemical displacement reaction that deposits stannous ions while displacing copper ions into the plating solution. The bath is considered self-limiting, because plating continues only until all the copper surfaces have been coated with a tin deposit. The presence of a complexing agent, thiourea, prevents the copper from interfering with the plating process. The complexed copper is removed as a precipitate from solution by decantation.

Step 5: Dry: A drying stage removes any residual moisture from the board to prevent staining and to ensure high metal quality in the through holes.

2.1.4 Chemical Characterization of Surface Finishing Technologies

This section describes the sources of bath chemistry information, methods used for summarizing that information, and the use of bath chemistry data. Publicly-available information, along with proprietary chemical information obtained from the chemical suppliers, was used to assess exposure, risk, and cost for the processes. This section does not identify any proprietary ingredients. Generic names have been submitted for the names of proprietary, confidential chemicals to mask their identity.

Use of Chemical Product and Formulation Data

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

- material safety data sheets (MSDSs);
- Product Data Sheets;
- proprietary chemical product formulations; and
- patent data, in isolated cases.

The chemical formulations identify the chemicals and concentrations present in the chemical products while the MSDS provides physical property and worker hazard information on the entire formulation. The Product Data Sheets describe how those products are mixed together to make up the individual process baths. Patent information, when available, provided insight into the mechanisms for chemical activity.

Table 2-1 presents all of the chemicals identified in surface finishing process lines and the technologies in which they were used. Generic names have been substituted for the names of proprietary, confidential chemicals to mask their identity. Although the confidential formulations included all of the chemicals listed below, a chemical was considered publicly-available if it was listed on a MSDS or patent.

Table 2-1. Use Cluster Chemicals and Associated Surface Finishing Processes

Chemical	HASL	Nickel/ Gold	Nickel/ Palladium/ Gold	OSP	Immersion Silver	Immersion Tin
Acetic acid				X		
Aliphatic acid A		X				
Aliphatic acid B		X	X			
Aliphatic acid D						X
Aliphatic acid E		X	X			
Aliphatic dicarboxylic acid A		X	X			
Aliphatic dicarboxylic acid C		X	X			
Alkylalkyne diol	X					X
Alkylamino acid A					X	
Alkylamino acid B		X	X			X
Alkylaryl imidazole				X		
Alkylaryl sulfonate	X					X
Alkyldiol	X	X	X			
Alkylimine dialkanol						X
Alkylphenol ethoxylate	X					X
Alkylphenol polyethoxyethanol	X	X				
Alkylpolyol			X			
Amino acid salt			X			
Amino carboxylic acid			X			
Ammonium chloride		X				
Ammonia compound A			X			
Ammonia compound B		X	X			
Ammonium hydroxide		X	X			

Chemical	HASL	Nickel/ Gold	Nickel/ Palladium/ Gold	OSP	Immersion Silver	Immersion Tin
Aromatic imidizole product [a]				X		
Arylphenol	X			X		
Bismuth compound						X
Citric acid	X	X	X			X
Copper ion				X		
Copper salt C				X		
Copper sulfate pentahydrate	X	X	X	X		
Cyclic amide						X
Ethoxylated alkylphenol	X	X	X	X		X
Ethylenediamine			X			
Ethylene glycol	X			X		
Ethylene glycol monobutyl ether	X					X
Fatty amine					X	
Fluoboric acid	X					X
Gum	X			X		
Hydrochloric acid	X	X	X	X		X
Hydrogen peroxide	X	X	X	X	X	
Hydroxy carboxylic acid						X
Hydroxyaryl acid	X	X	X	X		
Hydroxyaryl sulfonate	X			X		
Inorganic metallic salt A		X				
Inorganic metallic salt B		X	X			
Inorganic metallic salt C		X				
Lead	X					
Maleic acid			X			
Malic acid		X	X			
Methane sulfonic acid						X
Nickel sulfate		X	X			
Nitrogen acid					X	
Nonionic surfactant [a]					X	
Palladium chloride		X				
Palladium salt			X			
Phosphoric acid	X	X	X	X	X	X
Potassium compound		X	X			
Potassium gold cyanide		X	X			
Potassium peroxymonosulfate	X	X				X
Propionic acid			X			
Quantenary alkylammonium chlorides						X
Silver nitrate					X	

Chemical	HASL	Nickel/ Gold	Nickel/ Palladium/ Gold	OSP	Immersion Silver	Immersion Tin
Silver salt						X
Sodium benzene sulfonate	X					X
Sodium hydroxide	X	X	X	X	X	
Sodium hypophosphite		X				
Sodium hypophosphite mono hydrate		X	X			
Sodium phosphorus salt						X
Sodium salt		X	X			
Stannous methane sulfonic acid						X
Substituted amine hydrochloride		X	X			
Sulfuric acid	X	X	X	X	X	X
Surfactant [a]			X			
Thiourea						X
Tin	X					
Tin chloride						X
Transition metal salt [a]		X	X			
Unspecified tartrate						X
Urea						X
Urea compound B		X	X			
Urea Compound C						X
Vinyl polymer						X

[a] Dropped due to insufficient identification.

Determining Chemical Formulations

Determining the chemical formulations for each process step is critical for evaluating each surface finishing technology. Each surface finishing product line submitted for evaluation was divided into basic bath steps common to all the processes within that surface finishing category (e.g., both OSP product lines submitted were divided into cleaner, microetch, and OSP baths). The basic bath steps were combined to form a process flow diagram specific to each surface finishing technology, as shown in Figure 2-1. The recommended formula for creating a new bath, along with the individual formulations for each chemical product, were combined to determine the individual chemical concentrations in the final bath. 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} = chemical concentration, by weight, in the product, from chemical product formulations obtained from chemical suppliers (%)

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 ethylene glycol concentration in the cleaner bath is shown below for one supplier's OSP process. Each product's formulation lists the chemicals that are contained in that product on a weight percentage basis. For ethylene glycol, this is 40 percent, or 40 grams ethylene glycol per 100 grams of product (C_{CHEM}). The supplier's Product Data Sheet lists how much of that chemical product is used in the total bath make-up on a volume percentage basis: in this case, ten percent, or ten liters of product per 100 liters of the total bath (C_{FORM}). The remaining volume in the bath is made up of deionized water. The MSDS for the product lists the specific gravity or density (D) of the product, which was multiplied by the weight and volume percentages above to obtain the bath concentration (C_b) 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:

$$\frac{40g}{100g}\left(\frac{10L}{100L}\right)\left(\frac{1.27g}{cm^3}\right)\left(\frac{1000cm^3}{L}\right) = 50.8\frac{g}{L}$$

After the product formulation and Product Data Sheet data were combined in the above manner for each supplier's product line, a list of chemicals in each surface finishing technology category (HASL, OSP, etc.) was compiled. This list shows all the 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., OSP, nickel/gold, and immersion tin) 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 formulation data and are presented in Appendix B. Concentrations are for each bath in each surface finishing process alternative.

Data Limitations

Limitations and uncertainties in the chemical characterization data arise primarily from side reactions in the baths. 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 product formulation data, MSDSs or Product Data Sheets, but would affect bath concentrations over time. As a result, bath concentrations are estimated; actual chemical constituents and concentrations will vary by supplier and facility.

In cases where the formulation data was reported as a “ < ” or “ > ” value, the reported values were assumed in calculating bath concentrations. For example, if “< 5 percent” was reported for a constituent by a product formulation, it is assumed that product contained 5 percent by weight (or volume, where appropriate) of that constituent. Also, some data were reported as ranges. In these cases, mid-points for the ranges were used to estimate bath concentrations (e.g., if 20 to 30 percent by weight was reported, 25 percent by weight was assumed).

Chemical Properties

Appendix C contains chemical properties data for each of the non-proprietary chemicals identified in surface finishing 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. In order to protect the identity of confidential chemicals, chemical properties data was not included for proprietary chemicals.

2.2 ADDITIONAL SURFACE FINISHING TECHNOLOGIES

The surface finishing technologies described in Section 2.1 represent the technologies that were evaluated in the CTSA. However, additional surface finishing 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; or
- 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 surface finishing that accomplish the removal of lead from PWB manufacturing, which is a goal of the PWB manufacturing industry. A brief description of one surface finishing technology not evaluated in this CTSA is presented below. Other technologies may exist, but they have not been identified by the project.

2.2.1 Immersion Palladium

The immersion palladium process uses a three step process to deposit a thin surface finish of palladium on the exposed copper traces of the PWB. The process is similar to other wet processes presented earlier in this chapter. It consists of a series of chemical baths separated by a series of water rinse steps. The recommended bath sequence for the immersion palladium process is as follows:

- cleaner;
- water rinse;
- microetch;
- water rinse;
- immersion palladium;
- water rinse; and
- dry.

A mild alkaline cleaner is first used to clean the surface of copper, removing oil and debris from the boards' surface. The copper is then lightly etched to remove any copper oxide by the microetch, providing a pristine surface for palladium deposition. Finally, a three microinch layer of palladium is deposited onto the board by the immersion palladium bath via a chemical displacement reaction. During the reaction, palladium ions are deposited onto only the exposed copper surfaces of the board, displacing copper ions into the plating solution. Like other immersion processes, the palladium deposition is self-limiting, halting once all of the exposed copper has been covered by a layer of palladium. The displaced copper remains in solution, continuing to build in concentration, until an electrolyte in the bath causes the copper to precipitate out of solution, usually at a concentration of greater than 150 parts per million. The precipitate is then filtered out of the bath. The bath can be operated without replacement as long as the electrolyte and palladium content are maintained (Sedlak, 2000).

The immersion palladium process is typically operated in a vertical, non-conveyorized mode but can be modified to run in a horizontal, conveyorized mode. Immersion palladium finishes are compatible with SMT, flip chip, and BGA technologies, as well as with typical through hole components. The finish is also gold wire-bondable. Immersion palladium finishes are sensitive to some of the more aggressive fluxs, so milder fluxes (e.g., no-clean fluxes) are recommended. They can withstand four thermal excursions during assembly, and have a shelf life of at least 12 months. The immersion palladium process has been run successfully at two prototype facilities. However, the process could not be evaluated by the project because it could not be tested under full production at the time of the Performance Demonstration.

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