Printed Wiring Board
Pollution Prevention and Control Technology:
Analysis of Updated Survey Results

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DfE PWB Project Core Group members provided valuable guidance and feedback during the preparation of this report. Core Group members include: Kathy Hart, EPA (Core Group Co-Chair); Christopher Rhodes (Core Group Co-Chair) and Holly Evans, Institute for Interconnecting and Packaging Electronic Circuits (IPC); Dipti Singh, U.S. EPA (Technical Workgroup Co-Chair); Gary Roper, Substrate Technologies Inc. (Technical Workgroup Co-Chair); Michael Kerr, Circuit Center, Inc., (Communication Workgroup Co-Chair); John Lott, DuPont Electronics; John Sharp, Teradyne, Inc.; Lori Kincaid, Jack Geibig and Mary Swanson, University of Tennessee Center for Clean Products and Clean Technologies; Greg Pitts, Microelectronics and Computer Technology Corporation; and Ted Smith, Silicon Valley Toxics Coalition. We also thank the other industry representatives and interested parties who reviewed and provided suggestions for this report.

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1.0 Project Summary

1.1 Description of Project

This report presents results of a pollution prevention (P2) and control survey for printed wiring board (PWB) manufacturers and related information from literature and other sources. The survey was conducted by CAI Resources, Inc., with assistance from the Institute for Interconnecting and Packaging Electronic Circuits (IPC). The survey results were analyzed and this report was prepared by CAI Resources, Inc., under a subcontract to Microelectronics and Computer Technology Corporation (MCC). The Design for the Environment (DfE) Printed Wiring Board Project partners provided significant input to the final report. The work was funded by grant #X 823856 under EPA's Environmental Technology Initiative Program. This report is a follow up to a previous report that analyzed results of an earlier survey (ref. 1).

The DfE PWB Project is a voluntary cooperative partnership with EPA, industry, and other interested parties that promotes implementation of environmentally beneficial and economically feasible alternatives by PWB manufacturers. The ultimate goal of this project is to help the PWB industry increase efficiency and reduce waste generation by giving individual PWB manufacturers the information they need to make informed decisions that fit their particular needs. The initial focus of the project was to evaluate processes or technologies for "making holes conductive" (MHC), the process of depositing a conductive surface in drilled through-holes prior to electroplating. In support of these efforts, the DfE project conducted a Cleaner Technologies Substitutes Assessment (CTSA) of several alternative MHC processes and tests were conducted to evaluate the performance of alternative processes (ref. 2). The draft MHC CTSA was published in August 1997. The DfE PWB Project is now conducting a similar analysis of alternative surface finishes for PWB manufacturing.

1.2 Purpose of the Survey

The pollution prevention and control survey was performed to gather and organize information about the current state of environmental technology and practices for this industry segment. The focus of the survey was on determining the types of technologies and alternative processes used, the extent of their use, key factors with regard to implementation, including costs, and their success and failure rate. Pollution prevention and control technologies covered by the survey include substitute raw materials and manufacturing processes, reuse and recycle technologies, procedural changes, and innovative treatment/disposal methods that reduce chemical use or water use and/or prevent the production of hazardous waste material and its release to the air, water, or land.

The survey results are useful to all those associated with the PWB manufacturing industry. PWB manufacturers can use the results of the survey to compare their own manufacturing operations to those of the survey respondents. Using the survey results, manufacturers can evaluate how their operations compare in terms of chemical and other raw material usage rates, water use, waste generation, technology level used, and other key factors. The results also show which treatment, recovery, and bath maintenance technologies have been most successful, trends in chemical substitution, the identification of regulated pollutants, sludge generation rates, off-site waste recovery and disposal options, and many other pertinent topics. In addition to the manufacturing segment, the results will also be useful to companies that service the PWB industry, including engineering firms, chemical suppliers, manufacturers/vendors of pollution prevention and control equipment, and off-site recycling and disposal sites.

1.3 Survey Procedures

The survey of PWB manufacturing facilities was accomplished using a mailed questionnaire. To ensure that the survey adequately addressed the key production processes and pollution prevention methods, a draft form was prepared and reviewed by various industry participants, EPA, and other interested parties. The questionnaire was then tested by surveying a selected group of PWB facilities. Based on these responses, the survey form was revised. The final survey form was then distributed by IPC during 1995 to all IPC PWB manufacturing facility members (approximately 400).[1] There were 40 responses to the survey. A preliminary report was prepared to distribute the results of the survey (ref. 1). During 1997, a revised survey process was implemented in order to increase the response rate by PWB shops. The scope of the survey was reduced in order to shorten the amount of time necessary to complete the form. The second survey was distributed to 250 members of the California Circuit Association. An

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[1] The methodology employed during the PWB survey project and the format of the questionnaire employed were based on the experiences of a similar project conducted for the electroplating industry by the National Center for Manufacturing Sciences (NCMS) and the National Association of Metal Finishers during 1993 and 1994 (see reference 4). Permission to use the survey format and information gathering techniques of that study were given by the NCMS Project Steering Group.

additional 45 responses were received from the second survey. Therefore, a total of 85 different facilities responded to the survey.

Overall, there were few noticeable differences between the responses from the two surveys. One notable exception was a decrease in the use of the electroless copper method of making holes conductive. These results are discussed in Section 1.4.3. Raw data from the two surveys are presented in Appendix A.

The survey covered eight major areas:

- **Facility and Point of Contact Identification.** In order to maintain confidentiality, this portion of the survey form was kept separate from other portions of the form. Used only in the event that clarification to responses was needed, a procedure was employed that prevented anyone from connecting responses to their originator.

- **Facility Characterization.** Requested data concerning facility size, product type, base materials used, process capabilities, and technology level.

- **Wastewater Discharges.** Requested data concerning the type of discharge (i.e., direct, indirect, zero), flow rates, discharge limitations, compliance problems, and costs for water and sewer use.

- **Process Data.** Requested data concerning various elements of the manufacturing process, including etch resist, inner- and outer-layer etching, through-hole metallization, oxide, etchback/desmear, solder mask, and chemical usage.

- **Recovery, Recycle, or Bath Maintenance Technology.** Requested data concerning pollution prevention technologies, including costs, savings, labor needs, maintenance requirements, residuals generation, and other important information.

- **Pollution Prevention Methods.** Requested data concerning pollution prevention (P2) methods used by the facilities for improving operating procedures, reducing water use, preventing the loss of chemicals, and making other improvements.

- **End-of-Pipe Treatment.** Requested data concerning the type of treatment processes used, capital and operating costs, sludge generation, and compliance problems.

- **Identification of Problems and Needs.** Requested data concerning environmental and occupational health challenges, technology needs, and information needs.

1.4 Overview of Results

A total of 85 survey responses were received. Based on dollar sales, the 85 responses represent approximately 36% of the total U.S. PWB production (ref. 4). The following are some important findings from the survey.

1.4.1 Facility Characterization

Facility characterization data were collected as part of the survey to enable comparisons among the participants and as a way to relate the respondents as a group to the overall PWB industry population. Among the data collected are the facility size, production numbers, product mix, and the number of employees.

Comparison of Facility Sizes. Several measures of facility size were employed to help characterize the respondents and compare them to the overall PWB industry sector, including: annual sales in dollars, square footage of manufacturing facility, number of employees, and PWB production rate measured in square footage. The following is a summary of key information.

- Based on an IPC Technology Marketing Research Council survey conducted in 1994, facilities under $5 million represented 77% of all facilities and facilities over $50 million were only 2.1% of the total. The mix of respondents from the current Industry survey was substantially different than these industry figures. Among current survey respondents, 25.6% are small shops, while 14.1% are facilities with more than $50 million in sales. Any conclusions drawn from the current study should consider that the respondents may be more representative of larger facilities than the industry average.

- The mean sales reported among respondents is $20,958,000 and the median amount is $12,000,000.
- The physical size of the survey respondent's manufacturing facilities ranges from 4,000 sq. feet to 600,000 sq. feet. The mean size is 61,262 sq. feet and the median size is 31,800 sq. feet.
- Square footage of PWB production ranged from 1,100 square feet to 5,000,000 square feet. These values include single- and double-sided boards as well as multilayer PWBs. The mean and median values are 728,085 square feet and 273,000 square feet respectively.

Exhibit 1-1. Distribution of Annual Sales

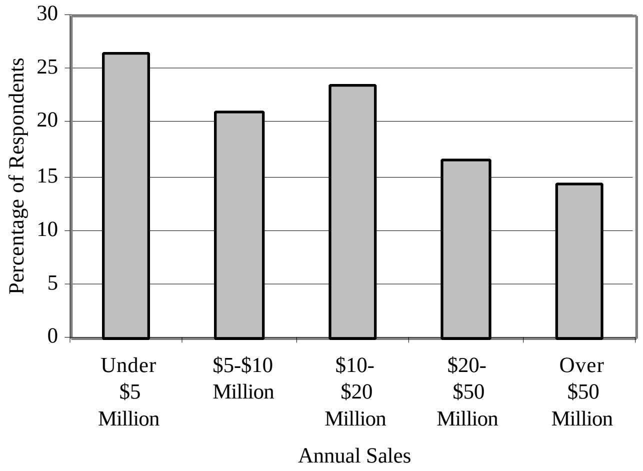
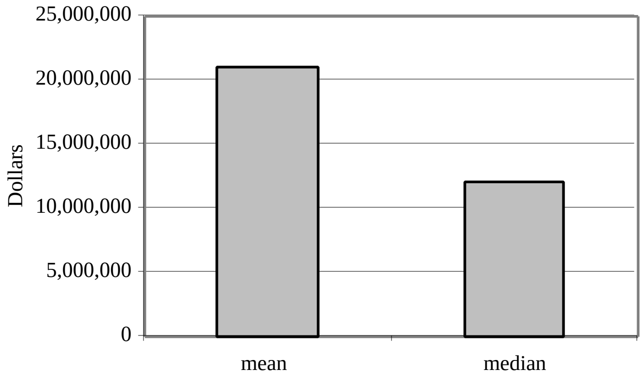


Exhibit 1-2. Mean and Median Sales



- Of the facilities responding to the survey, the number of employees ranges from 4 to 1,200. The mean is 191 employees and the median is 123 employees.
- For the respondents, a mean of 10.9 employees and a median of 10.6 employees are needed for each $100,000 of annual sales.

Exhibit 1-3. Mean and Median Facility Size of Survey Respondents

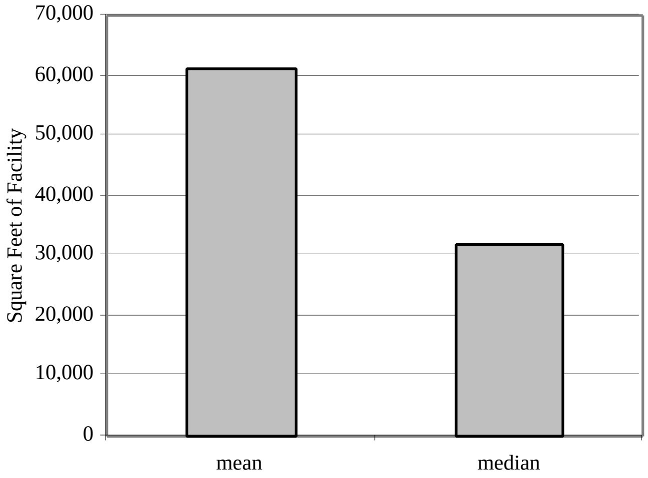
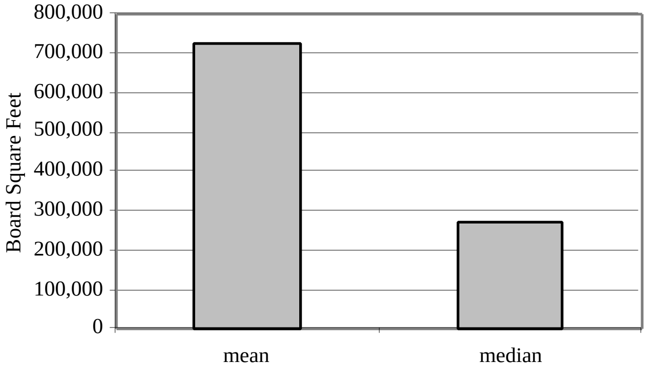


Exhibit 1-4. Mean and Median Production



1.4.2 General Process Information

The survey collected data for numerous process related topics. Some of the general process characterization data are presented in this section.

- PWB substrate can be rigid, flexible or a combination of the two. Rigid boards are the most common and are made exclusively by 88.5% of the survey respondents. Flexible circuits are made by 18.4% of the facilities and 11.5% make a combination of rigid/flexible (regi-flex) circuits.
- Another method of classification of PWB manufacturers is by the number of layers they are able to produce. Higher layer counts require more sophisticated equipment and processes. Double-sided boards are the most commonly produced boards among survey respondents (87.3% of respondents). Of the facilities that produce multilayers, 4-6 layer boards are the most common type (80.5% of respondents). Only 12.6% of the facilities produce multilayers with more than 20 layers.

Exhibit 1-5. Number of Employees

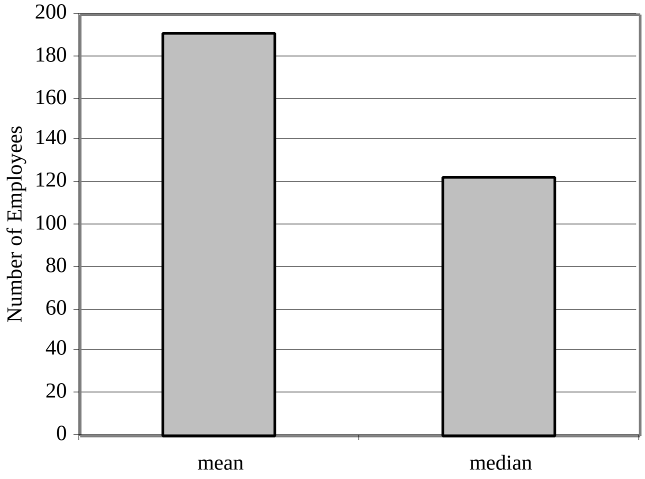


Exhibit 1-6. Employees Per $100K of Sales

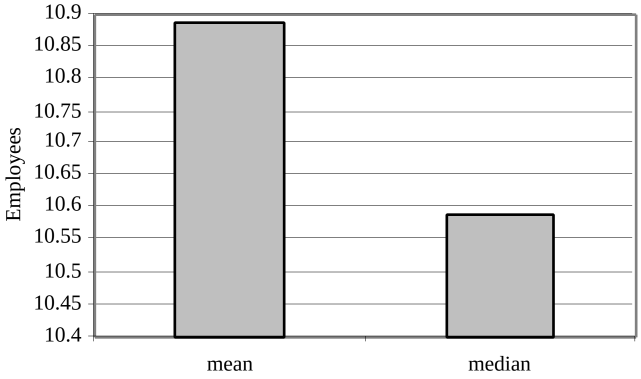


Exhibit 1-7. Distribution by Technology Level

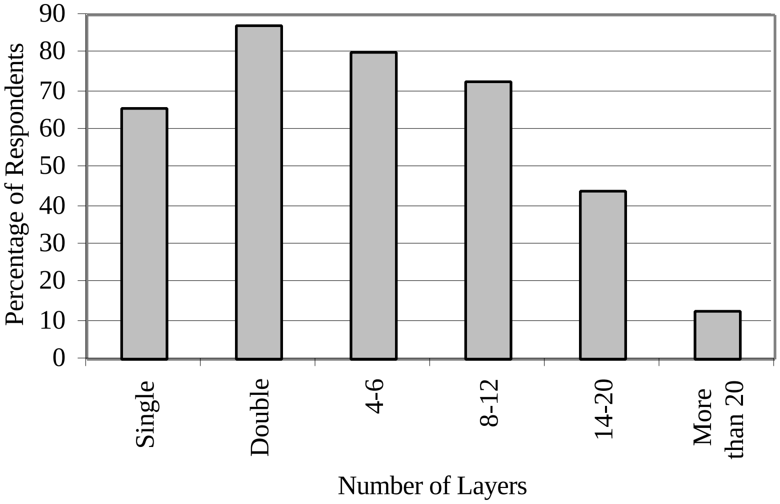
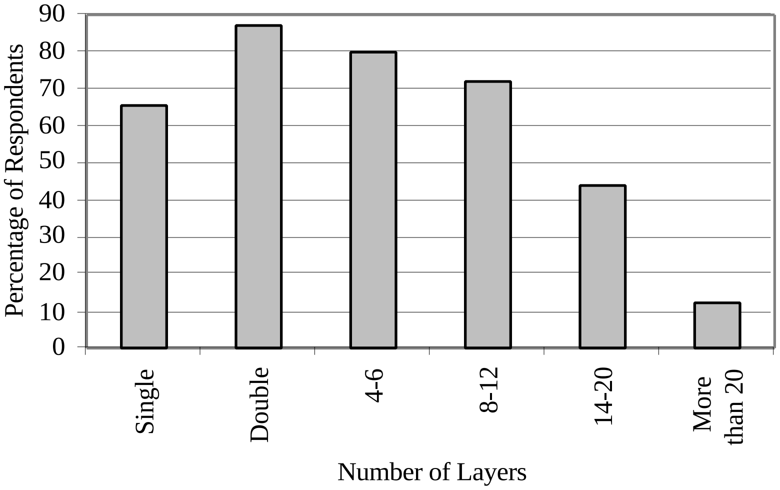


Exhibit 1-8. Distribution of Product Type



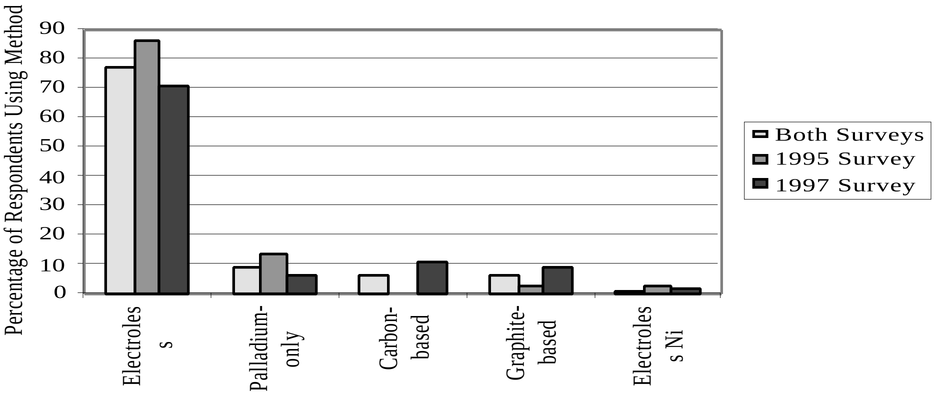
1.4.3 Production Methods and Materials

Certain manufacturing methods and materials used in PWB production are of particular concern with respect to waste generation or pollution prevention and are highlighted in this section. A detailed description of all applicable processes is presented in Section 3.

Making Holes Conductive. This process step has received much attention due to the chemicals used, the wastes generated and employee exposure concerns. Making holes Conductive (MHC) was the focus of the first Design for the Environment CTSA project (ref. 2). The draft MHC CTSA was published in August, 1997. Due to the emphasis placed on this process during the DfE project, both surveys (see description of survey process in Section 1.3) requested detailed information about making holes conductive from the PWB shops. Overall, there were few noticeable differences between the responses from the two surveys which were conducted approximately two years apart. However, with respect to making holes conductive, there appears to be some differences. Therefore, the data presented in Exhibit 1-9 show the individual survey results as well as the overall results.

During the making holes conductive step, a thin seed layer of conductive material (copper, carbon, nickel, palladium or other conductive material) is deposited to facilitate subsequent copper electroplating. Prior to the 1990's, few choices for making holes conductive existed other than electroless copper, which remains the predominate process. Due to the health risks and increasing regulation of formaldehyde, the waste treatment complications presented by EDTA or other complexing agents, and the complex pre-treatment line associated with electroless copper, interest in alternatives to electroless copper has been high. Considerable research has resulted in an array of substitute processes. Among the alternatives are palladium-based, carbon-based, graphite-based and electroless nickel processes. Each of these processes address some or all of the problems identified with electroless copper.

Exhibit 1-9. Through-Hole Metallization Methods



Although electroless copper remains the predominant method of making holes conductive, its use appears to have declined. Twenty percent fewer facilities from the 1997 survey employ electroless copper than did in the 1995 survey (electroless copper is used by 70% of the 1997 respondents, down from 86% in the 1995 survey). The carbon-based alternative, although not used by any respondents from the 1995 survey, is used by 11.4% of the respondents from 1997 survey. Use of graphite-based systems rose to 9% in 1997 from 2.7% in 1995. The use of palladium-based alternatives declined from 14% of the 1995 respondents to 6.8% in 1997. Electroless nickel use remained nearly unchanged at approximately 2%.

Design for the Environment (DfE) Printed Wiring Board Project participants are encouraged by this increase in the use of alternative MHC technologies, especially because it occurred while awareness of the alternatives was being increased by the MHC project. Additional increases in alternative MHC technology use can now be expected because the CTSA results were presented in seven seminars around the United States in 1997, and because the final MHC CTSA will be published in summer 1998.

Etch Resists. Etch resists are needed on any PWB manufactured using the subtractive process. The etch resist protects the underlying copper circuitry from being etched away. Dry film, screened ink, or a plated metal can act as a resist. Many facilities employ more than one etch resist.

Tin-lead has been losing ground to other resists for the last several years due to health and environmental concerns and the readily available substitute of tin-only plating (Exhibit 1-10). Tin-lead was still in use by 52% of survey respondents.

In the case of solder mask over bare copper (SMOBC) panels, tin plating easily replaces tin-lead since the etch resist is stripped after etching. Tin is used as an etch resist by 49% of the survey respondents.

Among other etch resists, dry film is used by 41% of the respondents and nickel-gold is used by 43%.

Exhibit 1-10. Outer-Layer Etch Resists in Production

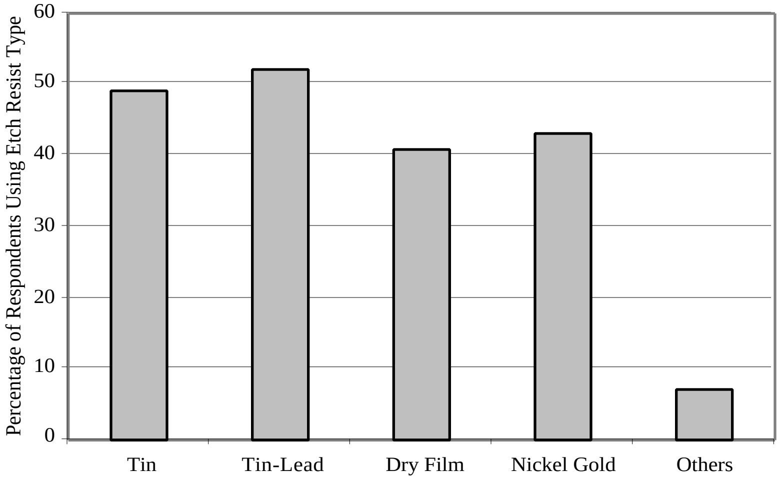
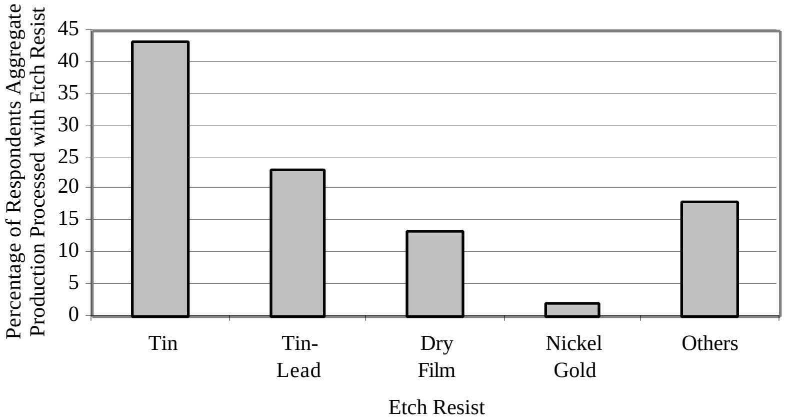


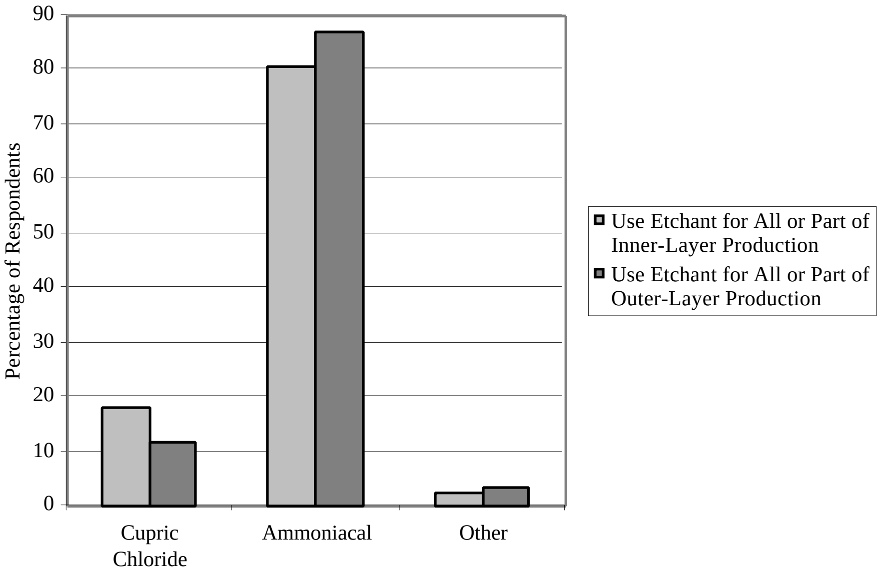
Exhibit 1-11. Outer Layer Etch Resists in Production (Aggregate)



When the aggregate production of all respondents who provided sufficient information is considered, the move away from tin-lead plating becomes apparent. Only 23% of the aggregate production (totaling more than 23 million ft^2) was produced with tin-lead versus 43% with tin-only. Dry film represented 13% and nickel-gold 2.1%. The major contributor to the "other" category shown on Exhibit 1-11 was a large, single-sided facility that used a screened-on ink etch resist.

Etchant. Although historically there have been many copper etchants employed by the PWB industry, the field has narrowed to just two chemistries in the modern shop: cupric chloride and ammoniacal etchants. The choice between these two etchants for outer layer etching is determined largely by compatibility with the various etch resists employed. Metallic etch resists are generally incompatible with cupric chloride, greatly limiting its use on outer-layers regardless of whatever advantages it may offer. Ammoniacal etchant is generally compatible with all etch resists and therefore is very common as an outer-layer etch resist and is the etch resist of choice for small shops that cannot justify the purchase and maintenance of two etching systems.

Exhibit 1-12. Etchants Used



Ammoniacal etchant is more widely used among the survey respondents; 81% of respondents indicated they use ammoniacal etchant for inner-layer etching and 87% use it for outer-layer etching.

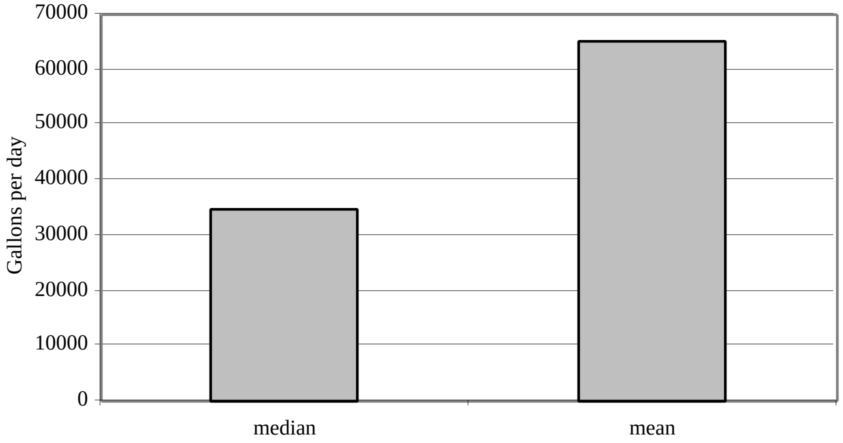
Solder Mask. Most PWBs, including nearly all high-technology circuits, require solder mask. The survey results show a very substantial use of liquid photoimageable masks (LPI). Seventy-six percent of respondents apply LPI to at least a portion of their product. Thermal masks are used by 74% of the respondents. Forty percent use dry film masks on at least some of their product. A significant percentage of respondents indicated that they use all three common mask types (26%).

1.4.4 Wastewater Generation and Discharge

The survey collected information about wastewater generation rates, discharge types, discharge limits, compliance difficulties, wastewater treatment methods, and other related information. Some key findings include:

- The survey data show that the majority of the respondents are indirect dischargers.[2] This is especially true for the small to mid-sized PWB manufacturing facilities. Seventy-seven percent of all respondents indicated that they are indirect dischargers, whereas 94% of the facilities with a production rate below 300,000 board ft^2 are indirect dischargers. None of the survey respondents indicated they are zero discharge shops.
- Average daily wastewater flow rates range from 5,200 gpd to 400,000 gpd.

Exhibit 1-13. Water Usage



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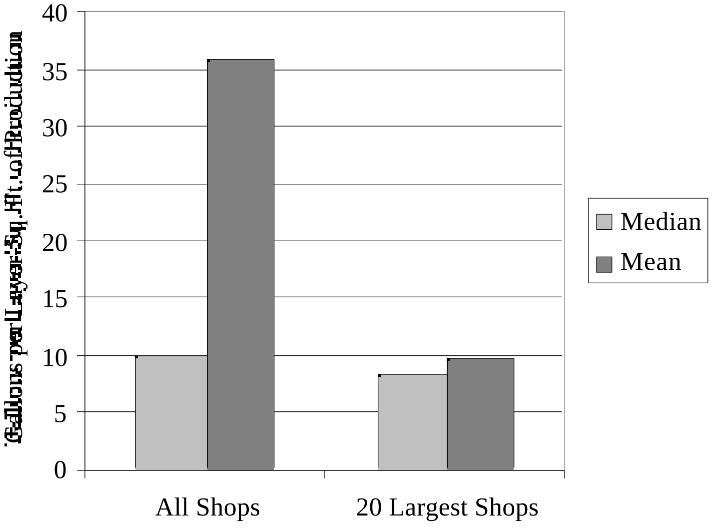
[2] For the purpose of this survey, the discharge type refers to the destination of wastewater discharges regulated by categorical effluent standards. The three possible selections in the survey questionnaire were direct discharge (i.e., to surface water such as a river or stream), indirect discharge (to a publicly owned treatment works or POTW), or zero discharge (no process wastewater discharge).

Exhibit 1-14. Production-Based Water Usage



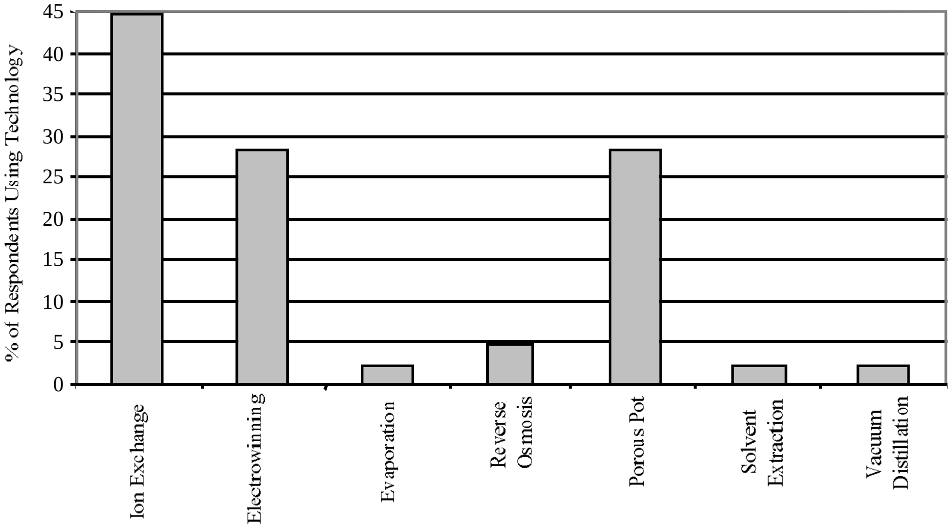
- Not suprisingly, the data indicate that overall water usage was related to the product mix of the shop, particularly the layer-count mix. Therefore, an adjusted, production-based flow rate was calculated. Comparing the adjusted production-based flow rates, the range of water use among respondents is extremely wide; 8% of respondents reported water usage of over 50 gallons/layer-ft^2, whereas 51% reported water use of less than 10 gal/layer-ft^2.
- A very sharp distinction can be drawn between the mean water use of larger and smaller shops. The largest 20 facilities in terms of production had mean production-based water usage rates less than one-third that of all respondents. Since facilities that did not have formal data were encouraged to estimate their water usage, it is possible that some of the very high usage rates among the smaller shops are a result of poor estimates of either the production rate or water usage. Following this line of reasoning, it is also possible that the rates shown in Exhibit 1-14 for the largest 20 facilities are a more accurate estimate of true water usage by this industry sector.
- There is a relationship between the adjusted production-based flow rates and the cost of water and sewer use. For facilities that have very high combined water and sewer costs, the adjusted production-based flow rates are very low. Variation of water and sewer use costs among survey respondents is likely due in part to geographical location, with higher costs in coastal and arid regions.
- Low water use rates are achieved by PWB facilities through the implementation of simple water conservation techniques and/or by using technologies such as ion exchange that recycle water.
- The data indicate that the use of water conservation methods does not always result in low water use. The four facilities with the highest production-based flow rates do not use ion exchange recycling, but they all indicated that they employ counterflow rinsing, plus some other methods of water conservation. In such cases, it is possible that water is simply being wasted by having unnecessarily high flow rates in the rinse tanks (e.g., flowing water during periods of non-production).
- The data indicate that the majority of respondents (63%) must meet discharge limitations that are more stringent than the Federal standards.
- Very few respondents reported any wastewater compliance difficulties. Of the respondents that reported difficulties, 11% reported difficulties with lead, 8% with copper, and 3% with silver. A large majority of respondents (86%) did not report any compliance difficulties. The majority of those reporting compliance difficulties have discharge limitations lower than Federal standards.

1.4.5 Recycle, Recovery, and Bath Maintenance

One section of the PWB survey form was devoted to gathering information concerning pollution prevention and recovery technologies that are applied for the purposes of recovering and recycling chemicals and improving the life-span of process solutions. Eighty-one percent (81%) of the respondents reported use of a recycle, recovery or bath maintenance technology, including ion transfer, electrowinning, ion exchange, diffusion dialysis, membrane electrolysis, evaporation, and solvent extraction. Exhibit 1-15 displays the technologies found amongst the respondents. They include:

- Electrolytic regeneration of permanganate desmear baths using a porous pot (or similar ion transfer designs) is employed by 28.2% of the survey respondents. This relatively inexpensive and simple technology is used for bath maintenance (i.e., extending the useful life-span) of permanganate desmear baths. In the conventional permanganate process, the permanganate ion is reduced by heat and contact with PWBs and is replaced by chemical addition. Also, during operation of this bath, by-products (including the manganate ion) accumulate in concentration causing a sludge to form and frequent disposal is necessary. The porous pot can be used to maintain a sufficiently low concentration of contaminants and thereby reduce the frequency of disposal.
- Ion exchange is a versatile technology that is applied by PWB manufacturers for various, sometimes overlapping purposes, including: water softening, chemical recovery, water recycle, solution maintenance, and waste treatment. Forty-five percent (45%) of the respondents reported using ion exchange as a water recycle/chemical recovery technology. Many of these respondents reported the same system as a component of their waste treatment system. In general, most of the waste streams discharged from PWB processes are compatible with ion exchange, and many facilities mix several similar rinse streams and treat them with a single ion exchange unit (e.g., sulfuric acid dips, micro-etch, and copper electroplating rinses are frequently combined). The ion exchange effluent may be discharged and the regenerant processed using electrowinning, thereby making ion exchange both an end-of-pipe waste treatment and a component of a metal recovery system.
- Electrowinning is a common metal recovery technology employed by PWB manufacturers to remove metallic ions from spent process fluids, ion exchange regenerant, and concentrated rinse water (e.g., drag-out rinses). Twenty-eight percent (28.2%) of the survey respondents reported using electrowinning as a recovery technology.
- Several other technologies are used by survey respondents, but to a much lessor extent than the porous pot, ion exchange or electrowinning. One respondent cited use of evaporation, which was employed to recover copper sulfate electroplating solution. One respondent reported using diffusion dialysis for bath maintenance on a tin-lead strip solution. Membrane electrolysis is used by one respondent as an on-line regeneration method for cupric chloride etchant. The same respondent also reported using solvent extraction technology for on-site regeneration of ammoniacal etchant (and drag-out recovery).

Exhibit 1-15. Recycle, Recovery and Bath Maintenance Technologies Used



1.4.6 Off-Site Recycling

The PWB survey gathered information regarding the types of wastes sent to off-site recycling firms, quantities, destinations, and associated costs. Off-site recycling is a commonly used alternative for PWB manufacturers as a means of managing spent etchant solutions and wastewater treatment sludges. Widespread implementation of this option reduces the quantity of wastes being disposed of in landfills. The following is a summary of key information regarding off-site recycling.

- Nearly all respondents reported using off-site recycling for disposing of spent process baths. By far, the most commonly reported spent process fluid that is sent off-site for recycling is spent etchant, particularly spent ammoniacal etchant. Eighty-three percent (83%) of the respondents who completed the off-site recycling section of the survey reported that they send spent ammoniacal etchant off-site for recycling. Spent ammoniacal etchant is created at a rate of roughly 1 gallon per 30 surface square feet of inner- and outer-layer panels. The reason that spent etchant is a popular waste for off-site recycling is due mostly to its high copper concentration, which is typically 150 g/l Cu (i.e., 15% Cu). Etchant that is sent off-site is processed to recover the copper and regenerate the etchant for reuse.
- Spent process baths other than etchant are less frequently sent off-site for recycling by the survey respondents. The next most commonly shipped waste product is tin and/or tin-lead stripping solutions. These solutions are listed by 20% of the respondents who completed this section of the survey form. Like etchant, spent stripping solutions have a high metal concentration that makes it a viable candidate for recycling. Also, stripping solutions are generated in relatively high volumes, furthering the economics of off-site recycling.
- Flux, solder dross from the hot-air-solder-level (HASL) process, and other lead-bearing solutions are shipped off-site for recycling by 20% of the respondents. However, the quantities of these materials that are shipped are relatively small.
- Micro-etchants are shipped off-site for recovery by only 8% of the respondents. Spent micro-etchants typically contain copper concentrations of 15 to 30 g/l Cu (i.e., 1.5 to 3.0% Cu). Other respondents reported electrowinning these solutions on-site, or treating them with conventional precipitation.
- Gold- and silver-bearing wastes are sent off-site by 15% of the respondents. Gold electroplating baths (usually gold cyanide) have a long life-span, and not surprisingly, the reported volumes were all 100 gallons per year or less. Solutions containing gold may include spent gold electroplating bath, or the contents of drip or drag-out tanks on the gold plating line. Silver is present in film developing fluids that may be reclaimed on-site (electrowinned), shipped off-site for metal reclamation, or combined with other waste streams and treated conventionally.
- Ten percent (10%) of the respondents indicated that spent rack stripping solution is shipped off-site. Plating racks are typically coated with a non-conductive substance to prevent electroplating from occurring on the rack surface itself. Due to use, this coating may degrade and plating can accumulate on the rack, especially near the clamps and contact points. This unwanted copper deposit is removed in a stripping solution such as dilute nitric acid. The volume of spent stripping solution can be significant.
- Nearly ninety percent (90%) of those who provided data concerning the destination of their sludges indicated that they ship the sludges to recycling facilities rather than landfills.

1.4.7 Wastewater Treatment

End-of-pipe treatment is, by definition, not pollution prevention (P2). However, it is an important aspect of pollution control and it sometimes competes financially with pollution prevention options when facilities are developing pollution control strategies. To make informed decisions about implementing P2 alternatives that include consideration of all applicable costs and potential savings requires accurate data. Therefore, the topic of waste treatment was included in the PWB survey project so that the true costs of treatment could be examined. The applicable portion of the survey form requested respondents to describe the type of waste treatment system currently in use at their facilities and to provide operating and cost data. The following is a summary of the end-of pipe treatment information provided by the respondents.

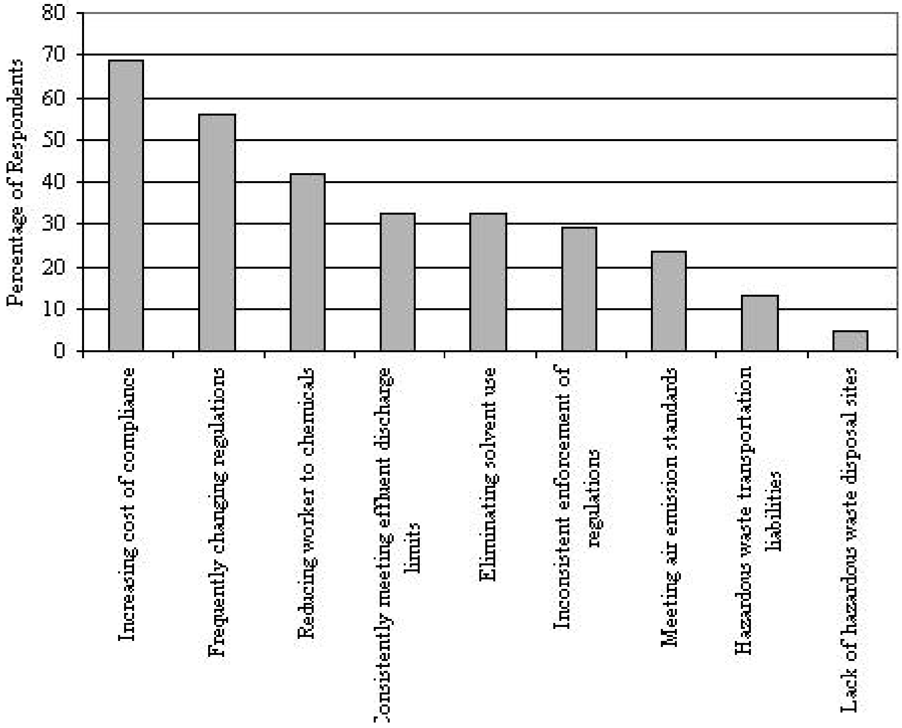
- The primary purpose of the wastewater treatment systems employed is the removal of dissolved metals. This is accomplished by the respondents through installation of conventional metals precipitation systems, ion exchange-based metals removal systems, and combined precipitation/ion exchange systems.
- Forty percent (40%) of the respondents reported using ion exchange as their basic waste treatment technology.

1.4.8 PWB Industry Environmental Problems and Needs

Checklists were included on the survey to identify sources of information, environmental and health challenges, and areas where insufficient information is available for the industry. The respondents were also allowed to fill-in items that were not covered in the checklists. The results are summarized below.

- **Environmental and Occupational Health Challenges.** Of the environmental and occupational health challenges on the checklist, the challenges most frequently cited were increasing cost of compliance (68.6%), frequently changing regulations (55.8%), and reducing worker exposure to chemicals (41.8%) (Figure 1-16).

Exhibit 1-16. Environmental and Occupational Health Challenges



- **Information Needs.** The most frequently cited P2 information need by survey respondents was chemical recycling (41.9%) (Exhibit 1-17). Other information needs frequently cited were water recycling (33.7%) and certified courses for pollution prevention (33.7%), fully or semi-additive process (30.2%), tin-lead alternatives (29.1%), smear removal alternatives (23.3%) and direct imaging (15.1%).
- **Source of Technical Information.** The survey indicates that PWB facilities draw on a variety of sources when seeking information (Exhibit 1-18). The sources of information that were identified most frequently by the respondents were in-house engineer (50.0%), vendors (48.8%), and professional journals (39.5%).

Exhibit 1-17. Information Needs

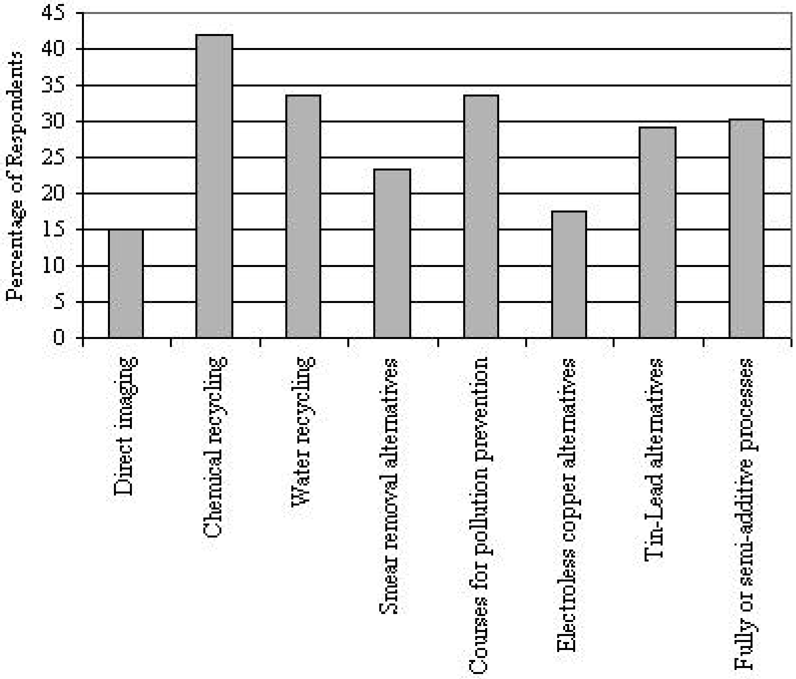
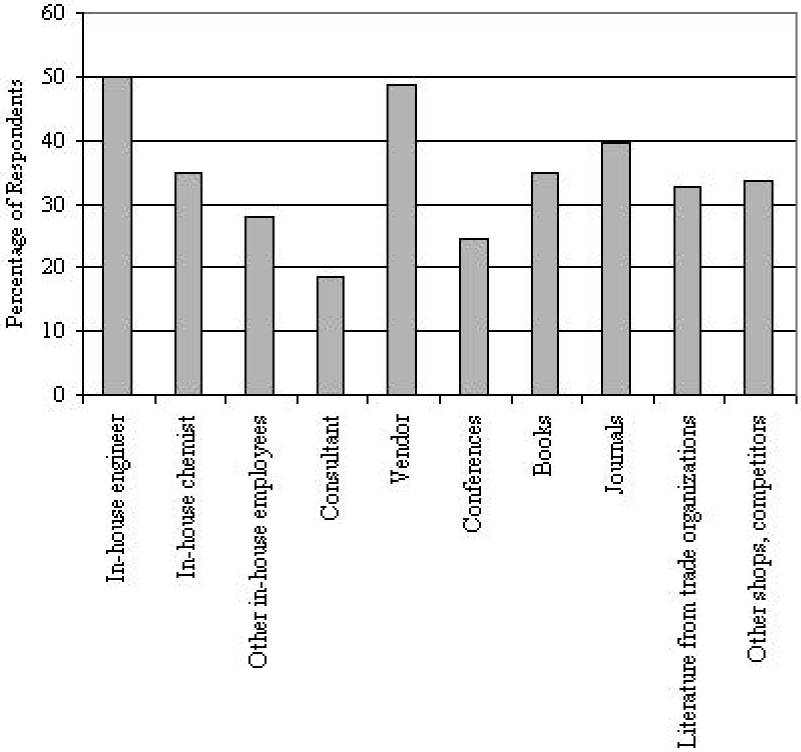


Exhibit 1-18. Sources of Technical Information Used



2.0 Laws and Regulations Affecting Pollution Prevention and Recycling for PWB Manufacturers

2.1 Introduction

Implementing a sound environmental protection strategy for a PWB facility may involve using a range of reduction and waste management methods that work in unison, including waste reduction, recycling, treatment, and disposal. Decisions regarding each facility's strategy are usually guided by a number of factors, including a desire to meet environmental regulations, reducing liability and operating costs, maintaining/improving the company's image and reducing risks to workers, the public, and the environment. Of these factors, compliance with environmental regulations is often the overriding factor. Understanding the influence of regulations and the need to move toward more environmentally sound pollution control practices and to encourage source reduction practices, Congress passed the Pollution Prevention Act of 1990 (PPA). The PPA declared it a national policy to prevent or reduce pollution at the source whenever feasible. This section of the report helps to understand the impact of the PPA and other federal, state, and local regulatory initiatives that promote source reduction and recycling.

2.2 Federal Laws and Regulations Affecting Pollution Prevention and Recycling

Several key federal laws and regulations affect decisions regarding implementation of pollution prevention, with the most influential being the Pollution Prevention Act of 1990, Emergency Planning and Community Right-to-Know Act (EPCRA, also known as SARA Title III), the Resource Conservation and Recovery Act (RCRA, which covers regulation of hazardous wastes), and the Clean Water Act (CWA, which covers regulation of wastewater discharges). The following overview of these laws identifies provisions that pertain to PWB manufacturing pollution prevention. A summary of this information is presented in Exhibit 2-1.

Exhibit 2-1. Summary of Federal Legislation Affecting Pollution Prevention and Recycling

Pollution Prevention Act of 1990 (PPA)	Formalized a national policy and commitment to waste reduction, functioning primarily to promote the consideration of pollution prevention measures at the federal government level.
Resource Conservation and Recovery Act (RCRA), including the Hazardous and Solid Waste Amendments (HSWA) to RCRA	Congress declared that the reduction or elimination of hazardous waste generation at the source should take priority over other management methods such as treatment and disposal. Hazardous waste generators are required to certify on their hazardous waste manifests that they have programs in place to reduce the volume or quantity and toxicity of hazardous waste generated to the extent economically practicable. Materials that are recycled may be exempt from RCRA regulations if certain conditions are met.
Emergency Planning and Community Right-to-Know Act (EPCRA, also known as SARA Title III)	EPCRA requires certain companies to submit an annual report (Form R) of the amount of listed "toxic chemicals" entering the environment. With passage of the PPA, new reporting requirements were added to the Form R. Source reduction and waste management information must be provided for the listed toxic chemicals.
Clean Water Act (CWA)	CWA regulations pertain to wastewater discharges. Most industries must meet discharge standards for various pollutants. Specific methods of control such as pollution prevention are not specified; however, many facilities use pollution prevention as a means of reducing the cost of compliance with federal regulations. State and local authorities generally have the responsibility to implement the provisions of the CWA. These authorities must enforce the Federal guidelines as a minimum, but may choose to enforce more stringent requirements. Some localities include pollution prevention planning requirements into discharge permits.

2.2.1 Pollution Prevention Act of 1990

Pollution prevention is a relatively new theme in environmental laws and regulations. In 1990, Congress passed the Pollution Prevention Act to promote the consideration and adoption of source reduction and recycling in both regulatory and non-regulatory settings. This statute is a foundation for future regulations and Agency initiatives, rather than a specific set of rules. The law obligates EPA to develop and implement a strategy to promote source reduction that includes:

- reviewing existing and proposed programs and new regulations to determine their effect on source reduction
- coordinating source reduction activities among Agency programs and other federal agencies
- streamlining public access to environmental data and foster the exchange of source reduction information
- establishing pollution prevention training programs for Federal and state environmental officials
- facilitating adoption of source reduction by businesses
- identifying and make recommendations to Congress to eliminate barriers to source reduction

Since the passage of the Pollution Prevention Act of 1990, EPA has implemented a diverse set of programs and initiatives to meet their obligations defined by the law. Key to EPA's approach is an array of partnership programs that are collectively referred to as Partners for the Environment. Through these efforts, EPA is utilizing voluntary goals and commitments to achieve environmental results in a timely and cost-effective way. This is being accomplished by building cooperative partnerships with a variety of groups, including small and large businesses, citizen groups, state and local governments, universities, and trade associations.

Examples of these collaborative efforts include programs such as 33/50, WasteWi$e, Climate Wise, Green Lights, Energy Star, WAVE, the Pesticide Environmental Stewardship Program, Indoor Air, Indoor Radon, Design for the Environment, the Environmental Leadership Program, and the Common Sense Initiative.

The Pollution Prevention Act of 1990 reinforced EPA's environmental management options hierarchy, where the highest priorities are assigned to source reduction, which is analogous to pollution prevention. This involves the judicious use of resources through, for example, product and process change, reuse of input materials during production, reduced water consumption, and energy efficiency.

The Pollution Prevention Act of 1990 is essentially a formalized national policy and commitment to waste reduction. However, even before passage of the PPA, some early consideration was given to waste reduction activities. Of the previous legislation, those most affecting P2 are the RCRA, EPCRA and the CWA.

2.2.2 Resource Conservation and Recovery Act (RCRA)

EPA regulates the management and control of all hazardous wastes from their point of origin to final disposal. These regulations are primarily the direct result of two congressional mandates: subtitle C of the 1976 Resource Conservation and Recovery Act (RCRA) (PL 94-580) and the 1984 Hazardous and Solid Waste Amendments to RCRA (PL 98-616). EPA has issued regulations, found in 40 CFR Parts 260-299, which implement Subtitle C. However, in many states, RCRA requirements are implemented through EPA-authorized State hazardous waste laws, which may be more stringent than Federal requirements. A facility should always check with the state when analyzing which requirements apply to their activities.

This section reviews some elements of the RCRA regulations that pertain to management of wastes from PWB manufacturing. In particular, RCRA rules regarding hazardous waste identification, requirements for generators, and aspects of recycling are covered. Also, note that all definitions in this section are intended to pertain solely to RCRA.

Identification of Hazardous Wastes. Each PWB facility has the responsibility for determining whether a waste it generates is hazardous and what classification, if any, applies to the waste. Part 261 of 40 CFR addresses the identification and listing of hazardous wastes. The facility must examine the regulations and undertake any tests necessary to determine if the wastes generated are hazardous. Wastes can be classified as hazardous either because they are listed by EPA through regulations that appear in the CFR or because they exhibit certain characteristics. Listed wastes are specifically named, for example, wastewater treatment sludges from electroplating operations (F006). Characteristic hazardous waste are wastes that "fail" a characteristic test, such as the RCRA test for toxicity.

When determining the status of a particular material, it is important to be familiar with the regulatory definitions of certain terms. Some of the important terms are defined in Exhibit 2-2.

Exhibit 2-2. Definitions of Terms Related to Waste Management/Recycling

Term	Definition
solid waste	Any discarded material that is not excluded under RCRA (exclusions are found in 40 CFR 261.2 and 261.4(a)) or by a variance granted under RCRA (procedures for variances are covered in 40 CFR 260.30 and 260.31).
hazardous waste	A solid waste that meets any of the RCRA hazardous waste criteria (described in 40 CFR 261.3) and is not excluded from regulation as a hazardous waste (exclusions are found in 40 CFR 261.4(b)).
spent material	Any material that has been used and as a result of contamination can no longer serve the purpose for which it was produced without processing (40 CFR 261.1(c)(1)).
by-product	A material that is not one of the primary products of a production process and is not solely or separately produced by the production process (40 CFR 261.1(c)(3)).
sludge	Any solid, semi-solid, or liquid waste generated from a municipal, commercial, or industrial wastewater treatment plant, water supply treatment plant, or air pollution control facility exclusive of the treated effluent from a wastewater treatment plant (40 CFR 260.10).
scrap metal	Bits and pieces of metal parts (e.g., bars, turnings, rods, sheets, wire) or metal pieces that may be combined together with bolts or soldering (e.g., radiators, scrap automobiles, railroad box cars), which when worn or superfluous can be recycled. (See 40 CFR 261.1(c)(6)). A material is "recycled" if it is used, re-used, or reclaimed.
excluded scrap metal	Includes home (40 CFR 261.1(c)(11)), prompt (40 CFR 261.1(c)(12)) and processed scrap metal. (See 40 CFR 261.1(c)(10)).

*Exhibit 2-3. Federal Regulatory Determinations**

Waste Type/Description	Regulatory Status under Federal RCRA
Unused/off-specification circuit boards: Manufacturers of computer circuit boards send unused/off-specification printed circuit boards off-site for reclamation.	As a matter of policy, whole unused circuit boards are classified as commercial chemical products and if recycled are excluded from the definition of solid waste. (See 40 CFR 261.2 Table 1).
Used whole printed circuit boards: Old electronic equipment may be disassembled and the usable parts salvaged. Salvaged circuit boards may be sent for reclamation.	As a matter of policy, unprocessed, spent printed circuit boards are classified as scrap metal and if recycled are exempt from the definition of hazardous waste. (See 40 CFR 261.6(a)(3)(ii)). Whole used circuit boards which contain mercury switches, mercury relays, nickel-cadmium batteries, or lithium batteries do not meet the definition of scrap metal. However, EPA does not intend to regulate under RCRA circuit boards containing minimal quantities of mercury switches, mercury relays, and/or batteries that are protectively packaged to minimize dispersion of metal constituents and that are part of a materials recovery program. (See 63 FR 28629).
Shredded circuit boards: Circuit boards are often shredded, for various reasons, prior to reclamation. The process of shredding circuit boards produces small fines from the whole board which are dispersible and do not meet the RCRA regulatory definition of scrap metal.	Shredded circuit boards being recycled are excluded from the definition of solid waste provided that they are: 1) stored in containers sufficient to prevent a release to the environment prior to recovery; and 2) free of mercury switches, mercury relays, and nickel-cadmium and lithium batteries. (See 40 CFR 261.4(a)(14)).
Circuit board trimmings: Manufacturers of computer circuit boards send board trimmings from the production process off-site for reclamation.	As a matter of policy, circuit board trimmings are classified as characteristic by-products. If reclaimed, they are excluded from the definition of solid waste. (See 40 CFR 261.2 Table 1).
Solder dross: Generated by the periodic skimming of molten solder baths used in the production of printed wiring boards to remove contaminants acquired through use of the molten solder baths.	As a matter of policy, solder dross is classified as a characteristic by-product. If reclaimed, it is excluded from the definition of solid waste. (See 40 CFR 261.2 Table 1).

Spent solder baths (pot dumps): Solidified pieces of tin-lead solder baths used in the production of printed circuit boards.	As a matter of policy, spent solder baths are classified as scrap metal and if recycled are exempt from the definition of hazardous waste. (See 62 FR 26013).
Sweeps: This term refers alternatively to a powdered material that is a residue of thermal recovery of precious metal-bearing secondary material (often ash that is crushed into particulate form in a ball mill or similar device) or particulate material that is collected from firms handling precious metals, such as jewelers and metal finishers.	As a matter of policy, sweeps are classified as a by-product. If hazardous solely by exhibiting a characteristic and being reclaimed, they are excluded from the definition of solid waste. If they are derived from a source material that meets the description of a listed hazardous waste, the sweeps are regulated as a solid and hazardous waste. (See 62 FR 26013).
Baghouse dust: Circuit boards are often sent to precious metal recovery furnaces for reclamation.	As a matter of policy, baghouse dust from precious metal recovery furnaces is regulated as a sludge. If hazardous solely by exhibiting a characteristic and being reclaimed, they are excluded from the definition of solid waste. If they are derived from a source material the meets the description of a listed hazardous waste, the sweeps are regulated as a solid and hazardous waste. (See 62 FR 26014).
Photoresist skins: Dry film resists are typically stripped in hot potassium hydroxide, which does not fully dissolve the resist material. The solids (photoresist skins) are filtered out to prevent clogging of spray nozzles, prevent redeposition on panels, and prolong the life of the stripper.	The determination as to whether or not photoresist skins are hazardous waste will depend on the analysis of the individual facility by the State or Regional regulatory authority.
Etchant: Commercial alkaline etchant is distributed for use to manufacturers of printed circuits. After a period of use, the alkaline etchant is reduced below acceptable levels and becomes “spent.” The spent material is then returned to the manufacturer of the alkaline etchant, where copper is recovered and the remainder of the etchant is then used as a raw material to produce additional alkaline etchant.	The determination as to whether or not spent etchant generated at a particular facility is hazardous waste will depend on the material, how it is managed, and the recycling process used. Generators should contact their State or Regional regulatory authority for assistance with making this determination.

*State laws may vary from Federal rules with regard to the classification of PWB wastes. Facilities are urged to contact their applicable state agency for the most recent information. State Agencies can be located using the Internet web site of the Printed Wiring Board Resource Center (http://www.pwbrc.org).

Although the RCRA regulations are fairly specific, there are some instances where clarification is necessary. Clarification or interpretations are often provided by EPA in direct response to requests. These responses are particularly useful when facilities are making determinations about specific types of wastes. Some of the clarifications and interpretations provided by EPA that apply to wastes generated during PWB manufacturing are summarized in Exhibit 2-3.

Requirements for Hazardous Waste Generators. Producers of hazardous waste (called generators) are ultimately responsible for the proper identification, pre-transport storage, and packaging and tracking of the waste. The generator first determines whether the waste is hazardous according to the criteria outlined above though, alternatively, the generator may simply declare the waste hazardous and treat it accordingly. If the waste is known to be nonhazardous, the generator need not test it. The responsibility for the accuracy of the determination of whether the waste is hazardous or not lies with the generator.

Generators of hazardous wastes are also responsible for notifying EPA and maintaining records of their activities, using appropriate containers, labeling the containers, and ensuring proper disposal. The law requires most generators of hazardous waste to use a manifest system to ensure the proper transport and disposal of the wastes. The manifest system records the movement of hazardous wastes from the generator's premises to an authorized off-site treatment, storage, or disposal facility. The generator must maintain original manifests for three years, and must report to EPA if the manifest is not returned to him within 45 days. An exception report must be completed for any non-returned manifests. Annual reports documenting shipments of all hazardous wastes originating during the report year also are required. All information submitted by a generator is available to the public to the extent authorized by the Freedom of Information Act and EPA rules related to that Act.

Recycling Aspects of RCRA. Certain recycling activities can be implemented by PWB facilities that may remove materials from RCRA regulation that otherwise would be considered hazardous wastes. Recycling can be accomplished in several ways, for example: (1) using or reusing materials in an industrial process to make a product, provided the materials are not being reclaimed (see definition of reclaimed material in Exhibit 2-2); (2) using or reusing the material as an effective substitute for commercial products; or (3) returning materials to the original process from which they are generated, without first being reclaimed (where the material is returned as a substitute for raw material feedstock).

Materials managed by these types of recycling are not classified as solid waste and therefore are out of the scope of RCRA Subtitle C regulation. However, materials recycled in other ways are considered solid wastes subject to Subtitle C, including: (1) materials used in a manner constituting disposal or used to produce products that are applied to the land; (2) materials burned as a fuel or for energy recovery; (3) materials that are speculatively accumulated; and (4) inherently waste-like materials (these materials include listed hazardous wastes that are always subject to RCRA regulation).

To assist the regulated community in determining whether a material that they recycle is a solid waste, EPA has released regulatory determinations that address specific production processes and wastes. By comparing their own situations to those in the determinations, industry personnel can develop a clearer understanding of the regulations and improve their waste management practices.

RCRA regulatory determinations that pertain to recycling at PWB facilities are summarized in Exhibit 2-3. These determinations address the following materials: etchant, photoresist skins, solder dross, pot dumps, off-spec boards and trimmings, and used printed circuit boards. Generators should check with their state regulating offices to determine if the Federal interpretations apply.

2.2.3 Clean Water Act Wastewater Regulations

Wastewater discharges from PWB manufacturing operations are governed by regulations developed under the Clean Water Act. Of particular importance are the categorical regulations that cover electroplating (40 CFR 413) and metal finishing (40 CFR 433). These regulations contain specific performance standards for contaminants discharged from PWB manufacturing processes. The wastewater regulations have been divided into several layers of categories: those for existing and new sources; and those for direct and indirect discharges. Direct dischargers are regulated by the National Pollutant Discharge Elimination System (NPDES), under which EPA or its state equivalent issues a separate permit to each discharger containing specific discharge limitations, reporting requirements, and compliance schedules. NPDES permits are renewable every five years. Indirect dischargers must conform to national pretreatment standards, both general and specific, which are enforced by the local government under EPA oversight authority.

While local governments must enforce the Federal discharge limits as a minimum, they have the authority to impose discharge standards that are more stringent than the Federal limits. As will be discussed, the enforcement of more stringent local limits is today more common than that of the Federal limitations.

For regulating purposes, electroplating plants, including PWB manufacturing facilities, have been divided into several categories. Facilities are first divided into captive and job shops. A captive shop owns more than 50 percent (annual area basis) of the materials undergoing metal finishing. A job shop owns 50 percent or less. PWB manufacturing job shops are referred to in the regulations as independent printed circuit board manufacturers (IPCBM). Facilities have also been labeled as existing sources or new sources, depending on when they began their operations. New sources are those facilities that began their operations after August 31, 1982.

Most of the PWB facilities responding to the P2 Survey are indirect dischargers whose applicable federal regulations are found in 40 CFR 413 (Electroplating Regulations) or 40 CFR 433 (Metal Finishing Regulations). These regulations are shown in Exhibits 2-4 and 2-5. The Part 413 regulations apply to independent PWB manufacturing facilities that were in existence since July 15, 1983. All other facilities are covered by Part 433 regulations.

The electroplating pretreatment standards for existing dischargers (Part 413) include an alternative mass-based standard for printed wiring board manufacturing facilities. The standard is expressed in units of milligrams per square meter of boards processed per operation. An operation is any “electroplating” step (e.g., electroless copper plating, copper sulfate plating) that is followed by a rinsing step. These standards can only be used upon prior agreement between a PWB facility and the regulatory authority. One purpose of mass-based standards is to encourage the implementation of pollution prevention. For example, a facility that has a concentration-based copper limitation has less of a regulatory compliance incentive to install a drag-out tank and counterflow rinse than a facility with a mass-based limitation. That’s because a facility with a concentration limit has to treat the wastewater to the same low concentration level regardless of the incoming flow rate and concentration. Alternatively, the facility with the mass-based standard may reduce the wastewater flow and mass of copper entering the treatment system and not have to achieve as low of an effluent concentration.

The CWA also has provisions for requiring best management practices (BMPs) in discharge permits. BMPs are typically baseline practices that are low in cost and easily implemented. Examples of BMPs include: good housekeeping, preventative maintenance, employee training, waste segregation, and use of specific P2 measures such as drip guards.

Exhibit 2-4. Pretreatment Standards for the Electroplating Category (40 CFR 413.84(b), (c),and (d))

Facilities Discharging <10,000 gpd

Pollutant	Daily Maximum, mg/l	Max. 4 Day Avg, mg/l
Cadmium	1.2	0.7
Lead	0.6	0.4
Cyanide (amenable)	5.0	2.7
Total Toxic Organics	4.57	--

Facilities Discharging >10,000 gpd

Pollutant	Daily Maximum, mg/l	Max. 4 Day Avg, mg/l
Cadmium	1.2	0.7
Chromium	7.0	4.0
Copper	4.5	2.7
Lead	0.6	0.4
Nickel	4.1	2.6
Zinc	4.2	2.6
Cyanide (total)	1.9	1.0
Total Toxic Organics	4.57	--

Facilities Discharging >10,000 gpd — Alternative Mass-Based Standards

Pollutant	Daily Maximum, mg/m^2 of Operation	Max. 4 Day Avg, mg/l
Cadmium	107	65
Chromium	623	357
Copper	401	241
Lead	53	36
Nickel	365	229
Zinc	374	232
Cyanide (total)	169	89
Total Metals	935	609

Exhibit 2-5. Pretreatment Standards for the Metal Finishing Category (40 CFR 433.15(a))

	Pretreatment Standards for Existing Sources (PSES)	
Pollutant	**Daily Maximum, mg/l**	**Max. Monthly Avg, mg/l**
Cadmium	0.69	0.26
Chromium	2.77	1.71
Copper	3.38	2.07
Lead	0.69	0.43
Nickel	3.98	2.38
Zinc	2.61	1.48
Silver	0.43	0.24
Cyanide (total)	1.2	0.65
Total Toxic Organics	2.13	--

Note: Pretreatment standards for new sources (PSNS) are identical to PSES except for the cadmium limitations which are 0.11 mg/l and 0.07 mg/l for the daily maximum and monthly average.

2.3 State Pollution Prevention Laws

A number of states have passed laws that incorporate aspects of pollution prevention into RCRA and EPCRA reporting requirements. Generally, these laws require industrial facilities that generate hazardous waste to develop a source reduction and waste minimization plan, including an implementation schedule, and to track and report waste reduction progress. A list of states with mandatory pollution prevention laws are presented in Exhibit 2-6. The following are some examples of provisions from state laws:

- Arizona, California and Minnesota have similar P2 requirement. The Arizona law applies only to facilities that must file the annual Toxic Chemical Release Inventory Form R required by EPCRA Section 313 or during the proceeding 12 months generated an average of one kilogram per month of an acutely hazardous waste. Minnesota's law has similar applicability. The California law only applies to facilities that generate more than 12,000 kilograms of hazardous waste or 12 kilograms of extremely hazardous waste in a calendar year. Each of the three programs requires facilities to perform pollution prevention planning that identifies waste sources and specific technical steps that can be taken to eliminate or reduce the generation of hazardous wastes. Each program requires that facilities submit progress reports with the length of time between reports ranging from one to two years.

- Texas has established a similar program; however, they have implemented a two-tier P2 system with source reduction as the primary goal and waste minimization as the secondary goal. The program has wide applicability in that it applies to all hazardous waste generators, exempt for conditionally exempt small quantity generators. Planning, tracking, and reporting requirements of the Texas law are similar to those of the Arizona, California, and Minnesota laws.

- A number of states have implemented voluntary pollution prevention programs. The foundation of these programs is generally educational outreach and technical assistance mechanisms.

2.4 Local Pollution Prevention Requirements

The Clean Water Act gives qualified local POTWs the authority to administer pretreatment programs, including regulation of industrial dischargers. These POTWs also have the authority to implement regulations that are more stringent than federal guidelines, such as 40 CFR 433. Many local agencies have used this authority to reduce the impact of industrial discharges on the operation of the POTW, reduce the concentration of toxic pollutants in POTW sludges and/or to reduce the mass of pollutants discharged by the POTW. This is typically accomplished by lowering the permissible concentration limits of industrial discharges below the federal standards. One local program, administered by the Palo Alto Regional Water Quality Control Plant (RWQCP), also incorporates P2 requirements into pretreatment discharge permits. This is one of the first examples of the use of such requirements in place of more traditional pollutant concentration limitations.

In response to its own stringent copper discharge limit, the RWQCP had to reduce the copper content of wastewaters received at the plant. This effort is focused upon all sources of copper, including stormwater runoff, as well as residential, commercial and industrial activities. Since most of the industrial copper in the Palo Alto area is discharged by metal finishing operations, particularly those associated with computer parts manufacture, the industrial portion of the copper source reduction efforts focused on printed circuit board manufacturing and other metal finishing operations.

Based on their new requirements, RWQCP formed a Metals Advisory Group, made up of volunteers from local industry, environmental awareness groups, the general public, and local officials. In collaboration, this committee made a decision to implement a unique plan to meet the discharge standards. The plan involved giving metal finishing and printed wiring board (PWB) manufacturers the choice between mass-based discharge limits or concentration limits that carry an additional P2 requirement. The mass-based limits could be met in any manner that the industrial discharger chose to implement. The mass-based limits were established on a facility by facility basis using data collected through RWQCP-conducted P2 studies. If a discharger selected the concentration limits (e.g., 0.4 mg/l Cu), they had to implement a specific set of P2 items that were referred to as Reasonable Control Measures (RCMs). The RCMs were established through a study performed at six volunteer metal finishing and PWB shops. The RCMs for PWB manufacturing facilities included:

- Minimize drag-out (e.g., spray rinsing, drag-out tanks, air knives, splash guards, drip bars, changing drip times)
- Counterflow rinsing (i.e., two stage with spray option)
- Positive flow control (e.g., conductivity, timer, contact switch)
- Extend bath life (e.g., purification, filtering, anode purity, change bath chemistry)
- Pre-treat spent baths (e.g., electrowinning)
- Control bath make-up (e.g., deionized water, control bath make-up and additions)
- Minimize drag-in (i.e., prevent bath contamination)
- Optimize wastewater treatment

There were a total of 13 metal finishing and PWB shops in the RWQCP service area in 1995. One facility made an unrelated decision to move out of the service area. Of the remaining 12 shops, eight facilities chose the concentration-based limits and installation of the RCMs.

Exhibit 2-6. State Pollution Prevention Programs

State Program	Statute
Mandatory P2 Programs	
Arizona	AZ Rev. Stat. Ann. 49-961 to-73
California	CA Health & Safety Code 25244.12 to .24
Georgia	GA Code Ann. 12-8-60 to -83
Louisiana	LA Rev. Stat. Ann. 30.2291 to .2295
Maine	ME Rev. Stat. Ann., tit. 38, 2301 to 2312
Massachusetts	MA Ann. Laws ch. 211, 1 to 23
Minnesota	MN Stat. Ann. 115D.01 to .12
Mississippi	MS Code Ann. 49-31-1 to -27
New Jersey	NJ Stat. Ann. 13: 1D-35 to -50
New York	NY Envtl Conserv. Law 27-0900 to -0925
Oregon	OR Rev. Stat. 465.003 to .037
Tennessee	TN Code Ann. 68-212-301 to -312
Texas	TX Title 30, Ch 335
Washington	WA Rev. Code 70.95C.010 to .240
Voluntary P2 Programs	
Alaska	AK Stat. 46.06.021 to .041
Colorado	CO Rev. Stat. Ann. 25-16.5-101 to -110
Connecticut	CT Gen. Stat. Ann Appendix Pamphlet, P.A. 91-376
Delaware	7 DE Code Ann. 7801 to 7805
Florida	FL Stat. Ann. 403.072 to .074
Illinois	IL Ann. Stat. Ch. 111 _, 7951 to 7957
Indiana	IN Code Ann 13-9-1 to -7
Iowa	IA Code Ann. 455B.516 to .518
Kentucky	KY Rev Stat. Ann. 224.46-310 to -325
Ohio	HB 147, HB 592
Rhode Island	RI Gen. Laws 37-15.1-1 to .11
South Carolina	SC Code Ann. 68-46-301 to -312
Wisconsin	WI Stat. Ann. 144.955

Source: Dennison, Mark, *Pollution Prevention Strategies and Technologies*, Government Institutes, Inc. Rockville, MD, 1996.

3.0 Prevailing and Alternative Printed Wiring Board Production Methods and Materials

3.1 Overview of PWB Manufacturing Processes

This section of the report addresses printed wiring board production methods and materials that are of particular concern with respect to waste generation and pollution prevention and control. This information will help the reader to relate the pollution prevention and control survey data to specific production steps. A brief overview of PWB manufacturing processes is presented in this section. This is followed by a more detailed discussion of rigid multilayer board manufacturing (Section 3.2), the most prevalent method of fabricating PWBs. The detailed discussion also contains information on alternative production methods and materials that may reduce waste generation and/or involve less hazardous materials. Section 3.3 presents information on waste generation rates, alternative processes and potential P2 technologies applicable to PWB manufacturing steps.

Printed wiring boards are categorized in several ways. When overall complexity is being considered, they are often categorized in terms of layer-counts, or the number of circuit layers present on a single PWB. PWBs fall into three layer-count categories: multilayer, double-sided and single-sided. The manufacturing steps for these different types of boards are shown in Exhibit 3-1. Multilayer PWBs contain more than two layers of circuitry (i.e., at least one layer is imbedded in the substrate between the top and bottom layers of the board). A multilayer PWB may contain 20 or more layers of circuitry, but more common layer counts are 4-10 layers. A typical motherboard for a Pentium personal computer is usually a 6- or 8-layer board. Double-sided boards have two interconnected layers and the manufacturing process is a subset of the multilayer process. Single-sided PWBs have only one layer of circuitry. Single-sided manufacturing is a small subset of the multilayer process with a considerable number of wet and dry process steps eliminated.

PWBs are also categorized by substrate, or base material, type and fall into three basic categories. Rigid PWBs are typically constructed with glass-reinforced epoxy-resin systems that produce a rigid board at thicknesses of less than 0.1" (0.062 is the common rigid PWB thickness although there is a trend toward thinner PWBs). Flexible (or flex) circuits are manufactured on polyimide and polyester substrates that remain flexible at finished thicknesses. A third category, rigid-flex, are a combination or assembly of rigid and flex boards laminated together during the manufacturing process often to produce three dimensional circuits.

There are two basic types of manufacturing methods, although hybrid methods exist. Most common is subtractive processing in which copper is selectively removed from a PWB; what remains forms the circuitry. What is referred to as the subtractive process does include additive steps (such as copper electroless and electrolytic plating) but the process of forming the circuit on the substrate is performed by subtracting (etching) copper. Additive processing refers to a process whereby the circuit is formed by selectively plating metal on a substrate thereby creating a circuit layer. In the fully additive process, no subtractive (etching) process occurs. Hybrid methods referred to as partially additive and semi-additive are essentially subtractive methods, but the amount of copper etched from the boards is much less than with the standard subtractive process.

Rigid Multilayer Manufacturing. This process is covered in detail in Section 3.2.

Rigid Double-Sided Manufacturing. Not unlike single-sided, double-sided PWB manufacturing is a subset of the multilayer process. The inner-layer image transfer, lamination, and hole cleaning are eliminated. The through-hole metallization process is required.

Rigid Single-Sided Manufacturing. Several process steps, including through-hole metallization, are not performed in this process. Furthermore, since no process step is unique to single-sided manufacturing, manufacturers of multilayer and double-sided boards often include single-sided manufacturing as part of their product mix.

The most common sequence of single-sided production is drill, print-and-etch, surface finish, and final fabrication. No inner-layer processing, through-hole plating, or hole-cleaning is performed.

Flexible PWB Manufacturing Overview. A flexible circuit is manufactured on materials that allow for bending or flexing of the PWB to create a three-dimensional effect or to allow for movement of a device to which the circuit is attached. Flex circuits can be designed to be flexed into shape once or a few times or to withstand thousands of flexing cycles. Flex circuits are found in printers, disk drives, automobile electronics, and a wide range of other common products.

Although similar to rigid manufacturing in many respects, the flexible circuit manufacturing process includes some unique processes and materials, and in general, is not integrated into a rigid PWB facility although data suggest a trend toward integration. Therefore, few rigid PWB facilities have expanded into flexible circuit manufacturing. On the other hand, manufacturers of flexible circuits often produce rigid boards as well, often as part of rigid-flex assemblies. Flexible circuits may be single-sided, double-sided or multilayer, although the dimensional stability of flexible circuit substrates generally complicates multilayer manufacturing.

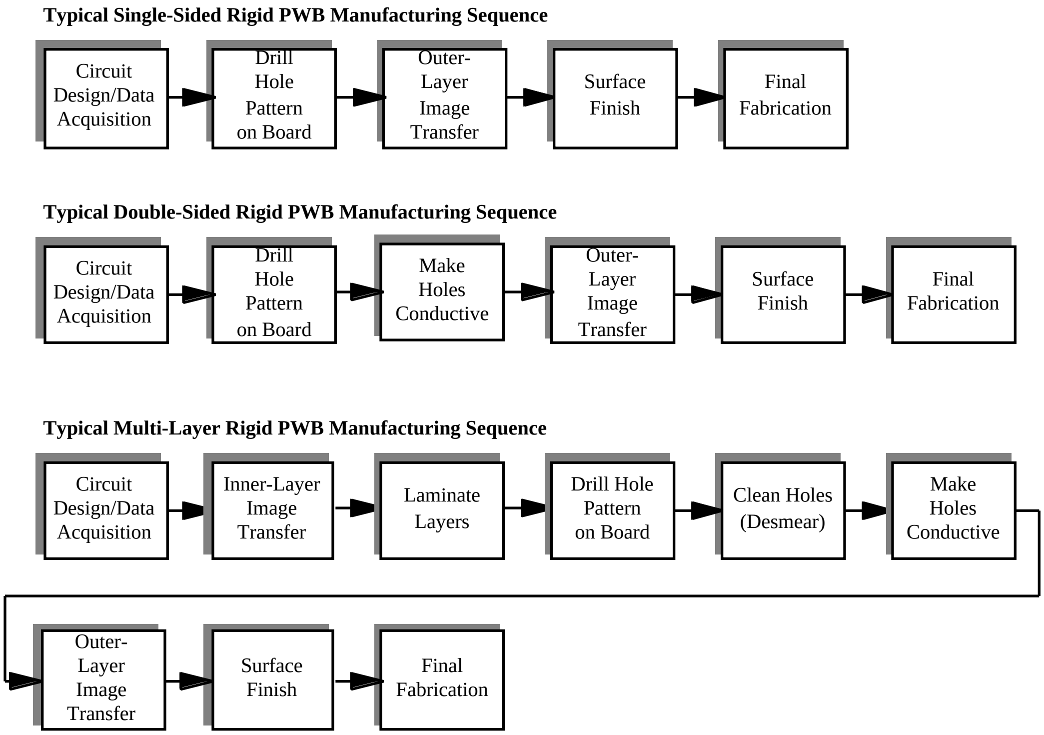
Image transfer, drilling (if any), and through-hole plating (if any) processes are similar but not identical to their rigid counterparts. Flex substrates are thin and unlike standard rigid materials. Thicknesses of a few mils are common compared to rigid material thickness of up to 31 mils for inner-layers and 62 mils for double-sided. Additionally, tooling and surface finishing processes for flexible circuits are quite different when compared to rigid. A cover sheet of similar material to the base film is laminated over the circuit of flexible PWBs whereas rigid PWBs are coated with soldermask. The coversheet is pre-punched to expose appropriate areas of the circuit for component soldering or device connections. Solder coating is performed with hot air solder leveling or hot oil reflow. Many flex circuits are nickel-gold coated.

3.2 Rigid Multilayer PWB Manufacturing

The remainder of Section 3 describes the individual processes that are used for rigid multilayer board manufacturing, the most common method of making PWBs. Each major step of the process is described using a "use cluster" approach. A use cluster is defined as a set of chemicals, processes, or technologies that may substitute for each other to perform a specific function. This approach is used by EPA to assess the potential health and environmental risks of alternative chemicals, processes, or technologies (ref. 2).

For purposes of this discussion, the fabrication of rigid multilayer PWBs has been subdivided into nine process steps (see Exhibit 3.1). These steps form a generic process flow, with many processes and potential alternative processes within each function. Each process is described below, identifying the most common processes, common alternatives, and the general technology trends.

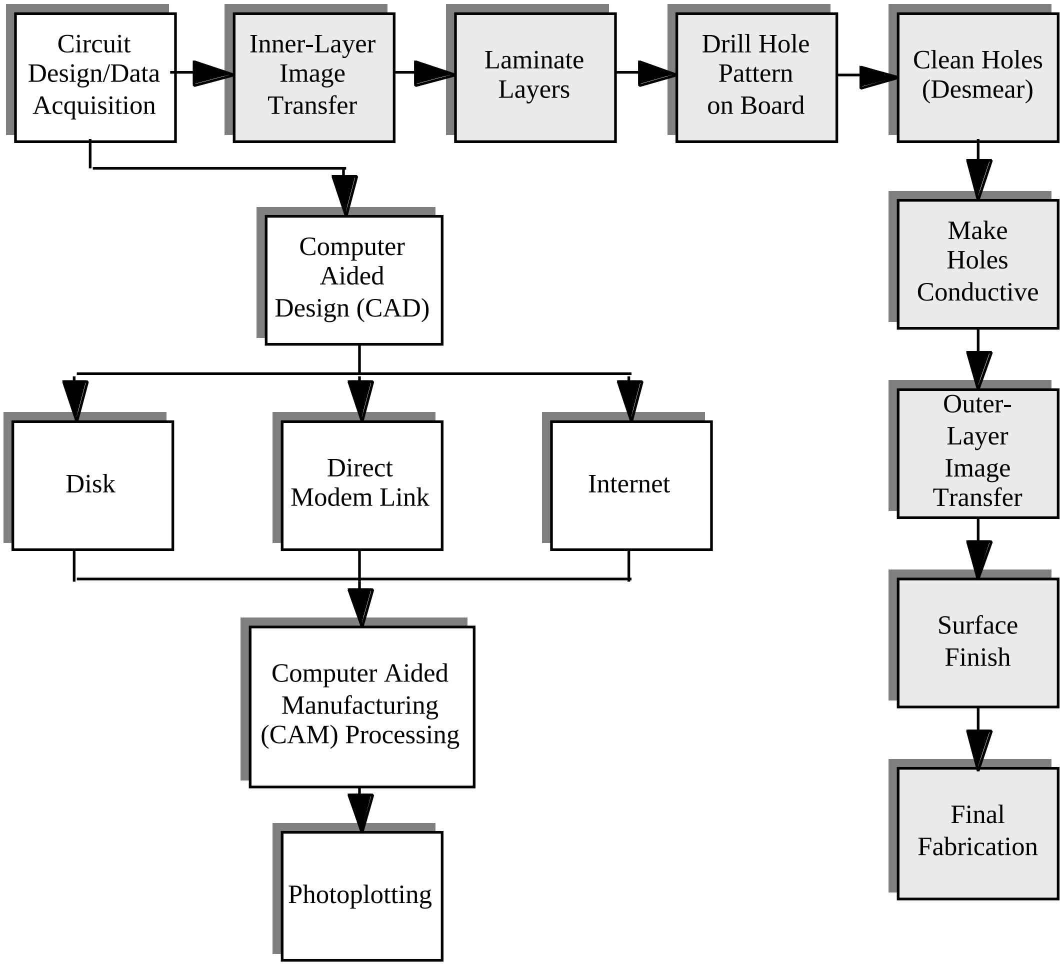
Exhibit 3-1. Typical Process Flow for Rigid Board PWB Manufacture



3.2.1 Circuit Design/Data Acquisition

Nearly all PWB design and layout is performed with Computer Aided Design (CAD) software, a relatively recent and dramatic development in the history of PWB manufacture (Exhibit 3-2). CAD packages for personal computers completely eliminated by the early part of this decade older methods of PWB layout. With the advent of CAD systems came a dramatic change in the materials provided to PWB facilities that specify the manufacturing and a new department, the CAM department, now exists in all PWB facilities to handle the incoming data.

Exhibit 3-2. Process Flow to Design and Produce Film with Data



Certain design aspects of PWBs affect the quantity and characteristics of wastes generated during manufacturing. The designer, through manufacturing specifications, has some control over the environmental impact the circuit will create. For example, specifying a tin-lead surface finish may generate more hazardous waste than using an organic solderability preservative.

Circuit layout also has some bearing on waste generation. For example, using blind/buried vias on multilayer boards makes more efficient use of the available circuit “real estate” and may eliminate some layers. This layout decision should be balanced against the additional wet processing required to make those holes conductive (i.e., more layers travel down the plating line and generate plating waste). A software package is currently being developed to take these manufacturing and environmental impact factors into account. With this software, “What if” scenarios can be run to compare the waste generated by one type of circuit and manufacturing process versus alternatives (ref. 9).

3.2.1.1 CAM Processing
Modern PWB facilities must transform CAD generated data into customized tools for the manufacture of the part, namely photo-tools, drill files and profile routing files. These functions are performed in what is usually called the CAM department.

Data files are transferred to PWB manufacturing facilities on magnetic media, via modem or via the Internet. These image files (native CAD files or, more often, "Gerber" files, so named for the company that created the format for its vector plotters) along with drill and rout files are analyzed and graphically displayed by CAM software for sales, quoting, and manufacturability purposes. Thereafter, the data are manipulated and edited to create the image, drill and rout files for necessary for photo-tool creation and fabrication. Step-and-repeat patterns, thieving patterns, stretching or shrinking to offset characteristic manufacturing dimensional shifts, registration and tooling marks, and other editing is performed to create the highly customized photo-tools. Higher-end CAM packages will also perform design-rule checking and other manufacturability analyses.

3.2.1.2 Photoplotting
CAM files are transferred to photoplotters for film imaging. Modern laser photoplotters can image a layer of circuitry in a few minutes or less. Silver-based high-contrast film, secured on a flat bed or a rotating drum, is passed under a laser source and the image created by the CAM software is reproduced on film. Developing is performed in a three- or four-chambered conveyorized developer that includes developer, fix, rinse and drying steps. The film generated in this step usually serves as the photo-tool for the image transfer process.

The film developing step does produce a small silver-bearing waste stream. The film itself contains approximately 0.0016 ounces per square foot and 80% of this silver winds up in the spent developer, fixant, and rinse (ref 10). Metallic replacement or electrolytic plating can be used to recover silver from the waste chemistry. With metallic replacement, the solution is passed through a steel wool cartridge where the iron in the steel wool reacts with the silver and replaces it. A silver sludge settles to the bottom of the cartridge. An electrolytic recovery system (referred to as electrowinning and discussed in Section 5) recovers silver by plating the silver in the solution onto cathodes.

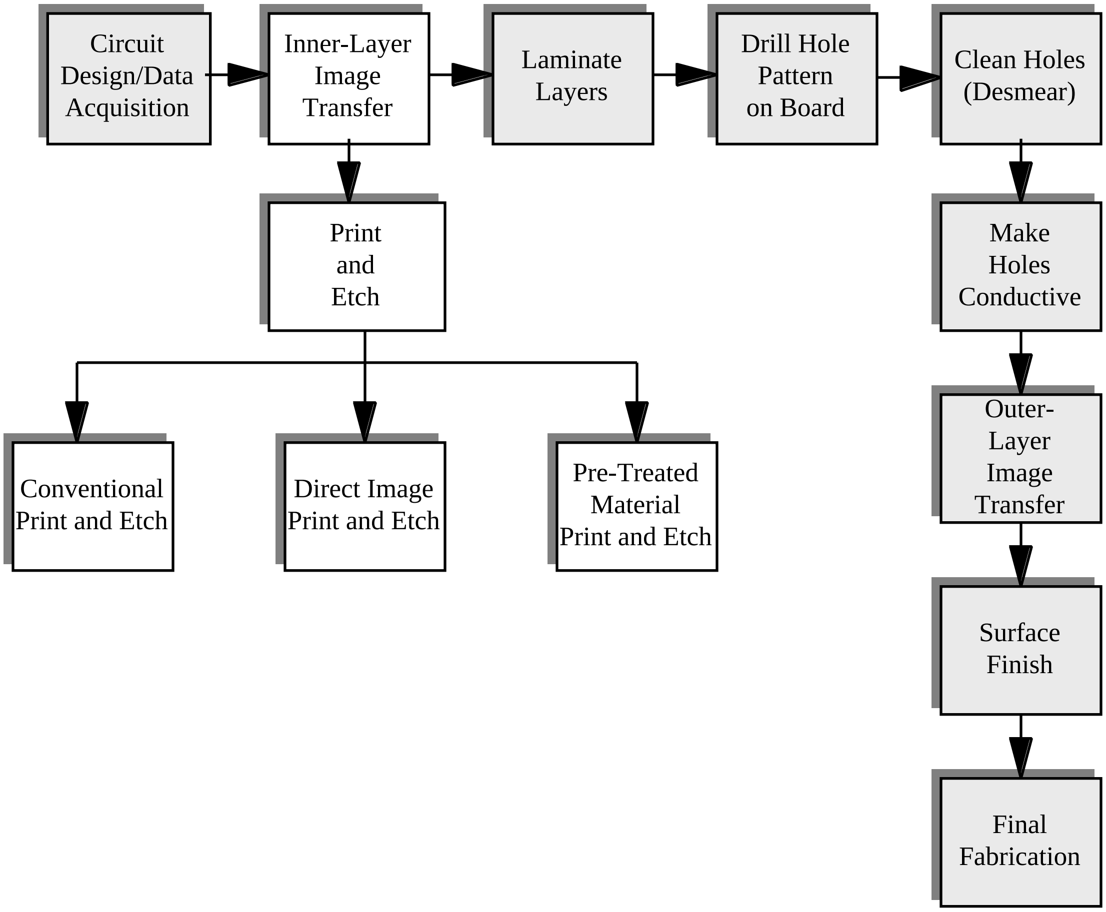
Photo-tools are ultimately discarded after the tool has served its purpose. Some facilities collect this film and ship it offsite for silver recovery although the small yields do not encourage such a practice.

A company has developed a new film that consists of a thin layer of bismuth chemically deposited onto a polyester base (ref. 11). The bismuth is then sandwiched by another polyester sheet that acts as a protective cover to prevent scratching. The bismuth layer, initially opaque, has the property of becoming clear when heated. Gerber Scientific Instruments has designed a laser photoplotter for this material that can also expose standard silver halide film. The PRISM-IR photoplotter uses a 10W Nd:YAG infrared laser for the bismuth film, combined with a red laser diode for silver film. This film requires no developing step, therefore, no waste stream is generated.

Registration systems, which maintain layer-to-layer alignment, usually include a film punch. The photo-tool is imaged with targets (added to the image files in the CAM department) that match fixtures in exposing frames employed in the image transfer step. The targets are punched in manual or automatic film punches. The film is then inspected for flaws, repaired if necessary, and is then ready to perform as a photo-tool.

3.2.2 Inner Layer Image Transfer
The purpose of this process step is to transfer a circuit image to the copper-coated base laminate of the PWB (Exhibit 3-3). Two basic strategies exist: subtractive and additive. The predominate method is subtractive which is accomplished through a series of steps known collectively as “print-and-etch.” Additive methods of multilayer circuit manufacture are briefly covered in Section 3.1.

Exhibit 3-3. Inner Layer Image Transfer



3.2.2.1 Conventional Print-and-Etch

Print-and-etch is a series of process steps that accomplish the goal of image transfer from the photo-tool to the copper foil layer of the base material. The "print" step includes the coating of the copper-foil-clad base material with a light-sensitive, organic photoresist. The photoresist (so named because in addition to being light sensitive, the coating will subsequently "resist" the etchant during a later step in the print-and-etch process) polymerizes when exposed to a light source of appropriate energy. The phototool, placed over the photoresist, acts to allow only an image of the circuit to be exposed, protecting the other areas of the photoresist layer. After exposure, the photoresist layer is developed; the exposed, polymerized areas remain, the unexposed areas (those which were under opaque areas of the photo-tool) are washed away, revealing the copper layer underneath.

The "etch" portion of print-and-etch removes exposed copper areas selectively from the panel, but cannot attack the copper residing under the photoresist. Thus, the image of the circuit is transferred from the photo-tool to the copper layer.

PWB Laminate. The PWB base material consists of a dielectric core that has been coated or impregnated with resin. The dielectric material is usually woven glass fibers or paper. Different combinations of these two materials and the substitution of various resin systems can alter the electrical, physical, performance, and cost characteristics of the material. The type of material employed for a specific part depends on the function of the PWB, design requirements, and how it will be manufactured. Some materials perform better in certain environments (e.g., extreme heat or high humidity), others are more suitable for a particular manufacturing process (e.g., punching), while others are chosen for their electrical properties (e.g., dielectric constant). FR4 is the designation given to the most widely used material for the printed wiring board industry. It is constructed of multiple plies of resin impregnated woven glass cloth. GI type material, also known as polyimide, is an example of a high temperature type material. Its resin system allows it to sustain temperatures of 200°C vs. FR4's 120-135°C.

Copper foil is rolled or electrolytically deposited on the base laminate. PWB facilities generally purchase sheets of copper-clad base laminate in sizes of 3x4 feet or larger.

Survey data relative to base materials used by respondents are located in Appendix A.

Material Preparation. The core material is sheared to panel size then cleaned mechanically, chemically, or by a combination of both. The purpose of this cleaning step, referred to as "pre-clean" or "chem-clean," is to remove surface contamination, including any anti-tarnish coating present and to condition the surface copper topography to promote the subsequent adhesion of photoresist.

Mechanical scrubbing methods include abrasive brush scrubbing and pumice scrubbing. Brush scrubbing removes a thin layer of surface copper, thus ensuring a clean surface, but tends to impart stress to thin core material by deforming it during the scrub. Brush scrubbing can also produce a surface not compatible with fine-line circuit designs. Pumice or aluminum oxide scrubbing imparts less or no stress to the material and produces a favorable surface for photoresist lamination, but is known to be ineffective at removing anti-tarnish coatings applied by laminate manufacturers. Thus, pumice scrubbing is often accompanied by chemical cleaning.

Chemical cleaning is usually accomplished in a conveyorized spray chamber. Two chemistries are sprayed onto the surface of the panel. The first is usually a proprietary product designed to remove anti-tarnish coatings. The second is a micro-etchant such as potassium persulfate, which is applied to further clean the surface and leave a desirable surface finish. A third chamber may include a mild anti-oxidizer.

Pre-treated material does not require cleaning and is discussed in Section 3.2.2.2.

The decision of which cleaning method to use is driven by a number of factors. Pumice scrubbing is claimed by some as the process that produces the best surface for photoresist adhesion (a critical consideration; poor photoresist adhesion is almost always fatal). But pumice scrubbing requires rather expensive and maintenance-intensive equipment. While rinsewater generated in the pumice scrubbing operation is usually free of metal (the surface copper is deformed during pumice scrubbing, not removed), pumice scrubbing is usually preceded by a chemical clean step designed to remove the anti-tarnish coating that laminate manufacturers apply and this step does produce a copper-bearing waste stream. Chemical cleaning produces a copper-bearing waste stream from each of the process tanks, but the micro-etchant chemisty is found in many processes and its associated copper recovery and treatment regimen is likely to already be in place in the shop. Mechanical scrubbing produces copper dust in its waste rinsewater stream which is easily removed by simple filtration. Mechanical stress imparted to thin core material during scrubbing and the difficulty of maintaining a precise topography as brushes wear tend to limit mechanical scrubbing of very thin materials.

Imaging. The imaging process includes three steps: photoresist application, exposing (or "printing") and developing. Photoresists are available as a dry film, currently the most common, and liquid resists. Dry film resists are usually sold in rolls ranging from 2 in. to 60 in. wide and 125 ft. to 1,000 ft. long. Resist thickness varies depending on the application. Resists less than 1 mil can resolve very fine lines. Resist thickness of 1 to 1.5 mils is common for imaging innerlayers. Thicker resists (1.5 to 2.0 mils) are used as plating, rather than etch, resists. The greater thickness allows the metal to plate up the sidewalls of the film without mushrooming over the top. This mushrooming effect will cause downstream problems during the resist stripping and etching steps (ref. 12).

The photoresist is applied with heat and pressure to the surface of the panel. This can be done with a hot-roll or cut-sheet laminator. A cut-sheet laminator cuts the resist slightly less than the panel dimensions thereby generating fewer resist trimmings than a hot-roll laminator. The photo-polymer film layer is sandwiched between a separator sheet that is automatically peeled away by the lamination equipment and a mylar cover sheet that is peeled away by hand when the panel is ready for development. This top coversheet also serves to protect the resist from scratches, keeps contaminants from the surface and prevents the phototool from adhering to the resist. Modern dry film resists for common print-and-etch functions are fully aqueous and are developed in a simple carbonate solution.

Although less common, liquid photoresists offer certain distinct advantages over dry film, and some disadvantages. Liquid resist coating equipment is more expensive than dry film lamination equipment, but offers greater production rates (250-300 panels per hour vs. 150 panels per hour with dry film) (ref. 13, 14). Liquid resist is more tolerant of surface topography, but requires a higher level of surface cleanliness. Since the coating does not include a cover sheet (the phototool rests directly on the photosensitive coating), resolution of fine lines is improved. Liquid resist is applied either by roller coating or by curtain coating. Roller coating allows double-sided coating and the equipment is less expensive than curtain coating. Development is performed in similar or identical chemistry as dry film.

The printing of the image is accomplished with a film or glass phototool being placed between the panel to image and a light source. A vacuum is drawn to remove air and to ensure the phototool is held securely against the panel before the light source is turned on. Hinged-glass frame fixtures have become common to expose panels. Pins can be set in the glass and when used in conjunction with holes punched in the film achieve precise layer-to-layer registration. One drawback with glass is its natural rigidity which can cause off-contact exposure (ref. 12). An alternative to glass is a polyester blanket which achieves a very good vacuum, but as the polyester conforms around the edge of the panel and contacts the bottom glass, it can isolate portions of the blanket from the vacuum source. “Bleeders” or “shims” must be used to maintain a constant source of vacuum to the surface of the panel (ref. 15).

Some facilities remove the mylar cover sheet from the photoresist prior to exposing when the traces are very fine. The removal of 1 more mil of separation between the photoresist and the phototool decreases the chances of light diffusion under the phototool. Also, there is less light scattering, which results in more light hitting the panel and better resolution of the image. Finally, any foreign particles that collect on the coversheet will be removed along with the coversheet. Using this method has enabled lines and spaces as fine as 1.5 mil (ref. 16).

Developing is performed in a sodium carbonate solution (1% to 2%). The same general developing chemistry can be used for both dry film and liquid resist. The spent developer stream is of considerable volume, usually the largest spent process fluid stream a PWB facility faces. Although copper is not usually present in the alkaline spent developer, this stream, along with the spent resist stripper, is the source of photo-resist solids, or skins. Resist solids from the developing of photo-resist does not generally fall into the category of F006 wastes because the process is not (usually) "in line or contiguous with an electroplating operation." Developing precedes plating steps and is separated from them by rinsing and drying steps, which is the basic consideration in determining the status of the solids (see section 2.2.21). The more complicated status of resist solids generated during resist stripping operations is discussed in Section 3.2.7.1.

Alternative image methods are discussed in Section 3.2.2.2.

Etching. Etching is required for any of the process alternatives within the subtractive process. Panels entering the etch process have been coated with an etch resist, usually a dry film photo-resist. The resist layer selectively protects the circuit areas from etchant, whereas the remaining copper foil is etched away.

Exhibit 3-4. Common Primary Etchants Used in PWB Manufacturing

Type	Applications	Advantages	Disadvantages	Cu Capacity
Cupric Chloride	For use with organic resists	Ease of regeneration Ease of copper recovery	Incompatible with metallic resists	15-20 oz
Ammoniacal	Organic or metallic resists	Continuous operation Ease of control	Regeneration is more difficult	18-24 oz.
Sulfuric-peroxide	Organic or metallic resists	Simple waste treatment Ease of regeneration Constant etch rate	Higher machine costs Employee safety concerns while handling concentrated chemicals	4-5 oz

Etchant sprayed onto the surface of the panel removes the exposed copper, but cannot significantly dissolve the copper residing under the resist. In this way, a copper circuit is formed. Etching is performed with conveyorized equipment that typically includes a main spray chamber, an etchant flood rinse, and several cascading water rinses. Long conveyorized units that include developing, etching, and film stripping are common only in large production shops. Acidic cupric chloride and alkaline ammoniacal are the most common etchants (sulfuric-peroxide, a common microetchant, is also employed as a primary etchant). Chromic acid and ferric chloride, dominant in the past, are now rarely found. A complex array of issues surround the choice between the remaining chemistries, and the decision is tied to downstream and upstream process material choices as well as economic considerations.

For example, cupric chloride is generally incompatible with the metallic resists (tin or tin-lead) which are commonly applied to outer layers, but may be selected for inner layers based on performance (for fine-line etching), waste minimization (ease of on-site regeneration and copper recovery), or other issues. In this example, two etching systems are required, cupric chloride for inner layers and ammoniacal for outer layers. Being a one-step conveyorized process, etching is not often a production bottleneck and two etching systems may be difficult to justify. For this reason, many small shops employ the more versatile ammoniacal etchant for both inner and outer layers.

Cupric chloride etchants consist of cupric chloride ($CuCl_2$) and hydrochloric acid. The simple etch reaction is driven by copper's two oxidation states:

$$Cu + CuCl_2 \rightarrow Cu_2Cl_2$$

The reaction with cupric chloride etchant is reversible chemically by chlorination, oxidation with peroxide or other oxidizer, or electrolytically. Several regeneration systems have been developed that reoxidize cuprous chloride and maintain total copper content at desirable levels (usually in the 15 to 20 ounce/gallon range) (ref. 69). Chlorination, the most common method, is performed in a closed-loop arrangement in which spent etchant is circulated through the chlorinator and back to the etcher sump. Copper oxide waste is produced. Since this etchant is acidic, no attack on the alkaline-sensitive dry film resists occur. Cupric chloride has a similar etch rate to ammoniacal but is not, as mentioned above, compatible with many metal resists.

Ammoniacal etchant is popular due to ease of use and general compatibility with most etch resists. Ammoniacal etchant systems are comprised mainly of ammonium hydroxide and ammonium chloride. Other ingredients are present to a lesser degree and serve a variety of functions. As with cupric chloride etchant, the etching reaction is driven by the cupric (Cu^{++}) ion:

$$Cu + (Cu(NH_3)_4)^{+2} \rightarrow (2Cu(NH_3)_4)^{+1}$$

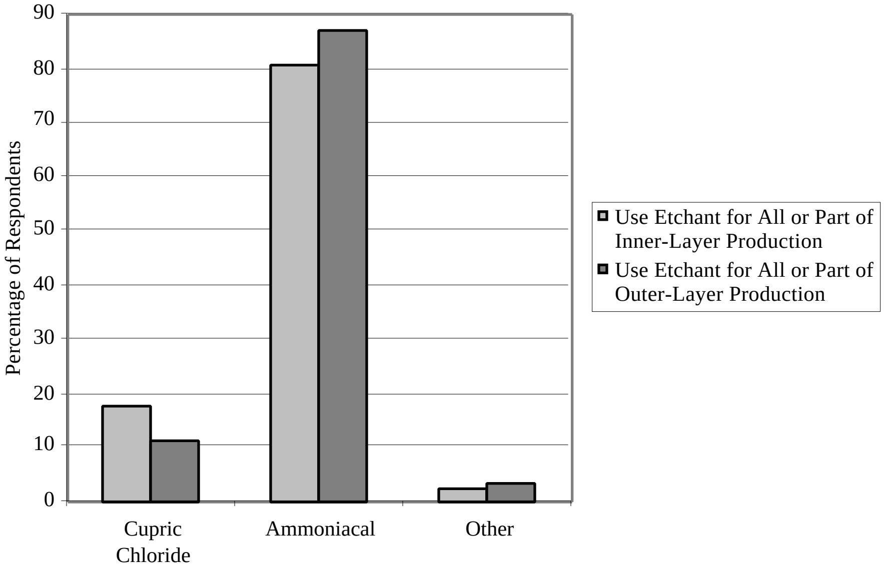
Ammoniacal etchants are maintained for continuous operation with a feed-and-bleed arrangement based on baume or specific gravity measurements. In this arrangement, a pump is connected to a baume-activated switch. When the baume of the etchant in the sump rises due to the increasing copper concentration, the pump is switched on. Copper rich etchant is removed from the sump while fresh etchant is introduced. In this way, a steady concentration of copper (critical in maintaining a steady etching rate) is maintained. In the absence of regeneration, the spent ammoniacal etchant stream is usually the largest waste stream shipped off-site by PWB shops.

Sulfuric-peroxide (i.e., sulfuric acid and hydrogen peroxide) is commonly used as a micro-etchant. This chemistry was reported in use by a small percentage of respondents as a primary etchant. Sulfuric-peroxide has a much lower copper-holding capacity than other etchants (approximately 4-5 oz/gal Cu vs. 15-24 oz/gal Cu or more for ammoniacal and cupric chloride) but is easily regenerated on-site and is compatible with metallic etch resists.

The survey results relating to etchants are presented in Exhibit 3-5. 81% percent of the survey respondents use ammoniacal etchant for inner-layer etching, while 18% use cupric chloride. Sulfuric-peroxide for inner-layer etching was in use by 2 respondents. 5 of the 10 largest facilities reported using cupric chloride. The disproportionate use of this etchant amongst larger facilities may be due, in part, to their ability to economically justify two etching systems (4 of these 5 facilities used ammoniacal etchant exclusively for outer-layer etching).

Outer-layer etchant use data are discussed in Section 3.2.7.2.

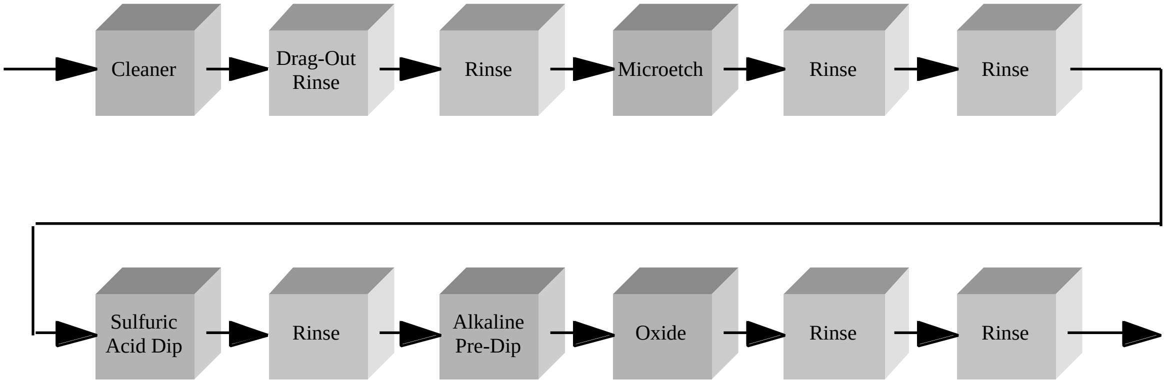
Exhibit 3-5. Etchant Use



Resist Stripping. The photoresist is stripped after etching. Stripping may be part of the conveyorized etching process with another spray chamber or done as a batch process in a stripping tank. A wide array of resist strippers exists. A hot potassium hydroxide (KOH) solution is one, but this process is inappropriate for spray operation because the resist is removed in strips and not dissolved. Monoethanolamine (20% by volume in an alcohol solvent) is the chemistry of choice for most applications. Other proprietary formulations abound. Photoresist developer and stripper wastes depend on the carrying capacities of the chemistries, the thickness of the resist, and the area to be developed or stripped. See the Photoresist Stripping subsection in Section 3.2.7.1 for a discussion of the regulatory status of resist skins.

Oxide. Oxide treatment is used in PWB manufacture to promote copper-to-epoxy adhesion in multilayer manufacture. The batch oxide process line usually contains four or five process tanks and three or four rinse systems (Exhibit 3-6). The process tanks consist of a hot alkaline cleaner, a microetch, and the oxide bath itself, which may include a dilute pre-dip for drag-in protection. The microetch may be persulfate- or peroxide-based. Oxide chemistries are usually proprietary—a common oxidizer is sodium chlorite with sodium hydroxide. Other ingredients vary from vendor to vendor. The oxide bath must be quite hot, usually 140 to 150°F or hotter. The process takes 15 to 30 minutes to complete.

Exhibit 3-6. Typical Oxide Line



One alternative is the conveyorized white oxide process that uses tin oxide as the adhesion promoter. Approximately four microinches of tin metal are plated by displacement on the copper surface in this self-limiting process (ref. 17).

Another alternative is a proprietary acid-based oxide replacement (ref. 18). This solution is most effective when used in conjunction with a new "drum-side treated foil," but it reportedly produces good results with conventional foils as well. This new foil has topography with more surface area than ordinary copper foil, which allows for greater deposition of the adhesion promoter. The proprietary oxide replacement is a sulfuric/peroxide-based system that is applied horizontally with conventional spray equipment. The process time is less than 10 minutes and the process bath temperature is 95-100°F. In addition to the increased productivity, some environmental benefits exist:

- Sulfuric peroxide is used as a microetch in many facilities and waste treatment may already be in place.
- Greater than 90% of the copper in the bath can be recovered with electrowinning or chilling whereas this is not possible with the oxide solution.
- Sulfuric-peroxide baths are quite likely to be found elsewhere in the facility and the treatment and copper recovery strategy already in place. Hypochlorite-based chemistry requires a distinct waste treatment strategy.
- The shorter process line and process time reduces the amount of rinse water used and wastewater generated.

The survey data indicate that all facilities producing rigid multilayer boards use the conventional oxide step for at least some of their multilayer product and 13% also purchase double-treated material for some of their product. Of the three exclusively flex manufacturers, one does not perform the oxide step at all, one does not use the oxide step for 98% of multilayer product, and the third uses double-treated material on all of its multilayer product.

3.2.2.2 Image Transfer Options

Pre-treated Material. A minority of facilities reported using laminate that is pre-treated by the laminate manufacturer with an oxide coating. This material, often referred to as "double-treat" material, comes ready to use. No scrubbing or chemical cleaning is needed, although some facilities will run the panels through tacky rollers prior to lamination. Eliminating the need for oxide treatment reduces chemical and water usage as well as process steps. This is attractive to smaller, quick turnaround shops.

Pre-treated material is not appropriate for several applications including blind and buried via processes, during which the oxide coating would be removed during the via metallization process. Furthermore, rework of pre-treated panels is often severely limited; for example, stripping photoresist and reapplying is a fairly common rework scenario that is not advisable with pretreated material simply because the stripping process includes a cleaning step prior to the reapplication of the photoresist and this step will remove the oxide coating. Automated Optical Inspection (AOI) performance can be negatively affected by the dark, nearly black surface of the oxided material. And finally, while positively affecting waste generation at the PWB shop, the strategy of purchasing pre-treated material simply pushes the oxide process and its attendant waste upstream to the laminate manufacturer.

Direct Imaging. Direct imaging is an alternative to using film or glass photo-tools. The panel is coated and developed the same as when using a photo-tool, but the exposing step is done with a laser in place of a photo-tool. Direct imagers are similar to photoplotters, except the photoresist-coated panel is imaged by laser rather than film (so similar are the two the direct imaging machines are usually designed to perform either task). The high capital costs, performance issues, and the fact that direct imaging takes longer than conventional exposing in most cases have historically impeded the penetration of this technology. However, advancements in photo-resist technology and improvements in laser technology are renewing interest in direct imaging.

In addition to the cost savings in film and developer chemistry, finished product yields may increase as well due to improved alignment between layers. Film photo-tools suffer dimensional instability from the environment where they are created, used and stored. Changes in temperature and humidity can cause characteristic and troublesome stretching and shrinking of film photo-tools. The dimensional instability of film is, in many cases, s the largest contributor to the overall registration tolerance of the manufacturing process. With direct imaging, only the positional tolerance of the imager (usually claimed to be less than 1 mil over 24 inches) contributes to misregistration. Furthermore, direct imaging eliminates the defects introduced by imperfections (dust, scratches) in the photo-tool that occur during photo-plotting or thereafter during handling and use.

Electrodeposited Photoresist. Recently a company has developed a positive acting, cathodically electrodeposited photoresist. Electrodeposited (ED) photoresists offer an alternative for imaging very fine lines and spacing while using the print and etch process. Lines and spacing at 2 mils have successfully been etched with ED resist. Conductive surfaces are completely and uniformly covered with resist by submerging them in an aqueous, micellular dispersion of the resist. Using a rectifier, the panel is charged to either a negative or positive potential and attracts the polymer micelles in the resist bath. The panels come out of the bath with a clear resist coat; there is no color pigmentation. The resist is non-tacky so phototools can be placed directly on the panel. The elimination of the coversheet, normally found with dry film resists, improves line and space resolution. The image is developed with an aqueous acid that differs from the standard resist developing chemistry.

This ED resist coating has some advantages over dry film photoresists: Dry film will tent over surface imperfections (e.g., pits and scratches) rather than conform to them, which could allow etching chemistry to etch out the underlying copper. Also, dry film is relatively thick (1 mil or greater) compared to ED resist (0.3 to 0.5 mils thick). This makes it more difficult to develop out the channels between closely spaced circuitry. Another useful feature of ED resists is the ability to make landless vias. Dry film tents over holes therby sealing off the hole barrel during etching but it requires a pad, or annular ring, to anchor the film to the surface surrounding the hole. ED resist coats the barrels of holes, as well as the surface, and eliminates the need for a pad (ref. 19).

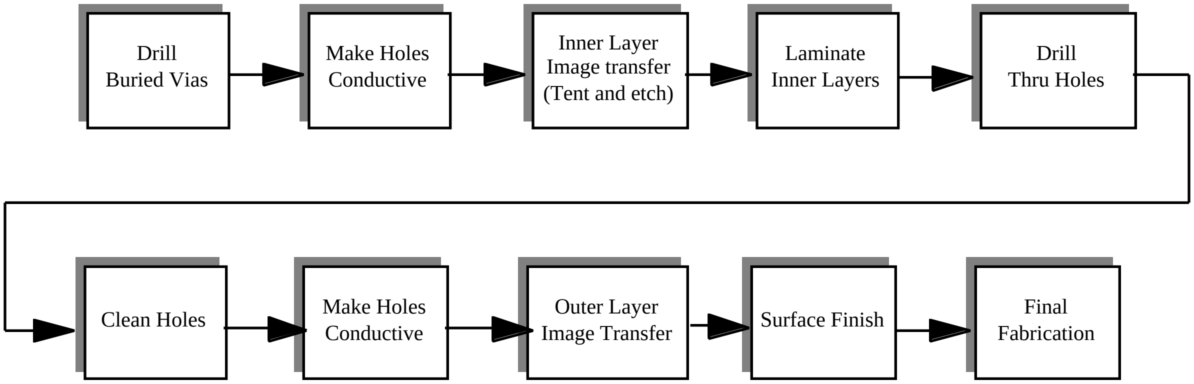
3.2.2.3 Blind/Buried Via Multilayer Manufacturing

These two technologies are specialty type multilayer manufacturing which have been devised to make more efficient use of circuit "real estate." Both methods are considerably more expensive to manufacture and are not recommended as a casual solution to circuit routing problems due to dense layouts. Buried vias are drilled through innerlayers and do not exit to either outer layer. Blind vias start at one surface layer but terminate prior to penetrating all of the layers.

Because of the surface preparation steps required prior to making holes conductive, pre-treated material cannot be used for blind or buried vias.

Buried Vias. The manufacturing process differs in that the innerlayer material must be drilled (Section 3.2.4) and the holes made conductive (Section 3.2.6) prior to exposing and lamination (Section 3.2.3). It is processed as a tent and etch outer layer (Section 3.2.7.1). This is performed for each pair of layers with buried vias. Then, they are then laminated together and afterwards, processed normally starting at drilling.

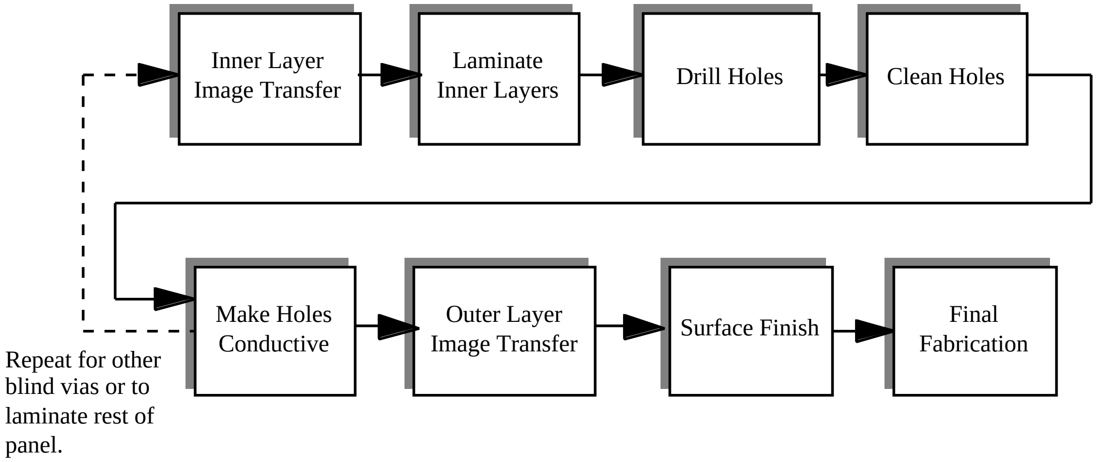
Exhibit 3-7. Process Flow for a Buried Via Processing



Complex sets of buried vias can greatly complicate the manufacturing process. For example, if the buried vias are designed to penetrate more than two layers, multiple or sequential lamination is required and the first four steps in Exhibit 3-7 are repeated one or more times.

Blind Vias. There are two methods for manufacturing blind vias, each with their own advantages and disadvantages. The first is to print, etch, laminate, and drill the innerlayers with the blind vias. After metallizing the holes, the next set of blind vias (or the remaining layers if there are no more blind vias) are laminated to the first assembly. This is also known as “sequential lamination” since the panel goes through multiple laminations for each set of blind vias (Exhibit 3-8). It is a reliable method for plating holes since the vias are plated as through-holes rather than as blind holes, but sequential lamination requires several time-consuming lamination cycles and increases the square footage usage of the metallization line, which increases waste generation.

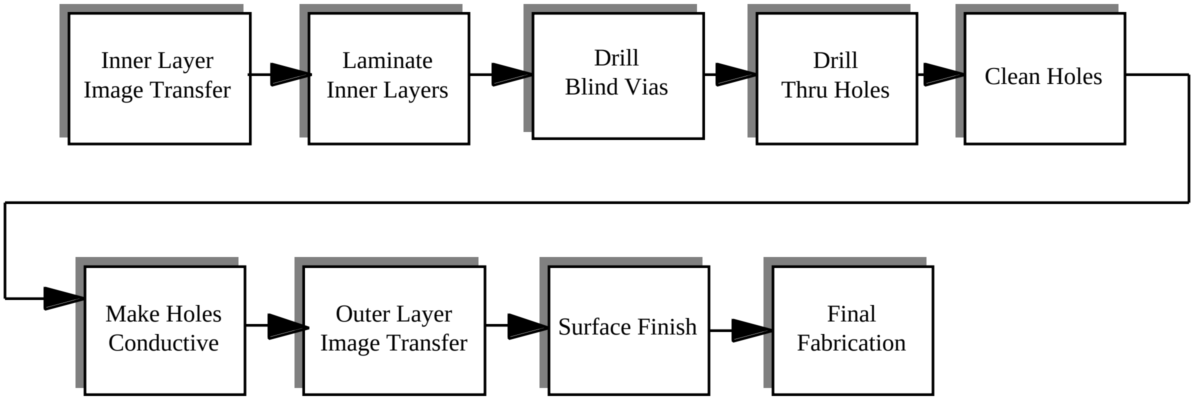
Exhibit 3-8. Blind Via Process Using Sequential Lamination



The alternative method to create blind vias is to use controlled depth drilling (Section 3-9). With this method, all of the innerlayers are laminated in one step, similar to standard multilayer manufacturing. The panels are then drilled with through-holes. Blind vias are drilled with precise controlled depth drilling. The panel is then sent to hole cleaning and the through-holes and vias are made conductive as with the normal multilayer process.

The efficiency of the controlled-depth-drilling method is considerable when compared to the aforementioned sequential lamination method, but process windows in both the drilling and plating steps are quite narrow. To accurately penetrate a panel with CNC drilling equipment, at a precise depth, depends on several factors, including: an intimate knowledge of the internal z-axis position of the layers in the multilayer panel; panel-to-panel and across-panel consistency of the z-axis position of the layers; and the accuracy of the z-axis control of the drilling machine. Plating blind holes is also challenging. Removing trapped air and providing fresh chemistry into the blind hole during the plating time is necessary to prevent voids and thin plating. In short, reject rates are higher with this blind via method.

Exhibit 3-9. Blind Via Process Using Controlled Depth Drilling



3.2.3 Lamination

During the lamination process the thin-core innerlayers are subjected to heat and pressure and compressed into a laminated panel. Sheets of material consisting of glass fibers impregnated with epoxy resin, known as pre-preg or b-stage, are slipped between the layers and bond the layers together. Pre-preg is available in different styles with varying amounts of resin and glass fibers, which allows the manufacturer to control the thickness between layers and to provide the appropriate amount of resin flow between circuitry.

Lamination steps are fairly consistent among manufacturers, although substitute lamination materials are available. All of the materials, including the innerlayers and pre-preg, are tooled to the same registration system and are held in place by tooling pins. Several panels can be pressed together in one set of heavy plates, creating what is known as a "book." Next to each copper outer layer is some sort of protective coversheet. Sheets of aluminum or a thin plastic sheet such as Paco-Thane® and a steel separator plate are used for this purpose. Foreign material must be kept from the copper surface or it will become pressed into the surface of the panel causing pits and dents. Dust and other contaminants can degrade the bondline between copper and the epoxy so cleanliness is essential. ,However, not all manufacturers perform this process in a cleanroom environment.

Copper foil can be purchased that is laminated to an aluminum separator sheet. The sheets are laminated in a clean room environment, which prevents any particle contamination on the copper surface. After the multilayer lamination cycle the aluminum is peeled away, revealing the copper sheet underneath. Commercial products of this nature are readily available (ref. 20).

Kraft paper, other fiber materials, or silicone rubber pads are used when the book is loaded into the press to evenly distribute the pressure and temperature (ref. 21). Modern presses have platens that are enclosed in a vacuum chamber to remove air and volatiles from the panels as the B-stage cures. If any air remains between layers, it will leave an air pocket or bubble that may lead to delamination of the panel. Another benefit of vacuum lamination is that less pressure is required, which reduces misregistration from the panels skewing under excessive force. Press cycles are usually computer-controlled. The specific cycle is dictated by the substrate employed; for FR-4, temperatures of 350°F (176°C) and pressures of 150 to 350 psi are common. The entire cycle from heating, curing, and cooling can take 2-3 hours for FR4 type material and as long as 5-6 hours with polyimide.

The heavy plates, steel separator plates, and silicone or rubber press pads are items that can be reused as long as they are performing satisfactorily. The Paco-Thane® and Kraft paper are discarded after one use. If aluminum sheets are used, they may be collected and sold for scrap or, depending on thickness, used in the drilling room as entry material. Coolant water used by the press is either discharged or reused.

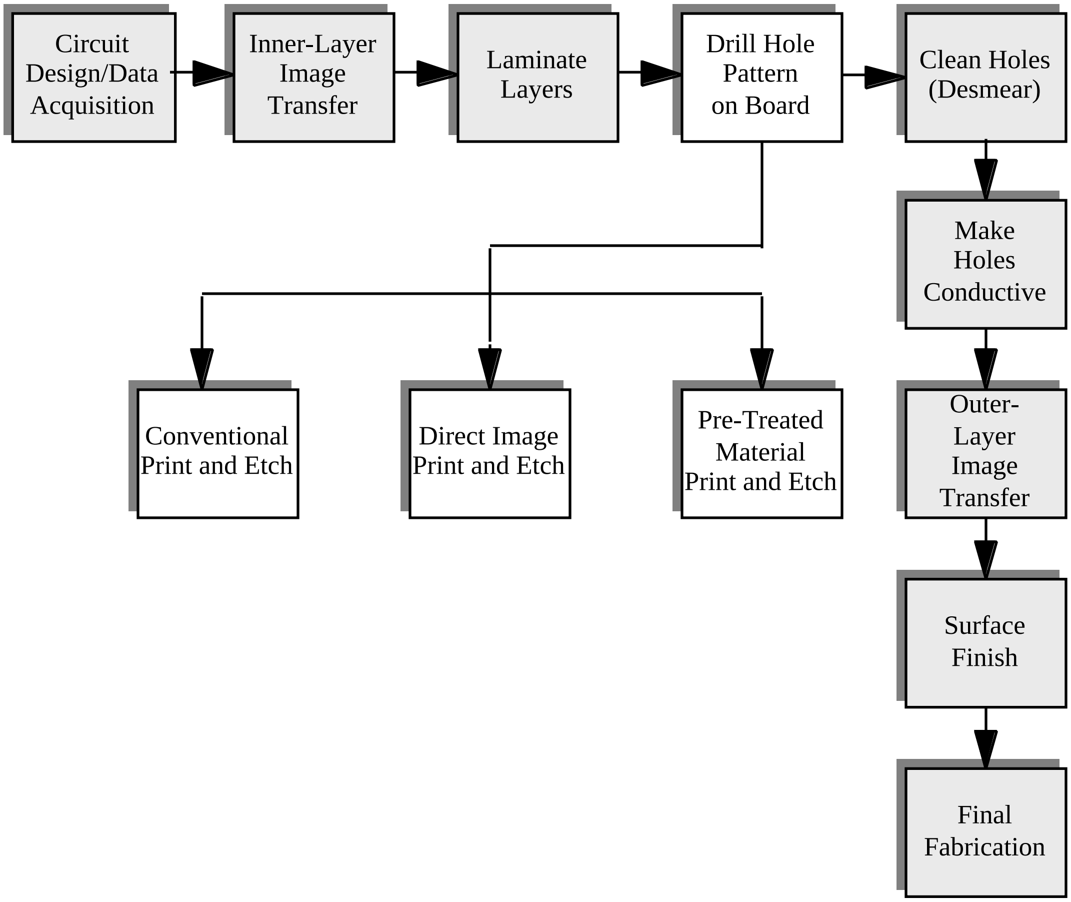
3.2.4 Drilling

Holes are drilled through the PWB to interconnect circuitry on different layers and to allow the insertion of components (Exhibit 3-10). The etched innerlayer pattern will extend to the barrel of the hole and therefore will be interconnected with the other layers when the hole barrel is made conductive in a later step. Most drilling is performed with computer numerical control (CNC) equipment, but as hole sizes less than .012" have become more common, other methods of making small holes are increasing in popularity. Two alternate methods are punching and laser processing. Entry and back-up materials vary between manufacturers, since there are several alternatives. These options are discussed below.

Dull drill bits can be sent for resharpening 2 to 4 times before being discarded. The backup material can be flipped over and used a total of 2 times before being discarded. Paper types of entry material are disposed of, while aluminum entry is collected and sold. The waste copper debris and fiberglass dust that is drilled or punched out of the material is carried by vacuum away from the machinery and work area and into a holding tank.

By using new and stronger materials, drill bits can drill 200 to 1,000 times more holes as ordinary bits. Punching holes eliminates the hole cleaning process and the need for entry material. Entry material and drill bits are unnecessary to laser process holes.

Exhibit 3-10. Drill Holes Process Step



3.2.4.1 Conventional CNC Drilling

Mechanical drilling is a mature technology that has reliably produced what have now become relatively large holes. As hole sizes have gotten smaller, mechanical drilling limitations, such as drill bit diameter and aspect ratios have emerged (ref. 22). Also, where drilling equipment technology surpassed that of drill bit metallurgical technology 10 years ago, that situation has now reversed. Older and poorly maintained equipment may not be able to drill small holes. One reason is the inability of the spindle to generate high enough rotational speed. Another is that drill runout and Z-axis slop are disproportionately large for these bits (ref. 25). Despite the smaller hole difficulties, mechanical drilling is how the majority of manufacturers create holes. High-end CNC drilling equipment has “lights out” features which allow automatic loading and unloading, broken bit detection, and tool cartridges that can hold hundreds of tools for automatic replacement at programmed intervals.

Entry Material. The top layer that the drill enters before PWBs are drilled is called “entry material.” The PWBs are drilled in stacks that consist of a sheet of entry material, one or more circuit panels, and back-up or exit material. Entry material is required to reduce or eliminate exit burring and to reduce drill wander, which is the tendency of the drill to briefly skate on the surface before penetrating. A variety of entry materials exist, the most common being paper-phenolic (10 to 24 mils thick), paper-melamine (10 to 24 mils thick), aluminum (7 to 15 mils thick), and an aluminum-clad material consisting of a phenolic, melamine, simple paper, cellulose, or other core. Some entry material is specifically made for small-hole drilling. One product consists of 1.5 mils of aluminum laminated to a 3.5 mil cellulose core. The alloy’s softness allows for easy and accurate penetration while the cellulose softens the impact of the drill bit (ref. 25). Entry material is discarded for recycle or disposal after use.

Back-up Material. The drill bit terminates its downward stroke with the point penetrating the back-up material in order to complete the drilling of the bottom panel in the stack. Back-up materials are generally 0.062 or 0.093

inches thick. Common materials are pressed wood products (pulp or fiber), paper-phenolic-clad with a wood product core, or aluminum-clad with a wood product core. Since the drill penetrates only halfway through back-up material, it is generally flipped over and used a second time before being discarded.

Drill Bits. Drill bit makers are now using materials such as diamond tipped bits and carbide alloys, which are 90% stronger than the older bits, to drill the smaller holes now being called out. Bits as small as 2 mils have been produced. Ordinary drill bits become unacceptably dull after 1,000 to 5,000 hits, but diamond tipped bits purportedly can drill one million holes if properly used. Drills are usually resharpened 2 to 4 times before being discarded. It is estimated that 70% of holes drilled are drilled with resharpened bits (ref. 22).

3.2.4.2 Punching

Punch presses have been used for years to make holes by the millions for paper-phenolic PWBs used in consumer items. It was discovered that punching could be used as a complement to the process of making high-density multilayer boards. It solves the mechanical drilling problem with small holes and is less expensive than laser processing. Punching is generally restricted to making small via holes on thin substrates (0.005” to 0.020”). Advantages to punching include:

- Better hole quality
- No hole cleaning process required
- No need for entry or backup materials (ref. 23)

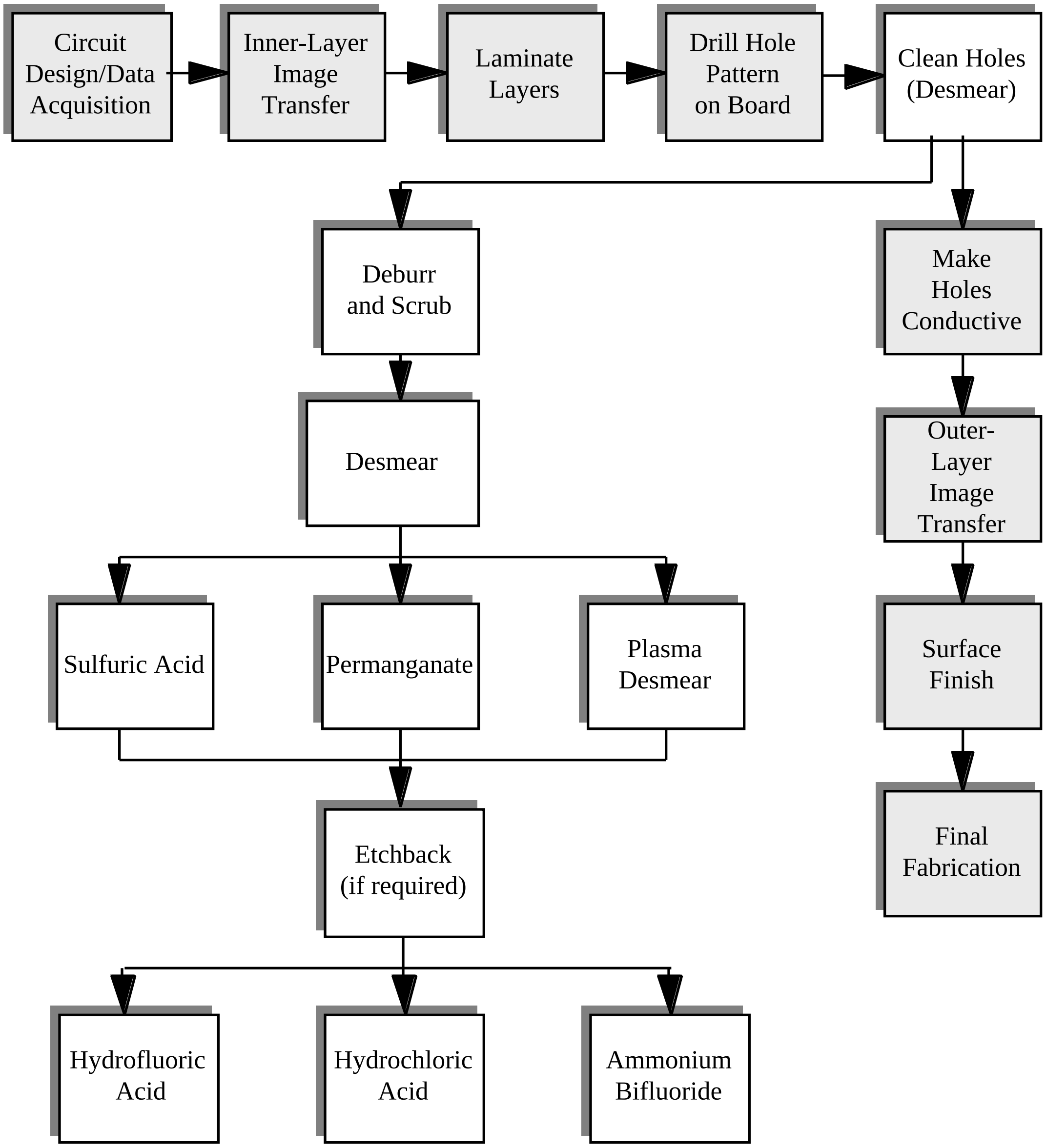
3.2.4.3 Laser Processing

A few technologies exist for making holes using lasers. One company manufactures a unit that can drill 4 mil holes and smaller in copper-clad and glass reinforced materials. Using a Nd:YAG laser, this unit can create up to 1,200 vias per minute (ref. 24). Another company uses a CO_2 multimode laser that is capable of drilling FR4, BT resins, and PTFE type materials at up to 1,200 holes per minute (ref. 23). A dual laser type system has also been developed. A computer controls the alternating ruby laser to drill through copper and CO_2 laser to clean out the epoxy (ref. 25).

3.2.5 Hole Cleaning

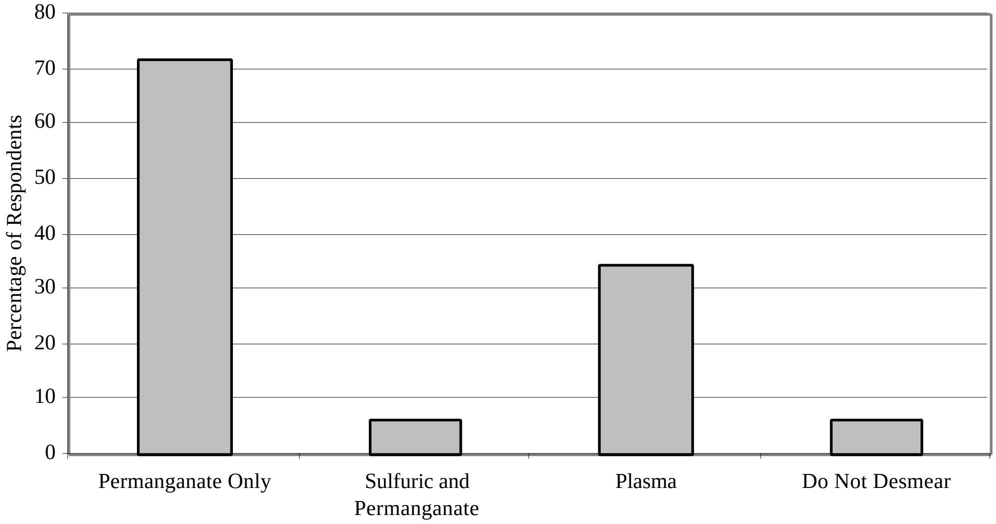
Hole cleaning generally refers to a process called desmear and/or the closely related process of etchback. Desmear removes the melted resin smear that results from the friction of the drill bit cutting through the material. If the smear covers the copper that extends to the barrel of the hole, it would prevent interconnection between it and the subsequently metallized hole. During etchback, in addition to removing resin smear, glass fibers are etched. The result is that the copper on the innerlayers protrudes out into the barrel of the hole. This allows for what is known as a “3-point” connection after metallization. Most of the demand for etchback stems from military specifications. Exhibit 3-11 summarizes methods of hole cleaning and Exhibit 3-12 displays the survey results for this process step. Detailed respondent data are found in Appendix A.

Exhibit 3-11. Clean Holes Process Step



Deburring and scrubbing are processes performed immediately before or after desmear or etchback. During drilling, copper burrs may be raised on both sides of the panel by the action of the drill entering and exiting the material. The burrs are sanded smooth on a deburring machine, which consists of a sanding wheel and a conveyor. In wet deburrers, copper dust is carried off in a waste stream. Dry machines usually are outfitted with vacuum units. Deburring is more correctly considered a surface preparation step rather than hole cleaning. Scrubbing is performed as a surface preparation step prior to electroless copper (and during other stages, such as before solder mask). Scrubbing may be performed similarly to deburring, except a much less aggressive surface abrasion occurs. Pumice or aluminum oxide scrubbers, which direct a high-pressure spray of abrasive particles at the PWB, are also used for surface preparation.

Exhibit 3-12. Distribution of Desmear Methods



3.2.5.1 Desmear

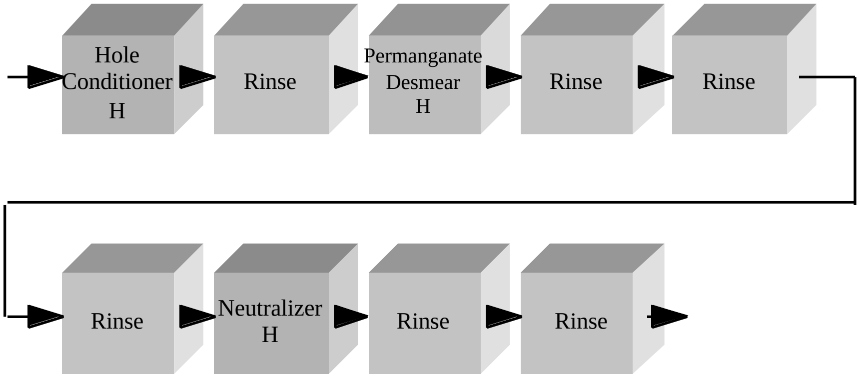
During drilling, drill bits become heated resulting in the melting and smearing of the epoxy-resin base material across the inner-layer copper surfaces within the hole barrel to which subsequent through-hole plating must connect. If not corrected the smear would constitute a dielectric layer between the inner-layer copper surfaces and the plated copper, and the circuit would be defective.

The desmear process is often grouped and sometimes confused with etchback because similar or identical chemistries can be used to perform both functions. Desmear is simply the removal of smeared epoxy-resin by-products from copper surfaces within the hole barrel to facilitate a connection with plated copper. Etchback is the significant removal of epoxy-resin (including smear) and glass fiber from the hole barrel in an effort to expose a greater copper surface and enhance the interconnection with the plating. The improvement and reliability of desmear chemistry has made etchback unnecessary.

Currently the most widely used chemistry is sodium or potassium permanganate when significant etchback is not required or specified. Permanganate-based systems remove a thin layer of epoxy-resin (typically less than 1 mil) and smear and are quite adequate for desmear-only applications.

The permanganate desmear is a three step process consisting of epoxy sensitizing, permanganate etch, and neutralizing (Exhibit 3-13). The sensitizer swells the epoxy and facilitates the subsequent removal. The permanganate solution etches the epoxy by oxidizing the covalent bonds within the polymer network. This bath is generally heated to 160°F or more with dwell times from 5 to 20 minutes. The neutralizing bath removes permanganate from the oxidized hole and panel surface. If the neutralizing bath is not used, voiding and poor adhesion can result during the metallizing of the holes.

Exhibit 3-13. Permanganate Desmear Process



One problem with the permanganate solution is that alkalinity at high temperatures causes the permanganate to decompose to manganate. As manganese dioxide builds in the bath, it accelerates the reaction of manganate to manganese dioxide until a black sludge (MnO_2) is formed that settles to the bottom of the tank. The epoxy etch rate is steadily reduced until the solution becomes unusable (ref. 26). Frequent analysis and additions of permanganate are necessary to counter this degradation in the etching rate. Electrolytic regeneration units are available to anodically re-oxidize the manganate ion back to permanganate (MnO_{4-}). These units consist of a porous pot, cathode, anode, and rectifier.

3.2.5.2 Etchback

During etchback, in addition to smear removal, the glass fibers themselves are etched back from the hole wall. The goal is to remove about 0.5 mil from the top and bottom of the innerlayer copper so that it will protrude out from the hole wall. This creates three surfaces (also known as a three-point connection) for the copper to bond to during the making holes conductive step. Glass etchants include hydrochloric acid, ammonium bifluoride, and hydrofluoric acid (rarely used). Etchback with plasma can be achieved by varying the type and amount of reactive gases.

3.2.5.3 Plasma Desmear/Etchback

Using plasma to desmear eliminates an entire wet process line, reduces chemical disposal costs, and reduces water usage and treatment costs. Labor costs are lowered as well since there are no baths to maintain. With plasma etching the panels are placed in a vacuum chamber, and gas is introduced and converted to reactive plasma by a power supply. The plasma reacts at the panel surface and volatile by-products (resin smear) are removed by the vacuum pump.

The addition of relatively inert gases, such as nitrogen or argon, stabilizes the plasma and controls the rate of ionization. Reactive oxygen species oxidize organic contaminants on the surface, creating volatile species that are pumped away. Etch rates are increased by providing more reactive species in the form of fluorine such as F_2, CF_4, or CHF_2.

3.2.5.4 Desmear/Etchback Alternatives

There are several desmear/etchback process alternatives. The applications and advantages/disadvantages of each are discussed in this section and summarized in Exhibit 3-14.

Exhibit 3-14. Desmear/Etchback Methods

Process	Applications	Advantages	Disadvantages
Permanganate	Smear removal	Better control.	Rapid chemical decomposition. Frequent bath analysis and maintenance
Concentrated Sulfuric Acid	Smear removal	Ease of operation.	Lack of control. Operator safety concerns with concentrated chemicals. Generally requires desmear.
Plate Forward	4-layer power/ ground plane multilayers	More easily controlled than etchback. Smoother holes.	Limited application.
Plasma Desmear	Smear removal/ etchback	Eliminates chemical line and waste treatment costs. No bath maintenance.	High capital cost. Uneven etch rate across panel.

Concentrated Sulfuric Acid. Concentrated sulfuric acid (usually 93%) is still in use, but generally requires a permanganate step for final hole cleaning, making it a significantly longer and more expensive process than permanganate alone. Handling the concentrated acid and operation of the line has proved to be a problem in many shops. The amount of epoxy-resin removed is controlled by the dwell time in the sulfuric bath, which must be precisely monitored. However, sulfuric acid does not etch glass and a second step is required to perform the glass fiber etch.

Plate Forward. This process has a narrow field of use (4-layer boards with ground/voltage plane innerlayers), but it represents a large portion of the multilayer market. To ensure the plating connection to the metallized hole surface is reliable, panels are electroplated prior to electroless plating. In order to accomplish this, the innerlayer planes are connected to the surface foil of the panel, which in turn is connected to the cathode bar. This plating step will extend the copper from the hole edge out into the barrel of the hole.

Plating forward is more easily controlled than etchback and leaves the hole barrels relatively smooth, whereas with etchback, hole interiors are roughened at an inconsistent rate. This process does not eliminate the desmear process (ref. 27).

Condensed Desmear/Metallization Process. A method exists to combine desmear and two processes from the plating through holes (PTH) electroless line into a single step. This process, which consists of a single process tank and associated rinse tanks, will neutralize the permanganate, clean/condition the hole walls, and microetch the surface. The reduction in process tanks lowers chemical maintenance costs, labor, and water usage, and simplifies the treatment of wastes. Excellent results have been reported from Asian and European manufacturers employing this technique (ref. 28).

3.2.6 Making Holes Conductive

To provide for the intended interconnection between layers, the holes must be coated or plated with a conductive substance. The PWB substrate itself is not conductive, so a non-electrolytic deposition method is required. Afterwards, electroplating is performed to plate the copper to the specified thickness.

Until recently, electroless copper has been used almost exclusively to metallize the holes. Direct metallization (DM) processes were introduced in the 1970s, but reports of higher costs and inconsistent quality kept manufacturers from experimenting with an unproven process (ref. 29). New interest in alternatives to electroless copper was ignited in 1992, when OSHA amended a standard for occupational exposure to formaldehyde, a probable carcinogen. With few exceptions, electroless copper uses formaldehyde as the reducing agent.

Alternatives to electroless copper now include palladium-based systems, carbon/graphite-based systems, electroless nickel, conductive polymer, and non-formaldehyde-based electroless copper. Based on the survey results, however, it is apparent that the electroless copper process is still entrenched as the predominant method of making holes conductive, although its use appears to be declining. Seventy-seven percent of all respondents reported using electroless copper for through-hole metallization, with the remainder split evenly among graphite-, palladium-, and carbon-based systems. One user reported testing an electroless nickel-based system on a small percentage of their product.

Design for the Environment (DfE) Printed Wiring Board Project participants are encouraged by this increase in the use of alternative MHC technologies, especially because it occurred while awareness of the alternatives was being increased by the MHC project. Additional increases in alternative MHC technology use can now be expected because the CTSA results were presented in seven seminars around the United States in 1997, and because the final MHC CTSA will be published in summer 1998.

The making holes conductive process step alternatives are shown in Exhibit 3-15. The advantages and disadvantages of the alternatives are discussed in the following section and summarized in Exhibit 3-16. Survey data relative to this process step are found in Appendix A.

Exhibit 3-15. Make Holes Conductive

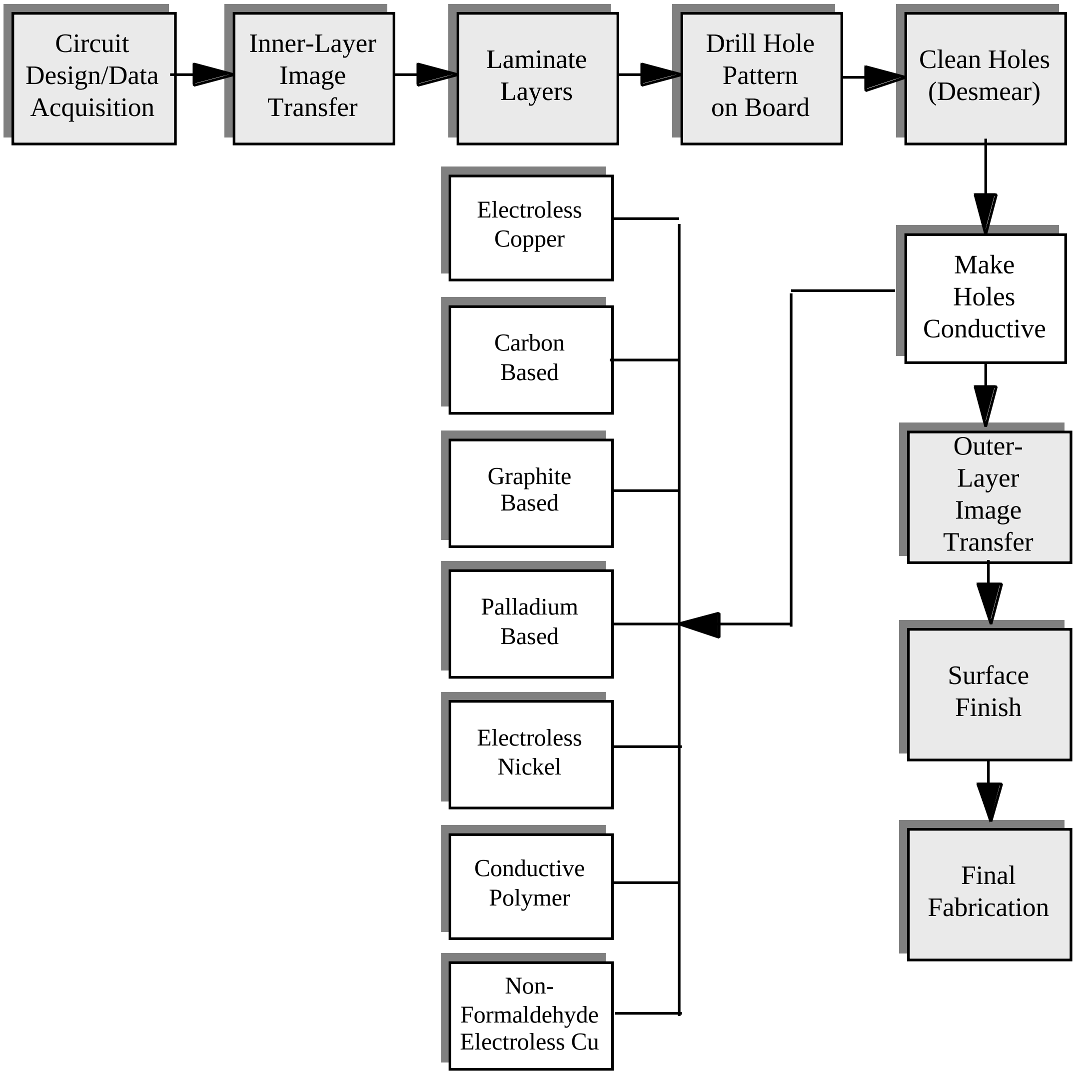


Exhibit 3-16. Comparison of Primary Alternatives for Making Holes Conductive

Process	Advantages	Disadvantages	Waste Generated
Electroless Copper	30+ years of reliable use.	Inherently unstable. EDTA complicates waste treatment.	Copper from microetchant Complexed copper from electroless bath. Eight process baths.
Carbon-based	Short application time. No formaldehyde. Less water consumption than electroless copper.	High capital costs.	Copper from microetchant. Five process tanks.
Graphite-based	Short application time. No formaldehyde. Conveyorized or vertical processing. Low water consumption and treatment.	None Identified.	Copper from microetchant. Three process tanks. Four if anti-tarnish used.
Palladium-based	No formaldehyde.	None Identified.	Copper from microetchant. Ten process tanks including desmear.
Electroless Nickel	No formaldehyde. No microetchant. Conveyorized or vertical processing.	None Identified.	Six process tanks including desmear.

3.2.6.1 Electroless Copper

Although electroless copper has been successfully used for more than three decades, limits on operator exposure to formaldehyde and difficulties in removing the electroless copper from the waste stream caused manufacturers to seek alternatives. Among the deficiencies are (ref. 30):

- Use of formaldehyde as reducing agent.
- The process is inherently unstable, requiring stabilizing additives to avoid copper precipitation.
- Environmentally undesirable complexing agents, such as EDTA, are used.
- The large number of process and rinse tanks causes high water consumption and energy use.

The electroless copper process consists of four basic operations: cleaning, activation, acceleration, and deposition (Exhibit 3-17). An anti-tarnish bath is common after deposition. Virtually all facilities purchase a series of proprietary chemistries from a single vendor that are used as the ingredients for the several process baths in the electroless copper process line. Only the micro-etch, its associated sulfuric dip, and the anti-tarnish baths are likely to be non-proprietary chemistries.

Cleaning. The cleaning segment begins with a cleaner-conditioner designed to remove organics and condition (in this case swell) the hole barrels for the subsequent uptake of catalyst, followed by a microetch step. The cleaner-conditioners are typically proprietary formulations, and mostly consist of common alkaline solutions.

A microetch step can be found on the electroless line, oxide line, pattern plate line and with chemical cleaning if that is the cleaning method used. Three chemistry alternatives are available. Sulfuric acid-hydrogen peroxide (consisting of 5% sulfuric acid and 1% to 3% peroxide) is most common, followed by sulfuric acid-potassium (or sodium) persulfate (5% sulfuric, 8 to 16 ounces/ gallon persulfate), and ammonium persulfate. In each case, the microetch bath is followed by a sulfuric acid dip, which serves to remove any remaining oxidizer. About 40 microinches of copper are etched for the making holes conductive process. Based on a 3-4 ounce copper carrying capacity, approximately 0.0183 gallons of microetch are used per square foot of product run. This figure does not include any solution that may be dragged out when the panels are moved to the next tank. The sulfuric-peroxide alternative has some attractive waste treatment and performance features (ref. 31):

- No spent etchant disposal. The etchant is replenished as it is used, and copper is removed with a recovery unit in the form of copper sulfate crystals. These crystals form when the solution is cooled to room temperature or lower. Smaller shops may use a batch treatment where the solution is pumped to another tank to cool and crystallize. After removing the copper crystals, the solution can be transferred back to the process line and reused.

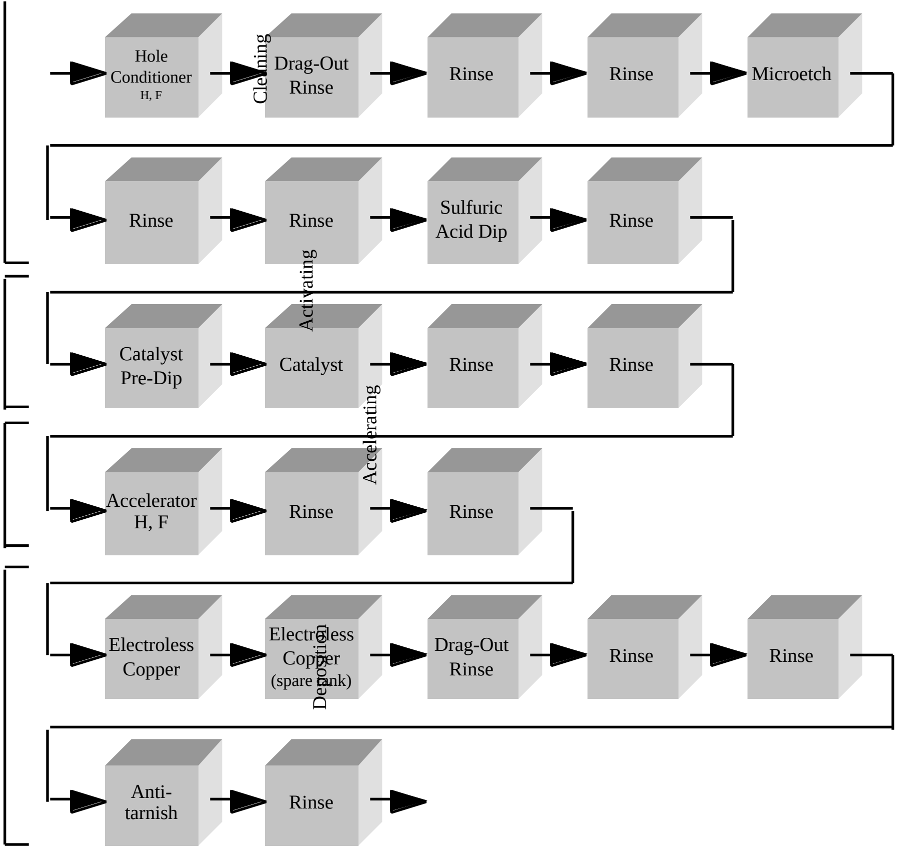
- Constant etching rate. The etching rate is dependent on temperature and hydrogen peroxide concentration, not the copper concentration.
- Simple waste treatment. No chelators are present in sulfuric-peroxide microetchants.
- A high copper capacity of 3 to 4 ounces/gallon.
- Efficient copper recovery. Copper sulfate recovery is usually 90-95% efficient.

Persulfate microetchants must be treated in-house or shipped to a licensed disposal facility. The etching rate is difficult to control since it declines as panels are processed and copper builds in the solution. Ammonium persulfate is uncommon due to high waste treatment costs.

Activation and Acceleration. Activation, through use of a catalyst, consists of two process tanks. A pre-dip, for the drag-in protection of the expensive activation (also called catalyst) bath, usually contains hydrochloric acid and possibly tin or sodium chloride. The activation bath itself consists of hydrochloric acid, tin chloride, and palladium chloride. The Sn^{+2} ion reduces the Pd^{+2} to Pd, which is deposited on the panel. The remaining Sn^{+2} and Sn^{+4} are selectively removed from the hole barrels by the accelerator (also called the post-activator). Fluoboric acid is a common accelerator, as is sulfuric acid with hydrazine.

Copper Deposition. Electroless copper baths can be divided into two types: heavy deposition baths (designed to produce 75 to 125 micro-inches of copper) and light deposition baths (20 to 40 micro-inches). Light deposition must be followed immediately by electrolytic copper plating. The more common heavy deposition can survive the outer layer imaging process, and copper electroplating occurs thereafter. The main constituents of the electroless copper chemistry are sodium hydroxide, formaldehyde, EDTA (or other chelator), and a copper salt. In the complex reaction, catalyzed by palladium, formaldehyde reduces the copper ion to metallic copper. Formaldehyde (which is oxidized), sodium hydroxide (which is broken down), and copper (which is deposited) must be replenished frequently.

Exhibit 3-17. Typical Electroless Copper Plating Line



Most heavy deposition baths have automatic replenishment schemes based on in-tank colorimeters. Light deposition formulations may be controlled by analysis. Formaldehyde is present in light deposition baths in a concentration of 3 to 5 grams/liter and as high as 10 grams/liter in heavy deposition baths.

When light deposition is applied, the next process step must be electrolytic copper plate. This is either a full panel plate (the typical 1 mil is plated in the holes and on the surface) or a “flash” panel plate, designed only to add enough copper to the hole barrels to survive the imaging process. Flash-plated panels return to copper electroplating after imaging to be plated up to the required thickness. This double plating step has made heavy deposition the more common electroless copper process.

Process Waste Streams. The electroless copper line typically contributes a significant percentage of a PWB shop’s overall waste volume. Water use is high due to the critical rinsing required between nearly all of the process steps. Copper is introduced into the wastewater stream due to drag-out from the cleaner-conditioner, micro-etch, sulfuric, accelerator, and deposition baths. Much of this copper is complexed with EDTA and requires special waste treatment considerations. Furthermore, waste process fluid generation is high. Micro-etch baths are exhausted when 2 to 4 ounces/gallon of copper is dissolved, and this bath life is usually measured in days. While the electroless copper bath is relatively long-lived (usually several weeks or months), a considerable bailout stream (including formaldehyde) is generated (several gallons of concentrated bath chemistry per day in production shops). This waste must either be treated in-house or shipped off-site, which adds another cost to using electroless copper.

3.2.6.2 Carbon-based Alternative

Black Hole® is a carbon-black dispersion method for metallizing holes. The advantages of this type of process versus conventional electroless plating are:

- Production rates are higher for Black Hole® since it is applied in about half the time required for electroless copper
- Formaldehyde is not a constituent of any of the process formulations
- Copper is dragged into the wastewater stream from only the microetch bath
- Overall water use is reduced

Although it has become more common in larger shops, this process is still an uncommon choice for small shops with sales of less than $5,000,000/year, which account for the majority of PWB facilities in the country. Capital costs for the Black Hole® conveyorized process line are much higher than for an electroless copper tank line, and represent a barrier of entry for small shops. Payback from production timesaving and waste reduction is likely to be quite long for small manufacturers.

After being cleaned and conditioned, non-conductive surfaces absorb the carbon deposits. The carbon deposition step is performed twice to ensure a good conductive surface. A microetching step follows to remove any carbon deposited on copper surfaces. At this point the panels can proceed to imaging or be copper plated. Without copper plating, the panels cannot be brush or pumiced scrubbed prior to exposing because carbon particles near the surface of the panel may be brushed off (ref. 30).

3.2.6.3 Graphite-based Alternative

The available graphite-based processes are Shadow® and Shipley Graphite 2000. In these cases, graphite particles suspended in a colloid are dispersed onto the surface and act as conductive pathway for electroplating. The four specific process steps for the Shadow® process are (ref. 32):

- Cleaning/conditioning
- Graphite (Shadow®) application
- Microetch
- Anti-tarnish (optional)

Graphite application can be done on conveyorized equipment or with an immersion (vertical) process. One pass through the graphite application step is sufficient to prepare holes for copper deposition. The vendor claims to be able to run this process from cleaning to lamination in less than 10 minutes (ref. 33). Graphite particles adhere well to the laminate surfaces and can tolerate mechanical scrubbing. The micro-etch solution is usually based on persulfate. Some facilities do not use anti-tarnish coatings on the copper surface if the dry film lamination process is done in-line, immediately following graphite application. Shadow® users include, buried and micro-via manufacturers with large layer counts up to 48 layers. Shadow® users process from 5,000 to 1,500,000 surface square feet per month.

Cleaning and Conditioning. Panels can be cleaned using conventional methods or in the conveyor line. Cleaning solutions used are similar to systems employed for electroless copper. As noted above, the cleaner-conditioner step is designed to remove organics and condition hole barrels for the subsequent uptake of graphite.

Graphite. The graphite is applied in the form of colloidal graphite. The particles are suspended in a slightly caustic colloidal solution (pH = 9). In the conveyorized process, surface activation is rapid, and solution that runs off the boards can be reused. In an immersion (vertical) setup, conventional process tanks are used to apply graphite. In this case, some efficiency is lost, but existing equipment can be used. Following the graphite application, the panels must be dried to dry the graphite on dielectric surfaces. This step is critical for obtaining good copper adhesion during subsequent copper plating. Drying is done with air knives, followed by a short bake (140 to 160^{o}F). The air knives used are run at close to room temperature; their principal function is to remove excess colloid from the surface and hole walls. No rinse is required after this drying step.

Microetch. Microetch follows graphite application. (See the Cleaning section under 3.2.6.2 Electroless Copper for a more detailed explanation of microetchants and available chemistries.) The drying step does a good job at removing colloid material from the field area of the panel. However, simply drying the solution does not remove graphite particles from exposed copper. The vendor recommends spraying a persulfate solution onto the panel surface. A filter below the panels prevents graphite from entering waste streams.

Anti-tarnish. Following microetch, the exposed copper is subject to oxidation. Because of this, an optional "anti-tarnish" step can be done. The system vendor recommends using a benzothiadzole-containing solution to protect copper surfaces. Some PWB manufacturers skip this step, in which case it is recommended that image transfer films be laminated onto the panels directly following micro-etch. Eliminating the anti-tarnish step should reduce chemical use, cost, waste, and cycle time. Effects on reliability were not reported but some commercial vendors use this approach (ref. 34).

Process Waste Streams. The quantity of wastewater produced by a typical horizontal conveyorized graphite application system is less than 5 gallons/minute. Also, wastewater is only produced when the system is running, rather than constantly, as in the rinse tanks used for electroless copper plating. In short, the graphite system seems to reduce both waste streams and costs from PWB manufacturing. There are five principal environmental benefits from using the graphite process instead of electroless copper. These include:

- Reduction in chelated copper and metal waste
- Elimination of formaldehyde
- Reduced water use
- Reduced treatment chemical use
- Reduced sludge disposal

3.2.6.4 Palladium-based Alternatives

Palladium-based alternatives offer the common advantages of the absence of formaldehyde, reduction in water usage, and the reduction in wastewater generated from the process. These alternatives can also be run with conveyorized equipment to increase throughput and lower costs. The panels typically are run through a desmear process prior to starting the palladium line.

The activator in these systems is palladium/tin. The accelerator removes stannous tin (Sn^{+2}) or reduces it to a metallic form (Sn). To improve conductivity and speed up the metallization of the hole, some systems have modified the acceleration step so that copper is deposited with the palladium, taking the place of the tin (ref. 30). A manufacturer has invented a modified palladium process called Crimson®, which has a conversion step after the activator. The palladium is changed to palladium sulfide, which is claimed to be more conductive for subsequent electrolytic copper plating (ref. 35).

Cleaner/Conditioner. During this "sensitizing" step, the holes are cleaned and a charged polymeric material is applied to the inside dielectric surface of holes. This charged material then receives a catalyst during subsequent processing. Chemical use and wastewater produced in the cleaning step of the palladium-based process is similar to volumes used for the carbon- and graphite-based processes. However, each step must be followed by a rigorous rinse to prevent contamination of the following steps.

Microetch. Microetch, which is performed using hydrogen peroxide (H_2O_2) and sulfuric acid (H_2SO_4), removes excess palladium sulfide from exposed copper surfaces without oxidizing the copper. This step enhances adhesion between exposed copper and electroplated copper added later, without degrading adhesion between laminate materials and plated copper. (See the Cleaning section under 3.2.6.2 Electroless Copper for a more detailed explanation of microetchants and available chemistries.)

Pre-dip. A base salt version of the catalyst (which does not contain catalyst metal) is applied to the panels.

Activator. After pre-dip, the catalyst (activator) is applied. In this case, the catalyst is palladium/tin in a colloidal solution. The catalyst adheres well to glass/epoxy laminates.

Accelerator. After the activator step, panels are rinsed with a caustic soda (accelerator or enhancer). The accelerator removes stannous tin (Sn^{+2}) or reduces it to a metallic form (Sn).

Acid Dip. The panels receive an acid dip and a final rinse, and are dried for lamination.

Process Waste Streams. There are two principal process waste stream considerations: first, formaldehyde is completely eliminated from the process of making holes conductive; and second, the amount of water used (and wastewater produced) is reduced when compared to conventional electroless plating. According to the manufacturer of one palladium-based process, the cost of this process is competitive with electroless copper plating.

3.2.6.5 Electroless Nickel

Ultra-Plate® 300 is a commercial metallization process that plates an electroless nickel deposit. This process does not use microetch, accelerator, or formaldehyde. Panels can be processed vertically or horizontally on conveyorized systems. This flexibility reduces cost barriers for converting since existing PTH equipment can be used. Fewer process tanks also reduce chemical usage, wastewater generation, and process time. With the Ultra-Plate® 300 process, the panels are sent to exposing after the palladium activator, and then are returned for selective electroless nickel. Subsequently, an electrolytic copper bath is used to plate through the holes and pattern plate the circuit.

Neutralizer/Conditioner. This mildly acidic solution prepares the hole wall surface for subsequent steps and acts as a neutralizer for the prior alkaline permanganate process tank.

Sensitizer/Activator. A 2-step process in which a palladium activator is deposited onto sensitized substrate areas. The sensitizer promotes the absorption of the catalyst onto the hole wall surface.

At this point, the panels are laminated with resist, exposed, and developed. The panel surface can be scrubbed or prepared as normal without detrimental effect.

Acid Cleaner. An acid copper cleaner is used to remove any residuals from the resist developing step.

Electroless Nickel. Electroless deposition is more rapidly initiated on palladium activated dielectric surfaces than on copper. A very conductive, high purity, thin layer of nickel is deposited on the hole walls that provides a low resistance path for subsequent electrolytic copper plating.

The electroless nickel process incorporates some steps from both the making holes conductive and outer layer image transfer use clusters. Since the circuit image is already pattern plated at the end of electroless nickel sequence, the process picks up at pattern plate etch resist in section 3.2.7.2.

Process Waste Streams. There are a number of items that impact the process waste stream when using electroless nickel. Among them are:

- Elimination of strong chelates
- Elimination of formaldehyde and cyanides
- Elimination of copper microetch
- Elimination of accelerator
- Reduced water use

- Reduced treatment costs

3.2.6.6 Conductive Polymer

Conductive polymers have been commercially available for years, but only one (polypyrrole) has been adopted as an alternative in making holes conductive. Polypyrrole, which was initially used in Europe, is very suitable for horizontal, conveyorized application. The conductive polymer builds on the standard permanganate desmear chemistry. As epoxy smear is removed from the holes, insoluble manganese dioxide is formed. The board is treated with a solution of pyrrole monomer, which is oxidized by the manganese dioxide to form the conductive polymer polypyrrole. The manganese dioxide is reduced to soluble manganese salts and is washed off. The full process line includes a microetch, cleaner/conditioner, catalyst, conductive polymer, and microetch, followed by a copper electroplate (ref. 35).

3.2.6.7 Non-Formaldehyde-Based Electroless Copper

At least two formaldehyde-free electroless copper systems exist. The first uses the standard electroless line with hypophosphite as the reducing agent in place of formaldehyde. The copper deposition is run in two modes: electrolessly as normal, then, while in the same tank, current is turned on to continue the copper deposition. Afterwards, the panels pass to an acid copper electroplating tank to complete the process.

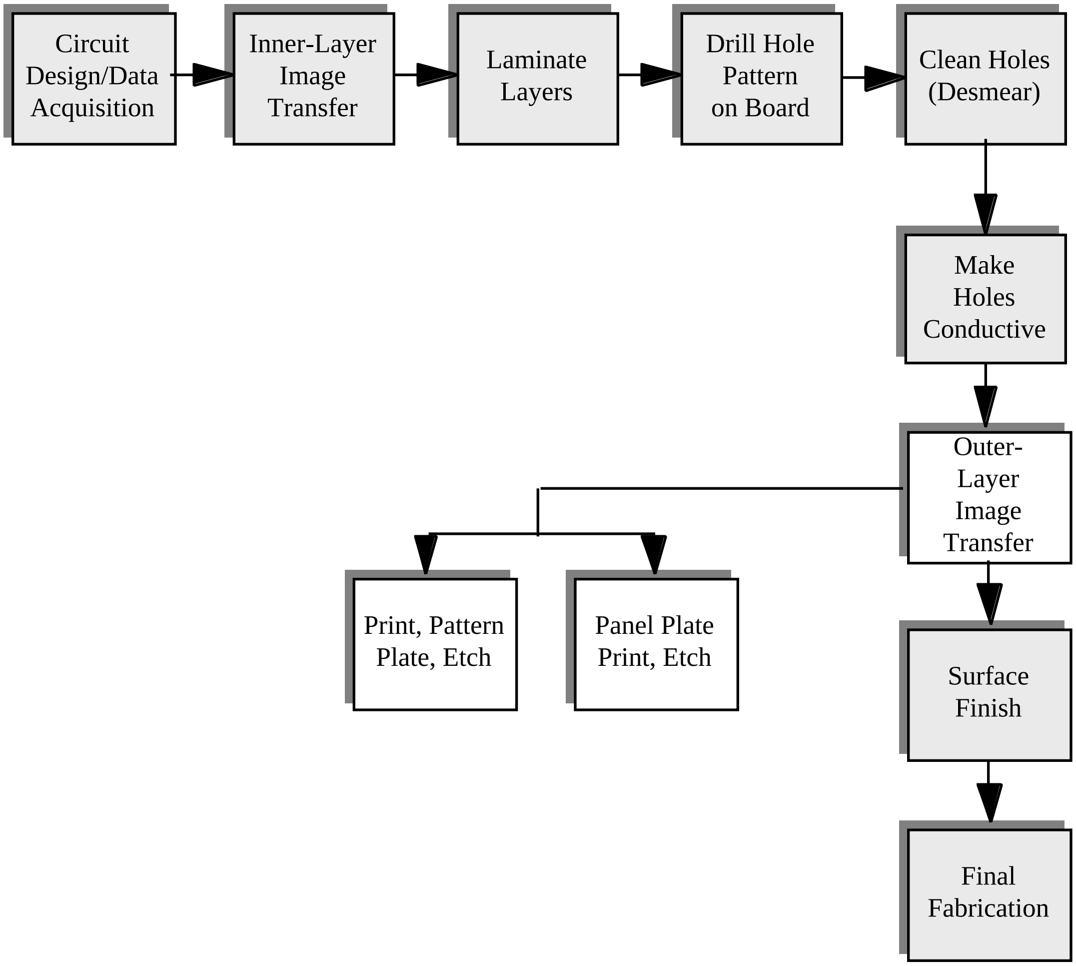
The second system uses the standard electroless process through catalyst application. The panels are then laminated, imaged and developed. The imaged panel is then placed in the electroless copper bath that deposits copper on the catalyzed surface and in the holes. The bath contains biodegradable complexing agents, and a boron compound acts as the reducing agent (ref. 35).

3.2.7 Outer Layer Image Transfer

This large cluster includes outer layer imaging, copper plating, etch-resist plating or application, etching, and etch-resist stripping (Exhibit 3-18). The cluster includes copper electroplating, a function not normally associated with image-transfer. Although arguably an independent function, copper electroplating is performed in a sequence determined by the overall image transfer strategy. Furthermore, with copper sulfate being the overwhelming choice of PWB shops, a cluster of alternatives does not actually exist (pyrophosphate baths, the other chemistry, have vanished). With the exception of process material improvements such as dry film photoresist, plating chemistries (copper sulfate vs. pyrophosphate, in particular), or the substitution of tin-only etch-resist for tin-lead, this cluster has remained essentially unchanged for many years. It also forms the core of double- and single-sided processing; thus many of the processes described here predate multilayer manufacturing.

Two major subtractive options, starting with copper clad laminate, are available to the PWB manufacturer. The majority of manufacturers in the U.S., Southeast Asia, and Europe use the print, pattern plate, and etch sequence. While copper pattern plating is a uniform process shop-to-shop, the etch-resist metal plated over the copper is not, and forms an interesting and important second-level cluster. Etching is theoretically a cluster of two chemistry options, but with most metallic etch-resists, only ammoniacal is possible. In Japan, the majority of manufacturers use the second method of panel plate, print, and etch. Copper is plated to full thickness over the entire panel prior to imaging. The photoresist imaged during the “print” process serves as the etch-resist precisely as in inner layer image transfer.

Exhibit 3-18. Outer Layer Image Transfer



It can be seen that the panel plate, print, and etch process (also referred to as “tent-and-etch” because the drilled holes are tented over and protected from the etchant by dry-film photoresist) eliminates process steps required in the more common pattern-plate process. There is no etch-resist plating (the photoresist serves as the etch-resist) or metal stripping; therefore, the tin or tin-lead problem is obviated. Furthermore, cupric chloride etching is an option when dry-film photoresist is the etch-resist. Unfortunately, it is the inefficiency of panel plating, along with certain technical limitations of this process, that prevent its widespread use. Most of the copper on a typical circuit panel is etched away; thus, most of the plated-on copper of this process is promptly removed during etching, unlike the copper added during pattern plating. Furthermore, the panel-plated copper can cause difficulty in etching, particularly fine-line etching. The thicker the copper to be etched, the greater the undercut. This problem has dampened the enthusiasm for tent-and-etch. On the other hand, layout design changes can easily rehabilitate tent-and-etch. One method referred to as “pads-only outer layers” eliminates difficulty of fine-line etching on outer layers (along with eliminating the need for solder mask) at the expense of requiring two extra layers of inner layer circuitry.

It should be pointed out that some of the etch resist options listed here are not true options, but rather alternative methods that may be required by customer specification or for end-product performance. Although tin and tin-lead perform identically as etch-resists, if reflow is the specified finish type, tin-lead plating must be used. Manufacturers need to decide if the small percentage of jobs requiring a reflow finish justify keeping a tin-lead plating tank, along with the worker exposure to lead and waste treatment difficulties that come with it.

3.2.7.1 Image, Pattern Plate, and Etch

Outer layer imaging is quite similar to inner layer imaging (see 3.2.2.2 Conventional Print-and-Etch for more detail). The panel is thicker and has drilled holes, but it is essentially processed through the same sequence of operations. Some shops, especially smaller ones, may use the identical photoresist product for both inner and outer layers for convenience. Photoresist thickness, not critical for an etch-resist, takes on significance as a plating resist. Most facilities use a thinner resist for inner layers (0.001 inches) and are forced to use thicker resist for outer layers (typically 0.0015 or 0.002 inches). Generally, the resist thickness should equal or exceed the thickness of the metals to be plated onto the pattern to avoid copper or tin-lead “mushrooming” over the top of the resist. Resists other than dry film are extremely uncommon for outer layer imaging.

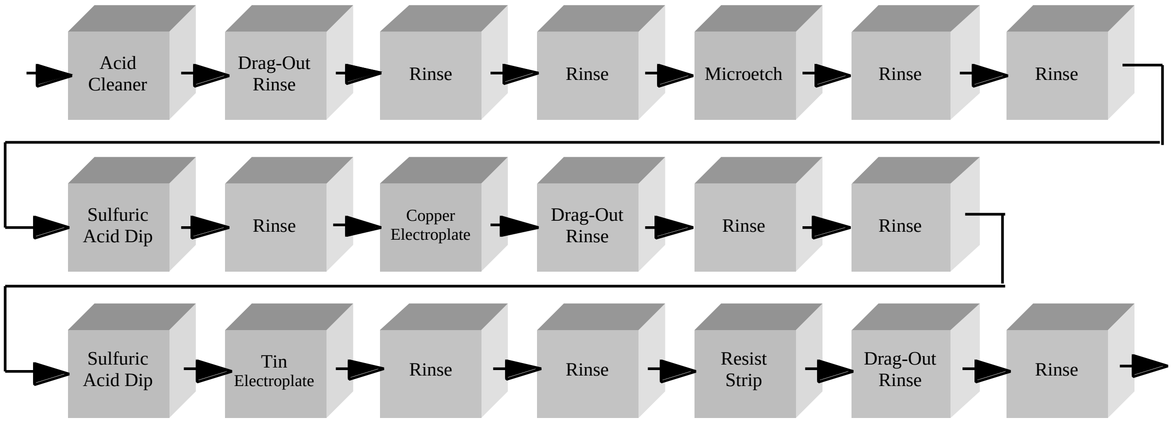
Exposing may be done with first-generation photoplotted phototools or with diazo, a reddish transparent film that allows for manual registration. With a diazo phototool, an operator can see through the dark areas of the film (the circuit pattern) and can align the phototool to the hole pattern, eliminating the need for tooling regimes. Although not practical for production shops, manual registration with diazo phototools is not uncommon in prototype shops. When pattern plating is to follow, outer layer phototools are positive images of the circuit. The circuit image is developed away exposing the underlying copper. The photoresist remaining on the panel is the plating resist for the pattern plate process.

Pattern plating is so named because only the circuit pattern and hole barrels are plated (Exhibit 3-19). Only the thin electroless copper layer has been deposited in the hole barrels up to this point in the process and it is far short of the typical 0.001-inch specification for copper thickness. None of the copper plated during this process is etched away, but rather, remains on the circuit and is part of the finished product. The copper is protected from the etchant by a metallic etch resist that is plated on during the next process step. The ordinary outer layer will have about 33% of the panel plated to a thickness of 1.5 mils of copper. This 1.5 mil target is to ensure a minimum thickness of 1 mil in the holes. The result is 0.6866 ounces of copper being plated per square foot of product run for a typical panel. This result does not account for the copper contained in the solution that is dragged with the panel.

Although a few copper electroplating chemistries exist, nearly all PWB facilities use basically the same copper sulfate bath composition. The bath is typically made with 10 ounces/gallon of copper sulfate, 25 to 40 ounces/gallon of sulfuric acid, and a small amount of hydrochloric acid to provide a chloride concentration of 30 to 90 mg/l. This bath has an extremely long life (measured in years) and is generally easy to maintain and control. Proprietary organic additives, usually referred to as brighteners, distinguish one vendor’s bath from another. The pre-plate line consists of an acid cleaner (dilute phosphoric acid is a common constituent), a microetch, and a sulfuric pre-dip.

High-performance copper plating is reliably performed at a current density range of 20 to 35 amperes/ft^2. Manufacturers generally plate from 0.0013 to 0.0017 inches of copper to ensure that all hole barrels meet the minimum of 0.001 inches in all areas of the panel. Dwell times depend on current density and target thickness, but generally range from 30 minutes to somewhat more than one hour. Although a source of copper in the wastewater stream, the copper sulfate plating process lends itself to recovery schemes. A drag-out tank, immediately following the plating bath, can be electrowinned (an electrolytic recovery process), which recovers copper in metallic form and reduces drag-out to the subsequent flowing rinses. Some facilities have employed ion exchange to create a closed-loop. In this arrangement, wastewater is processed and reused as rinse water and the cation regenerant can be returned to the copper sulfate bath.

Exhibit 3-19. Typical Pattern Plate, Etch-Resist, Photoresist Strip Process Line



Pattern Plate Etch Resist. Immediately after copper pattern plating, an etch resist is plated over the copper. The three most common etch resists are tin, tin-lead, and nickel-gold; however, other metals may be used depending on the customer's specifications. Tin is typically used on boards requiring solder mask over bare copper (SMOBC) finish since it serves no other purpose than acting as an etch resist. It is removed from the panel surface in a stripping step after etch. While the regulatory status of tin varies from locality to locality, it is safe to say that tin receives less scrutiny than lead. Some manufacturers have been able to eliminate tin-lead plating altogether since the majority of work is SMOBC. Manufacturers that serve military clients must maintain their tin-lead baths since some military specifications continue to call for tin-lead reflow finish.

Tin-lead is plated to a thickness of 0.0002 to 0.0005 inches. Assuming a thickness of 0.00035 inches and plating 33% of the panel, approximately 0.3028-ounce of tin-lead are plated per square foot of a typical panel. Tin-lead can be plated with one of the following baths:

Tin-lead fluoborate. This common bath consists of fluoboric acid, tin and lead fluoborate, and proprietary organic additives. Stannous tin (Sn^{+2}) is maintained at 2 to 4 ounces/gallon and lead at 1 to 2 ounces/gallon.

Methane sulfonic acid (MSA). MSA-based chemistry is not in wide use in the PWB industry due, in part, to the cost of MSA. The MSA-based bath is, however, generally considered to be more compatible with the environment and is less corrosive. Another advantage MSA has over the tin-lead fluoborate bath is that some local government regulations impose restrictions on the release of fluoborates to municipal wastewater treatment plants (ref. 35).

Tin is plated for etch resist purposes only, and a 0.0002-inch thickness is adequate. 0.2308 ounces of tin per square foot will be plated on a typical panel where 33% of the panel is exposed for plating. There are three possibilities for tin baths. A tin fluoborate bath exists, and some facilities have phased out tin-lead by simply replacing the tin-lead anodes in the fluoborate bath with tin anodes and allowing the lead concentration to gradually fall. Second, the tin sulfate bath consists of 20% sulfuric acid and enough stannous sulfate to provide 2 to 3 ounces/gallon of stannous tin. Last is an organic sulfonic acid (OSA) -based (usually MSA) tin bath. Most of the advantages of OSA-based chemistry are shared with the simple tin sulfate bath, and OSA chemistry has not found wide use in the PWB industry.

Nickel-gold is also pattern plated electrolytically as an etch-resist and surface finish. The nickel-gold plating line consists of a nickel pre-dip, the nickel plating bath, gold pre-dip, and the gold plating bath. The nickel plating chemistry of choice is nickel sulfamate or nickel sulfate. Nickel is relatively concentrated in either bath (e.g., 17 ounces/gallon in typical nickel sulfate formulations). Unlike many other process baths, many facilities use decades-old nickel plating formulations and do not purchase proprietary chemicals. Nickel is plated to any specified thickness, usually in the range of 50 to 500 micro-inches. Gold is then immediately plated over the nickel. Acid gold cyanide formulations are most common and are similar, but not identical, to the hard gold baths designed for edge connector plating. Sulfite-based alkaline baths are also in use. Gold is generally plated to a thickness under 100 micro-inches, and for many applications 10 to 30 micro-inches will suffice. The area to be plated on a typical gold panel is less than tin and tin-lead plated boards. The border areas are taped off in an effort to preserve gold and prevent it from being plated on areas where it is not necessary. On a typical square foot, 0.023 ounces of nickel and 0.05 ounces of gold will be plated. Both the nickel and gold plating baths are quite long-lived; barring unusual events, each may be maintained for several years.

Electrolytic soft gold is the surface finish of choice for certain performance considerations, including high corrosion resistance, low contact resistance (although wear resistance is poor), and long shelf-life. Electrolytic pure gold may be called for on circuits requiring wire bonding.

Metals such as rhodium or gold may be plated selectively over certain areas of a circuit, then masked off, and a conventional etch-resist is plated over the remainder. Rhodium is the metal of choice for maximum wear resistance.

The survey results indicate that 52% of respondents use tin-lead plate for at least a portion of their production (Exhibit 3-20), but tin-lead was used on only 23% of the aggregate production of the entire group of respondents. Tin-only plating was performed by 49% of the respondents and represented 43% of the aggregate production. It is clear from these data that many facilities are maintaining both tin-only and tin-lead plating operations, but are moving an increasing portion of their production to tin-only (Exhibit 3-21).

Exhibit 3-20. Outer Layer Etch Resist

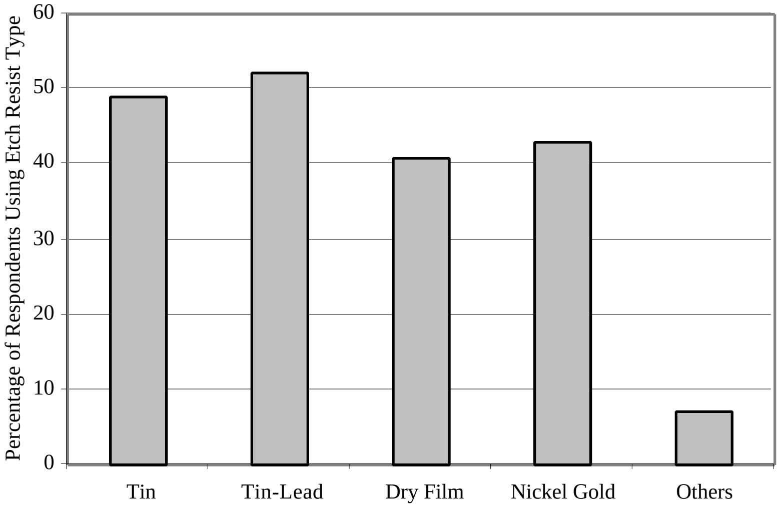
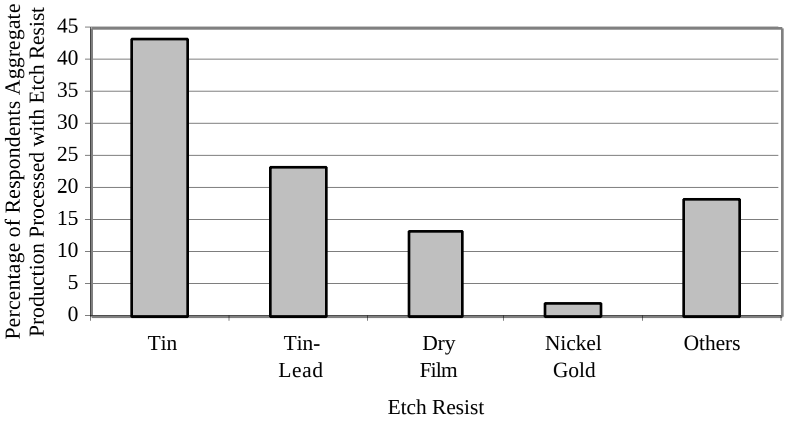


Exhibit 3-21. Percentage of Total Production with Various Types of Etchant Resistance



Photoresist Stripping. Dry film strippers break down the bond between the resist and the panel and cause it to detach. The chemical is usually alkaline and may be mixed with a solvent, such as ethylene glycol butyl ether or diethylene glycol butyl ether, which is needed to strip semi-aqueous resist. The solution is heated from 45 to 60°C (ref. 36). Stripping is accelerated at higher temperatures, but it also accelerates the attack on the tin or tin-lead coating, which is soluble at high pH. The stripping rate decreases as panels are processed and resist particles build up in the solution. Some facilities use a filter to remove the particles from the solution before they have a chance to dissolve, in an attempt to extend the life of the bath.

An EPA Resource Conservation and Recovery Act (RCRA) determination on photoresist solids has been issued that states they are to be considered a hazardous waste (see discussion in section 2.2.2). If the stripping process is in-line with an electroplating operation (not physically separated from the plating operation and the panels are not rinsed and dried prior to stripping), then the spent stripper solution itself becomes an electroplating wastewater. Thus, the resist skins would be considered an F006 waste. The belief is that the physical separation of the operations, along with the rinsing and drying of the panels, will serve to prevent hazardous contaminants from the electroplating tank or etcher from entering the stripping solution.

Resist skins from a tent-and-etch type process, which does not use a plated etch resist, would not be considered a hazardous solid waste as long as the boards are rinsed prior to being stripped (most etchers are equipped with rinse chambers). However, if tent-and-etch panels were stripped in the same tank as electroplated panels and those skins had already been determined to be hazardous waste, then the resist skins would be F006 waste.

Outer Layer Etching. Etching is described in greater detail in section 3.2.2.2, Conventional Print-and-Etch. Notable in outer layer etching is that cupric chloride etchant is not typically used for outer layers, due to its incompatibility with metallic resists.

Tin and Tin-lead Stripping. For solder mask over bare copper boards, the tin or tin-lead is only used as an etch resist and is stripped from the panel after etching. Tin-lead is left on boards and this step is skipped if the finish type is tin-lead reflow. Nitric acid, ammonium bifluoride, and peroxide-based systems are available as stripping solutions. If lead is present on the surface, the spent process fluid is a major source of waste lead. Tin-lead stripper is consumed at 0.0168 gallons per square foot of a typical panel. This figure does not account for the volume lost through drag out. When the saturation point of the stripper has been reached, this solution is usually is sent off-site for treatment/disposal.

3.2.7.2 Panel Plate, Print, and Etch (“Tent-and-Etch”)

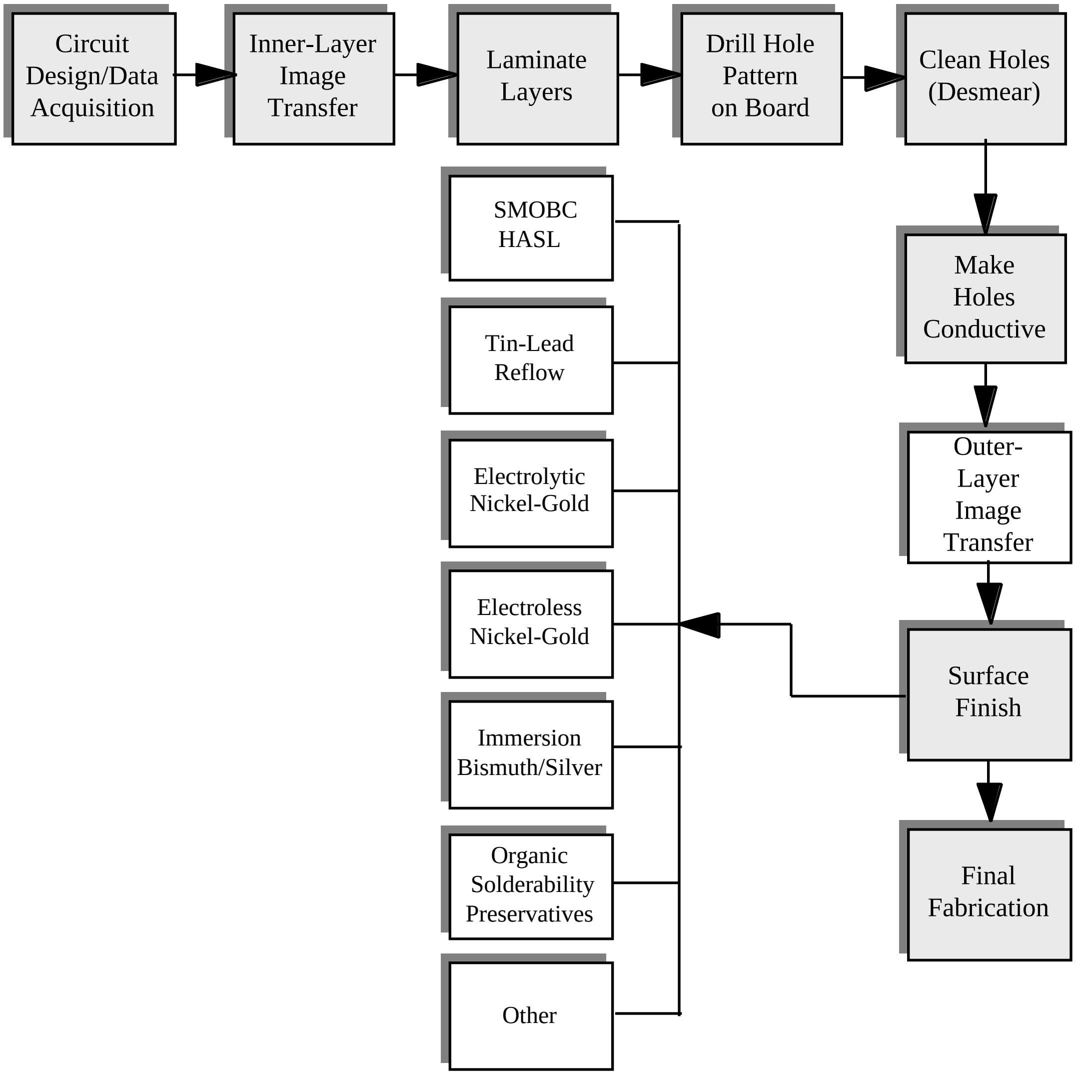
With the exception of the additional panel plating, this process follows the steps of innerlayer print and etch. Panel plating is less efficient than pattern plating since the entire panel is being plated rather than just the circuit. Most of what is panel plated is subsequently etched off. Either cupric chloride or ammoniacal etching systems can be used. Fewer steps and less process time are the advantages to using tent-and-etch.

The major disadvantage to tent-and-etch is the difficulty in etching through both the plated-on and base laminate. Circuit features are becoming smaller, and most facilities are required to produce line widths of less than 10 mils. To etch through 2 to 3 mils of copper, which is what the copper thickness can be after panel plating, the etching undercut will amount to a significant portion of the trace width. Another drawback is that panel plating can only be done where the surface finish will be bare copper or SMOBC. A surface finish of tin-lead, gold, or selective plating of a particular metal requires the use of pattern plating.

3.2.8 Surface Finish

For most parts, the functions of the surface finish are to prevent copper oxidation, facilitate solderability, and prevent defects during the assembly process. A number of metallic alternatives exist along with organic solderability preservatives (also known as OSPs or pre-fluxes). A variety of deposition techniques exist, including hot air leveling, electroplating, immersion, and electroless plating. The shelf life of immersion, electroless plated, and OSP coating alternatives are less than that of leveled or tin-lead reflowed boards (ref. 35). Other surface finishes are dictated by the environment in which the part will reside or by specific performance criteria.

Exhibit 3-22. Surface Finish Processes



Solder-mask-over-bare-copper (SMOBC) with hot-air-solder-leveling (HASL) has been the preferred surface finish for over 15 years (ref. 38). Nickel-gold, another popular finish, can be applied electrolytically as an etch resist, replacing tin and tin-lead, or electrolessly as a substitute for HASL. Other electrolytic plating metals include rhodium, palladium, palladium-nickel alloys, and ruthenium. Non-electrolytic deposition processes include tin immersion, tin-lead displacement plating, electroless nickel, electroless gold, immersion gold, immersion silver, immersion bismuth, and the previously mentioned OSPs.

3.2.8.1 Solder Mask Over Bare Copper (SMOBC), Hot Air Solder Level (HASL)

This method predominates for several reasons. Copper is a surface that lends itself to rigorous cleaning, which is essential for solder mask adhesion. If the solder mask were placed over tin-lead traces, the tin-lead would liquefy during soldering and may cause the mask to blister and peel. The hot air solder leveling process generally produces less wastewater and introduces less lead into the wastewater stream than tin-lead plating and reflow. The overall process begins with a solder-mask pre-clean, usually a mechanical or pumice scrub. Solder mask is then applied, followed by hot air solder leveling, nomenclature screening, and finally, gold edge plating if necessary.

Increasing circuit density, however, is causing some to look for alternatives to this difficult to control process. Maintaining planarity of fine-pitch surface mount pads across both sides of the panel is a challenge. Another is solder bridging on fine pitch pads. This tends to happen when pads are lined up in the same direction of travel as the panel as it is pulled from the solder pot. Increasing the pressure of the air knives may blow off the solder bridges, but it also reduces the thickness of the solder coat on all of the other features.

Solder Mask. The purpose of solder mask is to physically and electrically insulate those portions of the circuit to which no solder or soldering is required. Increasing density and surface mount technology have increased the need for solder mask to the point that, with the exception of “pads only” designs, nearly all parts require it. Manufacturers have had some autonomy in selecting masks. Many specifications do not call out a specific product or product type, and this has allowed the manufacturer to choose masks based on processing as well as performance issues.

Three basic types of masks are commonly applied: thermally cured screen-printed masks, dry film, and liquid photoimageable (LPI). Thermal masks have predominated for decades but are gradually being replaced by LPI, despite being the lowest cost alternative. Dry film has some specific advantages, such as ease of application, but its use seems poised to decline as well in the face of improving LPI formulations.

Hot Air Solder Level (HASL). The HASL process consists of a pre-clean, fluxing, hot air leveling, and a post-clean. Pre-cleaning is usually done with a micro-etch. However, the usual persulfate or peroxide micro-etch is not common in the process. Dilute ferric chloride or a hydrochloric-based chemistry is favored for compatibility with the fluxes that are applied in the next step.

Fluxes perform the following functions:
- Provide oxidation protection to the precleaned surface
- Affect heat transfer during solder immersion
- Provide oxidation protection during HASL

Higher viscosity fluxes provide better oxidation protection and more uniform solder leveling, but reduce overall heat transfer and require a longer dwell time or higher temperature. A balance in flux use must be struck between better protection with high viscosity fluxes and superior heat transfer with lower viscosity fluxes (ref. 38).

Hot air level machines consist of a transport mechanism that carries the panel into a reservoir of molten solder (460°F, 237°C), then rapidly past jets of hot air. All areas of exposed copper are coated with solder and masked areas remain solder-free. Boards are then cleaned in hot water, the only step in the SMOBC process where lead may enter the wastewater stream, albeit in very small quantities. Once cleaned, the panels may again enter the screening area for optional nomenclature screening, or proceed directly to the routing process.

Copper, flu, and other impurities build in concentration in the solder pot as panels are processed through the hot air leveler. These impurities can be removed to some degree by performing a procedure known as drossing. From the hot operating temperature, the temperature is reduced to 385°F (196°C) and the machine sits idle for 8 to 12 hours. The impurities will float to the surface of the solder where they are scooped out and placed in a dross bucket. This material can be returned to the vendor for reclamation of the metals. Some manufacturers go for years without changing the solder; they dross and make additions. When the time comes to change over the solder, vendors will issue credit on the purchase of new solder as long as the old solder is returned to them for processing.

The acid pre-clean will have some copper in solution and can be treated conventionally. The waste flux is collected and is sent off-site for treatment.

3.2.8.2 Reflowed Tin-lead

The reflow process uses the tin-lead plated as an etch resist to create the final surface finish. It is quite common in lower technology single-sided boards. Some military specifications require reflow and specifically exclude the use of SMOBC/HASL. The desire to remove lead from the plating process and tin-lead performance issues has lead to a decline in use. The performance concerns include difficulty in cleaning, a poor surface for solder mask, and the fact that it will liquefy during wave soldering, which may cause the mask to lift, among other downstream defects. Any spent flux generated during the reflow process is collected to be shipped off-site for treatment.

Four methods exist for tin-lead fusing (ref. 35):
- Infrared reflow uses IR rays to melt the tin-lead. This method is widely used since it can be conveyorized and gives consistent results. In-line are fluxing rollers, a pre-heat area, and the area of the oven where the actual melting of the tin-lead occurs, which is followed by cleaning and drying.

- Hot oil reflow has been around for years. The panel is fluxed and submerged in a pot of hot oil long enough to melt the tin-lead. It is not currently preferred due to its lower productivity vs. IR reflow, and because of the fire and safety hazards.
- Vapor phase reflow uses the principle of condensation heating. The panel is immersed in a saturated vapor, which condenses on the board, causing heating and subsequent tin-lead melting. The heat transfer liquids are very costly.
- The hot air leveling machine can be used to melt the tin-lead as well. It is dipped in the molten solder, the same as a SMOBC-type board, and air knives blow off the excess solder.

3.2.8.3 Nickel/Gold

Nickel-gold finishes may cover an entire circuit or be selectively plated onto certain areas of a circuit. Nickel-gold formulations can produce hard gold, with the addition of cobalt or another metal being co-deposited in small amounts, or they can produce soft gold, by utilizing pure gold.

Hard Gold. Hard gold is electrolytically plated. The most common application of hard gold is edge connectors, but hard gold may also be plated over circuit areas as well. Automated edge plating machines are common since manual plating is quite labor-intensive. Typically, a plater's tape is applied to the board masking off all of the circuit above the edge connector. The panel is then processed through a nickel-gold plating line, with just the edge connectors immersed in the plating fluid. Nickel is plated first, Watts or sulfamate nickel is common. Cyanide gold is the most common gold electroplating chemistry.

Soft Electrolytic Gold. Soft gold is a pure gold coating over a nickel deposit. It may be electroplated over the entire circuit or selectively over certain portions of a circuit (excluding edge connectors, which require hard gold). Selective electroplating requires a combination of masking and bussing (providing current to the portion of the circuit being electroplated). Selective gold applications include contact points (which may require hard gold), press pads, wire bond sites, or portions of a board that may reside in a corrosive environment. Selective gold plating can be labor-intensive and is not frequently specified for production lots (all gold plating is often substituted; the labor savings offset the extra gold required).

Electroless Nickel/Immersion Gold. The electroless nickel/immersion gold process is another method of applying soft gold. Electroless plating can be conveniently performed after etching because no bussing is required. Therefore, these all-gold boards can be processed with a standard tin etch-resist and processed identically as SMOBC, except the gold plating step replaces the HASL step. This process has advantages over SMOBC/HASL and electrolytic gold plating. When compared to SMOBC/HASL, electroless all-gold circuits have a much longer shelf life. The flat surface profile of the electrolessly plated surface-mount pad and overall excellent solderability make electroless nickel/gold ideal for surface-mount technology. When compared to electrolytic gold, electroless has the advantage of full copper encapsulation because plating is performed after etching, not before, as with electrolytic gold plating. Selective gold plating is made somewhat easier by the electroless plating method since no electrical bussing is required. Cost is the main disadvantage. Immersion gold and electroless nickel process baths are short-lived compared to electrolytic formulations, and maintenance and control of these baths is more difficult. The main application of electroless nickel-gold coatings is chip-on-board technology, where component leads are ultrasonically or thermosonically bonded to gold pads rather than soldered.

3.2.8.4 Immersion Bismuth/Immersion Silver

Two non-precious metal coatings have been developed that are less expensive and require fewer steps than their precious metal counterparts. No base nickel is necessary, which eliminates that step. However, both immersion technologies require that the surface is cleaned and microetched to remove surface oils and improve topography for subsequent deposition. Testing has shown that these two immersion metals provide better solderability than organic coatings (ref. 39).

Immersion Bismuth. Bismuth resists oxidation and provides solderability similar to that of unoxidized copper. The bismuth coating does not form any intermetallic alloy with copper and readily diffuses throughout the solder joint during soldering since it melts at nearly the same temperature as tin-lead.

Immersion Silver. Immersion silver is deposited in conjunction with an organic coating. After surface preparation the panels are transferred to the immersion silver. Since bare silver surfaces tarnish and oxidize, the organic component is added as a protective coating for the silver.

3.2.8.5 Organic Solderability Preservatives (OSPs)

The OSP coatings are applied to bare copper after solder mask (they can be applied to the finished board after routing). Their function is to protect the copper from oxidation and to provide long-term solderability. The coatings can usually be applied in immersion, spray, or flood mode (ref. 35). OSPs offer an environmentally friendly alternative, low capital equipment expense, lower maintenance costs compared to HASL, and are safer for employees to handle. However, HASL has a very long and reliable track record, which is a deterrent to change. For such a change to occur, PWB facilities and their customers need to be convinced that OSPs are a viable alternative. Some may be forced into trying OSPs as designs call for finer pitch surface mount pads. HASL is notorious for depositing uneven and unlevel amounts of solder on surface features, while OSP-coated features have good pad coplanarity. Care must be taken, however, while handling and storing OSP-coated boards. The surface is not very durable and is susceptible to scratches that will expose the copper underneath and allow oxidation to occur.

A cost comparison completed at a large facility concluded that the OSP process costs one-third that of HASL. Among the costs associated with HASL are:

- High equipment maintenance costs
- Cost and maintenance of safety equipment for HASL operators
- Hazardous waste disposal of the tin-lead frames after the panels are routed
- High electricity costs to keep the solder pot heated
- Labor cost involved with the masking and subsequent cleaning of gold edge contacts
- Added cleaning necessary to pass surface insulation resistance (SIR) testing when using dry film

While companies converting to OSPs report success, they indicate that facilities must be prepared for process alterations. New “optimum” operating parameters will need to be established. During assembly, for example, different flux formulations, pre-heat temperatures, and solder pot temperatures may be necessary. They recommend a coordinated effort between the PWB shop, assembly shop, and the customer to educate one another on process issues and what is or is not an acceptable final product.

3.2.9 Final Fabrication

Non-plated features are added to the board during the final fabrication process. These may include tooling holes, cutouts, and countersink holes. Numeric controlled routers run profiling programs that are output from the CAM systems with all of the features needed according to specifications.

Finally, the circuit is either completely routed from the panel or partially depanelized. Partial depanelization is common with production lots or when board assembly will be performed by machine. Most of the circuit is routed out of the panel, but tabs remain to hold the circuit in place. This allows the assembly machine to populate multiple boards at once. Afterwards, the circuits can be snapped or broken out of the panel. Such panels are often referred to as “breakaways,” “snaps,” or “arrays.”

An alternative to breakaways is to have the panel V-scored. This allows more circuits to be placed on a panel since no spacing is necessary for the routing bit. An array of circuits is routed as if it were a single image. The V-scoring machine has a thin rotating scoring blade that will rout across the top of the panel 30-40% of the thickness of the panel. This is repeated on the bottom side. Some scoring machines have two blades and both sides can be scored in one pass. The remaining 20-40% of the panel not routed will hold the panel together through assembly and can then be easily broken apart.

Drilling and routing produces dust from the material that is being drilled or cut. Most of the material is the glass and resin core. However, copper is laminated to the core, and in the case of routing, there may be tin-lead or another metal plated to the surface. A toxicity characteristic leaching procedure (TCLP) can be performed on a sample of router dust to determine how the dust needs to be treated. In most cases it can be treated as non-hazardous industrial waste. If the lead concentration in the dust were greater than 5 mg/L, the router dust would be considered hazardous and would have to be managed in compliance with Resource Conservation and Recovery Act (RCRA).

The "frames" that remain after the boards are routed from the panel may have a tin-lead or gold coating. These frames are collected and sold as scrap.

3.3 Waste Generation and Pollution Prevention Methods

A summary of waste volume estimates for common PWB manufacturing processes is presented in Exhibit 3-23. Potential substitute processes that may reduce the quantity of waste generated or the hazardous characteristics of the waste are presented in Exhibit 3-24. Potential bath maintenance and recovery options applicable to common PWB manufacturing processes are identified in Exhibit 3-25. Detailed information relative to these technologies can be found in Section 4.

Exhibit 3-23. Selected Waste Volume Estimates from PWB Processes

Process	Waste	Volume (based on 1000 board ft^2 of 4 layer boards)
Etching, Inner and Outer Layers	Spent Etchant	140 gallons
Dry Film Resist Developer	Spent Developer	200 gallons
Dry Film Resist Stripper	Spent Stripping Solution	6 gallons
Tin-Lead Stripper	Spent Stripping Solution	17 gallons
Soldermask Developer	Spent Developer	60 gallons
Microetch; Inner and Outer Layers	Spent Micro-Etchant	16 gallons
Sulfuric Acid Dips	Spent Sulfuric Acid baths	12 gallons
Electroless Copper	Waste Electroless Cu Bath	26 gallons
Board Trim	Waste Copper-Clad Material	187.5 square feet 49.2 lbs Cu

Assumptions:
0 Ammoniacal etchant used for both inner- and outer-layers, 70% of copper foils etched, 1 oz copper used on all layers, and 20 oz/gal carrying capacity of etchant.
1 Fifty percent of film developed (30% outer, 70% inner), developer carrying capacity of 3 mil-ft2/gal, and 1 mil film is used throughout.
2 Fifty percent of film stripped (70% outer, 30% inner), stripper carrying capacity of 100 mil-ft2/gal, and 1 mil film is used throughout.
3Thirty percent metal area, tin-lead resist is 0.3 mil thick and stripper capacity of 15 oz/gal of metal.
4 Thirty percent of mask developed, 1 mil thickness, 10 mil-ft2 carrying capacity.
5Oxide, electroless Cu, and pre-pattern plate microetches (50%, 100%, and 30% of surface area etched, respectively) considered. Many facilities may employ additional baths.
6 microinches average etch and 4 oz/gal carrying capacity.
7 Bath life of 1 gallon/500 ssf, 3 sulfuric dips (oxide, electroless copper, and pattern plate lines).
818x24 panels with .75-inch thief area and .25 inch spacing of 6 step-and-repeats, outer layer 2 oz copper (80% of trim area), inner layer 1 oz copper (50% of trim area).

Exhibit 3-24. Potential Substitute Processes for Common Multilayer PWB Manufacturing Processes

Most Common Process	Substitute Processes	Advantages	Disadvantages
Chemical Clean	Pumice Scrub	Eliminates portion of chemical preclean line (anti-tarnish remover and anti-oxidant remover may still be necessary) Does not produce copper-bearing waste from scrubbing operation	Maintenance-intensive equipment
	Mechanical Brush Scrub	Eliminates chemical pre-clean line	Imparts stress to thin layers--usually not an option of very thin inner-layer material Introduces a waste stream bearing copper dust
Photo-tool creation	Direct Imaging	Eliminates photo-tooling (film, film punches, film developing) Eliminates defects introduced by photo-tools (film dimensional instability, handling defects)	Very high capital costs Current models are slower than conventional photo-tool exposures
Oxide	Use pre-treated or "double-treat" material	Eliminates oxide process line	Material is more expensive Simply moves oxide process upstream to laminate vendor

Permanganate Desmear	Plasma desmear	Eliminates desmear process line Completely "dry" process Process control is more precise	Slower, limiting use among production shops Higher capital investment
Electroless Copper	Various metallization alternatives (see details in Exhibit 3-16)	Eliminates formaldehyde Some shorten process line from 7-8 process tanks for electroless Cu to 3-5 tanks for alternative Some eliminate high concentrations of EDTA and other complexing agents Carbon and graphite-based alternatives have only one copper-bearing process tank and rinse stream--micro-etch	Far less mature--many early versions of the alternatives had narrow process windows Some alternatives require conveyorization which generally has associated higher capital costs than tank lines
Pattern Plate Copper	Panel-Plate Copper	Facilitates use of organic (dry film) etch resist as opposed to metallic Shorter process--pattern plate pre-clean line is eliminated along with tin-plate line	Inefficient--most of copper plate is subsequently etched away Copper incidentally plated on surface excludes use for fine lines due to etching undercut.
Pattern Plate Tin-Lead	Pattern Plate Tin	Eliminates lead from process No performance loss as etch resist. Tin sulfate bath also eliminates flouborates	Some specifications require tin-lead, forcing facilities to maintain both lines or a tin-lead line only; Issue is of considerable importance to small and very small shops
Solder Mask Over Bare Copper (SMOBC) followed by Hot Air Solder Leveling (HASL)	SMOBC, E'less Nickel/Immersion Gold	Eliminates lead and maintenance and capital intensive HASL When used with tin-only etch resist, manufacturing process becomes lead-free Provides excellent solderability, shelf life	More expensive Considerable additional process chemistry and time
	SMOBC, Organic Solderability Preservative (OSP) Coating	Eliminates lead and maintenance and capital intensive HASL Opens new process sequence options (OSP can be applied immediately after solder mask or later in the process) Lower overall costs	OSP coating is soft, scratches easily, which can lead to defects Requires some co-ordination with assembly houses

Exhibit 3-25. Potential Bath Maintenance and Recovery Options Applicable to Common PWB Processes

Common Process Sequence (wet processes only)	**Tank Name**	**Common Tank Chemistry**	**Process Waste**	**Common Bath Maintenance & Recovery Options**
Inner Layer Image Transfer				
Chemical Clean*	Anti-tarnish Remover	Mixed strong acids	Rinsewater contains Cu Spent bath contains 1-10 g/L Cu	Bath: Consider use of bath maintenance technology such as diffusion dialysis or acid sorption.
	Microetch	Persulfate-based or Peroxide/ sulfuric	Rinsewater contains Cu Spent bath contains 20-40 g/L Cu	Rinse: Recycle using ion exchange. Bath: Peroxide sulfuric can be chilled, causing copper sulfate to crystallize for recovery and sale. Decanted solution can be reused. Persulfate baths can be reduced, then electrowinned to recover copper.
	Sulfuric Acid	5% sulfuric	Rinsewater contains Cu Spent bath contains 1-2 g/L Cu	Rinse: Recycle using ion exchange. Bath: Acid purification for bath life extension (usually economical for large shops). Cu concentrations usually too low for Cu recovery using electrowinning.
	Anti-tarnish	Weak acid (citric)	Rinsewater contains Cu Spent bath contains 1 g/L Cu	None identified.
Imaging*	Film develop, fix		Spent developer, fixant	Small quantities of silver can be recovered with electrowinning or metal replacement technologies.
	Resist developer	Sodium carbonate	Rinsewater generally free of metals Process solution contains dissolved resist	Square footage analytical-based replacement rather than time-based, which is frequently employed for this bath.
Etching	Etchant	Acidic cupric chloride or alkaline ammoniacal	Rinsewater contains Cu. Spent etchant contains 140 or more g/L Cu	Rinse: Cu-free etchant flood rinse to lower Cu-rich dragout. Rinse can be recycled with ion exchange. Bath: Bath regeneration with chlorination is common with cupric etchant. Copper can be electrolytically removed from ammoniacal etchants, reinjected with ammonia and oxygen, and reused. Other regeneration techniques include membrane-based technologies (electrodialysis).
Resist Strip	Stripper	Potassium-hydroxide/ solvent	Rinsewater contains dissolved and solid resist, but no metal Spent stripper contains dissolved resist	Bath: Filtration can be used to remove solids and extend the bath life.

Oxide*	Microetch	Persulfate-based or Peroxide/ sulfuric	Rinsewater contains Cu Spent bath contains 20-40 g/L Cu	Rinse: Recycle using ion exchange. Bath: Peroxide/sulfuric can be chilled, causing copper sulfate to crystallize for recovery and sale. Decanted solution can be reused. Persulfate baths can be reduced, then electrowinned to recover copper.
	Sulfuric Acid	5% sulfuric	Rinsewater contains Cu Spent bath contains 1-2 g/L Cu	Rinse: Recycle using ion exchange. Bath: Acid purification for bath life extension (usually economical for large shops). Cu concentrations are usually too low for Cu recovery using electrowinning.
	Pre-Dip	Sodium hydroxide	No rinse; Little or no Cu in bath.	None identified.
	Conventional Oxide	Caustic and hypochlorite	Rinse contains Cu Spent process solution contains low concentration of Cu	Consider new chemistries not based on hyprochlorite.
Clean Holes				
Permanganate* Desmear	Hole Conditioner	Various organic solvents, amine acids	Rinse with no Cu Process solution with no Cu	None identified.
	Permanganate	Potassium permanganate, caustic	Rinsewater contains little or no Cu Process solution contains little or no Cu	Bath maintenance technology (e.g., porous pot) extends bath life.
	Neutralizer	Sulfuric acid	Rinse contains Cu Process solution contains 1-5 g/L C	None identified.
Make Holes Conductive				
Deburr and Scrub	Mechanical Scrub		Rinsewater contains copper dust and spent brush fibers	Filter rinse to remove Cu particles.
Electroless Copper*	Cleaner	Triethanolamine or other caustic	Rinse contains some Cu; Process solution contains 1-5 g/L Cu, also may contain complexer such as EDTA	None identified.
	Microetch	Persulfate-based or Peroxide/ sulfuric	Rinsewater contains Cu Spent bath contains 20-40 g/L Cu	Rinse: Recycle using ion exchange. Bath: Peroxide sulfuric can be chilled, causing copper sulfate to crystallize for recovery and sale. Decanted solution can be reused. Persulfate baths can be reduced, then electrowinned to recover copper.
	Sulfuric Acid	5% sulfuric	Rinsewater contains Cu Spent bath contains 1-2 g/L Cu	Rinse: Recycle using ion exchange. Bath: Acid purification for bath life extension (usually economical for large shops). Cu concentrations usually too low for Cu recovery via electrowinning.
	Pre-dip	Hydrochloric acid	No rinse; Spent bath contains 1-2 g/L Cu	None identified.

	Catalyst	Hydrochloric acid, stannous chloride and palladium	Rinse contains Cu, Pd, Sn; Process solution contains <1 g/L Cu, <1 g/L Pd and ~5 g/L Sn	Rinse: Recycle with ion exchange. Bath: Long-lived bath can be extended further by maintenance of pre-dip.
	Accelerator	Fluoboric acid or sulfuric acid-based	Rinse contains Cu and Sn Bath contains 2-5 g/L Cu and Sn	Rinse: Can be recycled with ion exchange. Switch to sulfuric-based chemistries that can be electrowinned for Cu recovery.
	Electroless Copper	Copper sulfate, caustic, formaldehyde, EDTA, other Some formulations include CN	Rinse contains Cu and formaldehyde Bath contains Cu (3-7 g/L)	Rinse: Can be recycled with ion exchange. Bath: Cu from solution can be recovered with activated foam canisters. Switching to an alternative metallization method removes some Cu sources, eliminates formaldehyde, and reduces water consumption.
	Anti-tarnish	Weak acid (citric)	Rinsewater containing Cu Spent bath containing 1 g/L Cu	Rinsewater contains Cu. Spent bath contains 1 g/L Cu.
Outer Layer Image Transfer				
Imaging	Developer	Sodium carbonate	Rinsewater generally free of metals Process solution contains dissolved resist	Square footage analytical-based replacement rather than time-based, which is frequently employed for this bath.
Pattern Plate Copper*	Cleaner	Ethylene glycol		None identified.
	Microetch	Persulfate-based or Peroxide/ sulfuric	Rinsewater contains Cu Spent bath contains 20-40 g/L Cu	Rinse: Recycle using ion exchange. Bath: Peroxide/sulfuric can be chilled, causing copper sulfate to crystallize for recovery and sale. Decanted solution can be reused. Persulfate baths can be reduced, then electrowinned to recover copper.
	Sulfuric Acid	5% sulfuric	Rinsewater contains Cu Spent bath contains 1-2 g/L Cu	Rinse: Recycle using ion exchange. Bath: Acid purification for bath life extension (usually economical for large shops). Cu concentrations usually too low for Cu recovery via electrowinning.
	Copper Sulfate	Copper sulfate, sulfuric acid	Rinsewater contains Cu. Bath contains 10-20 g/L Cu	Rinse is excellent candidate for dragout/electrowin setup for copper recovery. Remaining Cu-bearing rinse can be recycled with IX.
Pattern Plate Etch Resist*	Tin-lead	Stannous fluoborate Lead fluoborate Boric acid Fluoboric acid	Rinsewater contains Sn and Pb Bath contains 20-30 g/L of Sn and Pb	Rinse: Since bath is not heated, simple drag-out configuration is not effective. Point source ion exchange to remove metal or to recycle water is effective in removing lead from entering general waste streams to conventional treatment.

Strip Photoresist	Stripper	Potassium-hydroxide/ solvent	Rinsewater contains dissolved and solid resist, but usually no metal Spent stripper contains dissolved resist	Bath: Filtration can be used to remove solids and extend the bath life.
Etch Copper	Etchant	Acidic cupric chloride or alkaline ammoniacal	Rinsewater contains Cu. Spent etchant contains 140 or more g/L Cu	Rinse: Cu-free etchant flood rinse to lower Cu-rich dragout. Rinse can be recycled with ion exchange. Bath: Bath regeneration with chlorination is common with cupric etchant. Copper can be electrolytically removed from ammoniacal etchants, reinjected with ammonia and oxygen, and reused. Other regeneration techniques include membrane-based technologies (electrodialysis).
Strip Etch Resist	Tin, Tin-lead strip	Various chemistries used, including nitic-based and ammonium biflouride	Rinsewater contains Sn and Pb; bath contains 50-100 g/L Sn and Pb. Bath may contain small but significant amounts of arsenic and other tin/lead anode impurities.	Switch to tin-only plating to eliminate lead from this waste.
Surface Finish				
Solder Mask	Developer	Sodium carbonate	Rinsewater generally free of metals Process solution contains dissolved resist	Square footage analytical-based replacement rather than time-based which is frequently employed for this bath.
Hot Air Solder Level*	Acid Cleaner	Hydrochloric acid	Rinsewater contains Cu Bath contains 1 g/L Cu	None identified.
	Flux	L-Glutamic acid HCL, Polyalkylene glycol, other		None identified.
	Solder Immersion	Tin-lead	Dross, rinsewater, trace amount of dissolved Pb; some metallic Pb and Pb salts may also enter rinsewater stream	Dross is generally recyclable off-site (to solder bar vendor).

* See Table x-x for common process substitutions

4.0 Wastewater Generation and Fundamental Waste Reduction Practices

4.1 General

Section 4 presents a discussion of wastewater data provided by survey respondents. It also covers fundamental waste reduction practices used in the PWB manufacturing industry. These practices were identified from the survey and a review of literature. Implementation of these practices is considered the first step in an effective pollution control program. These pollution prevention (P2) methods are relatively inexpensive to implement and they reduce the need for the more expensive recovery, recycle and treatment technologies which are discussed in Sections 5 and 6.

The fundamental waste reduction practices are categorized into the following three groups:

- Good Operating Procedures
- Drag-Out Reduction and Recovery Methods
- Rinse Water Use Reduction

Descriptions of these practices, along with summaries of relevant survey responses, can be found in Sections 4.3 through 4.5.

4.2 Wastewater Survey Data

This section of the report contains a discussion of wastewater data provided by survey respondents, including discharge type, flow rates, and costs for raw water and sewer use charges. Additional wastewater data, including discharge limits, compliance difficulties, and treatment methods employed by survey respondents, are found in Section 6.

4.2.1 Discharge Types

For the purpose of this survey, the discharge type refers to the destination of wastewater discharges regulated by categorical effluent standards. The three possible selections in the survey questionnaire were direct discharge (i.e., to surface water such as a river or stream), indirect discharge (to a publicly owned treatment works or POTW), or zero discharge (no process wastewater discharge from PWB manufacturing).

The survey data (see Exhibit 4-1) show that the majority of the respondents are indirect dischargers (69%). One facility indicated they are at zero wastewater discharge. That particular facility is a small PWB shop operated by the US Navy (ID# 36). Based on the information in their survey form, it appears they achieve zero discharge by implementing good operating procedures and using an evaporative technology, and shipping concentrated residual wastes off-site for disposal.

4.2.2 Discharge Flow Rates

Wastewater discharge data are summarized in Exhibit 4-1, columns 6 to 9. Average daily flow rates for respondents range from 400 gpd (ID# 36) to 400,000 gpd (ID# 740500). The mean and median flow rates of respondents were 64,459 gpd and 35,000 gpd, respectively. The vast majority of water used in PWB facilities is used for rinsing. The quantity of rinse water used is dependent on numerous factors, including types of boards manufactured, production rate, cost of water and sewer use, drag-out rate, use of pollution prevention measures (e.g., extended draining time), the rinsing configuration (e.g., single rinse vs. counterflow rinse), and water use control method (e.g., continuously running rinses vs. those controlled by conductivity controllers). Some of these factors are examined in this section.

The values in column 8 express water use in terms of production. These values are calculated as the average flow rate in gallons per square feet of “wetted surface.” The wetted surface area was calculated based on the total surface area of all layers of boards manufactured. Because these adjusted production-based flow rates account for multiple processing and rinsing steps, they are a good method of comparing water use among respondents.

Not suprisingly, the data indicate that overall water usage was related to the product mix of the shop, particularly the layer-count mix. Therefore, an adjusted, production-based flow rate was calculated. Comparing the adjusted production based flow rates, the range of water use among respondents is extremely wide; 8% of respondents reported water usage of over 250 gallons/layer-ft^2, whereas 69% reported water use of less than 75 gal/layer-ft^2.

A very sharp distinction can be drawn between the water use of larger and smaller shops. The largest 25 facilities in terms of production had water usage rates less than one-third that of all respondents. Since facilities that did not have formal data were encouraged to estimate their water usage, it is possible that some of the very high usage rates among the smaller shops are a result of poor estimation of either the production rate or water usage. Following this line of reasoning, it is also possible that the rates shown in Exhibit 4-1 for the largest 25 facilities are a more accurate estimate of true water usage by this industry sector.

There is a relationship between the adjusted production-based flow rates and the cost of water and sewer use. For facilities that have very high combined water and sewer costs, the adjusted production-based flow rates are very low. Variation of water and sewer use costs among survey respondents is likely due in part to geographical location, with higher costs in coastal and arid regions.

Exhibit 4-1. Water Use and Wastewater Discharge Data

Resp.
ID
Prod.
(board ft^2/yr)

Direct

In-direct

Zero
Avg Flow
(gpd)
Max. Flow
(gpd)
Flow
(gal/
layer-ft^2)
Cost of Water
($/Kgal)
Cost of Sewer
($/Kgal)Cost of Water & Sewer
($/Kgal) 36930A-X27,00000.951.452.40955099-
X120,000140,000nrnr12.4055595-X20,00022,500nrnr44486-
X100,000130,0001.620.792.41955703-X98,000108,0001.700.552.2513-
X30,00033,000 37-X10,00012,000
1.51.352.85154,000X13,50017,000516.2386,800X3,0004,00060.44.63.48.
003610,000X4008002.8 5410,625X80,000120,000477.5
5111,000X9,50011,700114.61.51.352.854112,000X230,000275,000618.30.71.1
21.82671015,000X10,56021,12012.01.503.505.002215,000X10,00018,00058.8
5715,000X40,00050,000
2.335.304816,000X12,00030,000102.61.342.363.701216,788X17,00024,0001
19.73.183.181717,000X18,00021,00076.3 1917,500X275,000310,000677.
61.2534.252818,000X40,00051,000260.32.352.795.144718,000X25,00032,000
44.52.661.44.065218,000X21,00032,00034.7
1120,000X32,50052,00061.12.242.875.114222,000X25,00040,00051.8
4522,500X25,00030,00049.60.002025,000X3,5005,00022.5
3525,000X31,00039,00076.93.23.817.013925,000X95,000115,000125.10.00
2726,480X25,00028,00051.7
2628,500X77,00080,000291.50.003129,500X60,00090,00056.31.230.792.02
1830,000X40,00042,00049.61.31.552.853330,000X45,00070,000197.955.00
4030,000X60,00090,00075.8
3433,000X70,00085,00076.31.290.51.795035,000X39,00050,00069.1
4435,625X35,00040,00077.43.53.501036,000X30,00033,00041.8

1636,000X200,000171.30.860.41.2694774540,000X13,00018,00028.61.501.50
3.004340,000X51,62872,28899.91.330.331.664465742,358X6,000180,0008.31.
982.294.274644,000X45,00060,00044.8
2345,000X130,000157.8213.002155,000X113,000175,000
2.80.63.402971057,000X74,000124,00091.2nrnr
50210060,000X35450.08nrnr
5564,500X168,900168,900192.31.212.613.825669,000X50,00065,00043.811.
005370,000X35,00040,00035.10.003271,064X215300
1.742.864.603248275,000X31,00054,00036.41.94nr1.942575,000X110,000130,
00036.9112.002975,000X34,000150,0007.833.002550390,000X5,0006,5009.
9nrnr 3693096,000X00nrnr 49120,000X64,00085,00099.0
965874175,000X21,00027,00016.91.721.032.75953880180,000X35,00045,00013.9
1.332.603.9333089200,000X16,00025,00011.61.322.283.60T3200,000X20,000
30,0006.2nr4.004.003470240,000X20,00030,0009.20.060.0643841250,000X38,
00050,0009.93.542.576.11279250,000X5,2005,5004.37.565.8213.3814250,000

30250,000X2.52.50237900273,000X105,000125,00015.61.430.612.042737
01280,000X25,00030,0008.61.411.352.7641739300,000X57,12565,00017.90.801.
602.40959951320,000X20,00030,0007.1nrnr
42692360,000X100,000125,00023.90.03nr0.03358000500,000X9,00012,0000.9nr
nr
43694500,000X30,00040,00011.61.000.781.7837817540,000X6,00011,0002.41.2
00.211.4142751540,000X140,000160,0007.01.603.104.70T2600,000X48,00062,4
004.21.612.704.31133000600,000X160,000200,00013.72.732.335.06T1936,000X
160,000185,0005.21.632.924.557405001,800,000X400,0001,000,0009.62.223.085.30
9465871,900,000X200,000250,0004.30.580.731.3130232,300,000X145,000160,000
2.23.785.249.02318383,000,000X280,000420,0002.31.851.903.754628003,750,000
X26,00031,0001.813.803.4017.201073005,000,000X250,000300,0006.31.501.963.46
Mean64,459—
8.20*1.602.283.18Median35,000—12.42*2.162.604.07
*For largest 25 shops.

Low water use rates can be achieved through the implementation of simple water conservation techniques and/or by using technologies such as ion exchange that recycle water. ID# 462800 has achieved the lowest production-based flow rate without the use of any sophisticated recycling technology. Rather, it uses flow controllers, rinse timers, and reactive or cascade rinsing.[3] The data also indicate that facilities that have implemented the ion exchange technology within their processes have a lower average flow rate than those that have not implemented this technology.[4]

The data also indicate that the use of water conservation methods does not always result in low water use. The four facilities with the highest production-based flow rates do not use ion exchange recycling, but they all indicated that they employ counterflow rinsing, plus some other methods of water conservation. In such cases, it is probable that water is simply being wasted by having unnecessarily high flow rates in the rinse tanks (e.g., flowing water during periods of non-production).

4.3 Good Operating Practices

Good operating practices are organizational and procedural activities that reduce the generation of waste. Generally, these are not equipment-oriented methods of waste reduction, although the implementation of some good operating practices can result in significant capital expenditures when implemented plant-wide. Many of the good operating practices identified will provide product quality improvements and operating cost reductions in addition to reducing waste generation. Also, they will generally improve the working environment of a shop, including health and safety aspects. Exhibit 4-2 contains the survey results for good operating practices.

Exhibit 4-2. Good Operating Practices

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[3] Water conservation methods such as these were covered in Section 6 of the PWB survey form. The responses to these questions are summarized in Section 6 of this report.

[4] Based on six facilities (ID#'s 25503, 3470, 43694, 37817, T1, 31838) that have installed ion exchange and have an average adjusted production-based flow rate of 5.4 gal/ssf, vs. an average for all facilities of 12.4 gal/ssf.

Drag-Out Reduction or Recovery Method	No. of PWB Respondents Using Method	% of PWB Respondents Using Method
Maintain records of analysis and additions	81	93.1
Perform in-house regular process bath analysis	80	91.9
Dump process baths based on analysis rather than schedules	74	85.0
Control inventory levels and access	72	82.7
Have preventive maintenance program for tanks	63	72.4
Conduct employee education for pollution prevention	62	71.2
Look for opportunities to reduce energy consumption	61	70.1
Have a formal policy statement regarding pollution prevention	53	60.9
Have a formal pollution prevention program	48	55.1
Have overflow alarms in process tanks	40	46.0
Have a leak detection system	20	23.0
Recycle non-contact cooling water*	1	1.1

*Added by respondent under “Other.”

4.3.1 Employee Awareness and Education

Employees are often the fundamental cause of waste generation and, conversely, they are in the best position to employ pollution prevention and control. Without employee cooperation, even the best efforts of management will be ineffective or futile (ref. 23). Of the 87 PWB facilities responding to the survey, 62 (or 71.2%) indicated that they conduct employee education for pollution prevention.

Employee awareness and education begins with a clear company policy with regard to the environment and plans for pollution prevention and control. The policy must be conveyed to the employees and reinforced in various ways in order to create a sufficiently positive attitude toward meeting the company's environmental goals.

There are three stages to instilling a pollution prevention attitude in employees and providing them with the knowledge needed to perform successfully. These are prior to job assignment, during job training, and on-going education throughout employment (ref. 40). This training should include the following elements:

- How, why, and where waste is produced and how to minimize it (e.g., good rinsing practices)
- Preventive maintenance methods that reduce waste generation (e.g., tank/liner inspection and repair)
- Company rules for handling process chemicals and making process (tank) additions
- Procedures for handling spills/leaks
- How to operate pollution prevention and control technologies in their working area
- Where to go for assistance with a non-routine problem
- Capabilities and capacities of waste treatment processes
- Environmental regulations and how they relate to the processes the employees operate
- Why pollution prevention is important (cost, regulations, health and safety, improved working environment, improved environment)
- How related waste management operating costs (e.g., chemicals, water, waste treatment, hazardous waste) impact employee wages

The advantages of establishing company rules and employee training will be reduced or eliminated unless the program has a method of measuring success and can deal with those who refuse to participate. Success should be quantified, whenever possible. This means companies should collect chemical use and waste generation data, maintain records, and periodically evaluate the records. Data collection and record keeping are discussed in Section 4.3.2.

One PWB company that was experiencing high HCl use (HCl bath serving as a microetch on a preclean line) implemented an education program that kept employees informed about process specific chemical and water costs. On their high production line, some incidents of misuse represented a cost of $2,000 to $5,000. By immediately informing the employees after each incident of high water/chemical use was detected, the incidents were brought under control in a matter of months and eventually were eliminated (ref. 41).

Bonuses, awards, plaques, and other forms of recognition are often used to provide motivation, and to boost employee cooperation and participation. In some companies, meeting waste minimization goals is used as a measure for evaluating the job performance of managers and other employees (ref. 42).

4.3.2 Chemical Tracking and Record Keeping

The major sources of pollution from plating operations are process chemicals. Process chemicals become pollution through both use and misuse, resulting in wastewater generation, spills/leaks, spent solutions, sludge, and air emissions. To be fully effective, a pollution prevention and control program must track and record chemical purchases, chemical use, and waste generation. The following is a list of chemical and waste data that merit consideration for record keeping (ref. 3):

- Chemical purchases
- Chemical inventory
- Bath analyses
- Process bath reformulations and chemical additions
- Partial tank discharges (i.e., decanting, bleed and feed) and total tank discharges (i.e., batch dumps)
- Water use per rinse tank or process line
- Total wastewater flow
- Wastewater treatment chemical use
- Spent process solution analyses
- Waste treatment sludge analyses
- Specific incidents of high chemical use

To increase the utility of the chemical use and waste generation data, corresponding production data should also be collected and recorded. These data can be used to identify variability of chemical use and waste generation that are due to production changes rather than operational practices. As discussed in Section 4.3.1, chemical use data should be shared with employees in an effort to educate them.

Several survey questions were related to chemical tracking and record keeping. Records of analyses and additions are kept by 93.1% of the shops. This item had the highest response for good operating procedures. In-house bath analysis is second with 91.9% of the shops. Controlling inventory levels and access is performed by 82.7% of the PWB shops.

4.3.3 Chemical Purchasing, Storage, Usage, and Handling

Proper purchasing, storage, usage, and handling of chemicals increases the percentage of raw materials that reach their intended process without spills, leaks, or other types of losses that could result in waste generation. Some basic guidelines for good operating practices include (ref. 40):

Purchasing:
- Standardization of materials (i.e., using the minimum number of materials in all operations). Many times the decision to use one material over another is based on operator preference, rather than on a technical or economic requirement. Written specifications can improve purchasing and reduce waste.
- Avoid over-purchase of materials.
- Avoid collecting free samples of process chemicals from vendors. Only accept amounts needed for testing purposes.

Storage:
- Utilize a dedicated/protected storage area.
- Space containers in storage areas to facilitate inspection.
- Label all containers.
- Stack containers according to manufacturers' instructions to prevent cracking and tearing from improper weight distribution.
- Separate incompatible materials in storage, such as cyanides and acids.
- Raise containers off the floor in the storage area to inhibit corrosion from sweating concrete.

Handling/Use:
- Establish written procedures for process (tank) formulation and additions.
- Use specifically assigned personnel to formulate baths and make tank additions.
- Perform routine bath analyses and maintain bath analysis logs and tank formulation/addition logs.
- Use process baths to the maximum extent possible (do not employ a dump schedule).
- Implement multiple use of certain materials.
- Implement statistical process control (SPC) to improve the efficiency of chemical use.

Survey results show that process bath dumps based on analysis rather than a schedule is performed by 85% respondents. Overflow alarms in process tanks are used by 46% respondents.

4.3.4 Preventive Maintenance

In general, preventive maintenance is an important element in operating and maintaining a PWB facility. With regard to pollution prevention, preventive maintenance can minimize chemical losses due to leaks and can reduce the potential for a catastrophic loss due to a tank failure. Specific areas where preventive maintenance can reduce pollution generation include:

- Periodic inspection of tanks and tank liners with replacement or repair of damaged or corroded units
- Regular replacement of seals on chemical pumps and filter systems
- Inspection and repair of racks, particularly focusing on loose coatings that can hide drag-out and copper nodules that can dissolve in process tanks
- Regularly checking tank bottoms for panels, fixtures and other materials that have fallen and will corrode

4.3.5 Leak/Spill Prevention and Control

Chemical losses from leaks and spills can equal or outweigh the losses due to routine production operations. If small leaks from pumps, filters or tanks go unnoticed or ignored over a long time, the overall loss can be very significant. Catastrophic losses, such as a tank failure caused by corrosion, will cause more immediate results. Several methods for reducing the potential of chemical losses from these sources were identified from the literature and survey. These include:

- Conduct preventive maintenance of pumps, filters, tanks, etc., as discussed in Section 4.3.4.
- Employ a controlled method of adding make-up water to process tanks (do not permit use of unattended hoses).
- Install overflow alarms on all process tanks and especially on tanks that are heated and require regular evaporative replacement.
- Install double-walled tanks and for added protection; install a sight tube that will indicate if a leak of the inner wall has occurred.
- Implement company rules for tank additions and other chemical transfers.
- Construct secondary containment with segregation that would permit reuse of spilled material. For example, install berms around process tanks, external filter systems, and pumps.
- Install pH, ORP, moisture sensors, and/or conductivity sensors with an associated alarm system in bermed areas, sumps, drain lines, or around treatment tanks.

Of the PWB facilities responding to the survey, 72.4% indicated that they have established a preventive maintenance program for tanks, and 23% use a leak detection system; 46% have installed overflow alarms in process tanks.

4.4 Drag-out Reduction and Recovery Methods

For the typical PWB shop, the drag-out of process solutions and the subsequent contamination of rinse waters are the major pollution control problems. This section explains the basic principles of drag-out theory and explores the function and applicability of the various drag-out minimization techniques in use today.

By reducing drag-out before it gets into the waste stream, less water is required to maintain clean rinses, water and sewer charges are reduced, and treatment costs are lowered by treating reduced volumes of water.

4.4.1 Drag-Out Reduction Principles

The viscosity of a plating process solution can be described as its resistance to flow or removal by another liquid (in this case, rinse water), caused by molecular attraction forces. The difference between high and low viscosity can be demonstrated with paint and water. A much thicker film will form on a knife dipped in paint than on one dipped in water. Paint, therefore, has the higher viscosity because of its cohesive and adhesive qualities.

Surface tension is another physical phenomenon that has a significant effect in the PWB shop. According to kinetic theory, molecules of a liquid attract each other. At the surface of a solution, such as a copper plating bath, the molecules are subjected to an unbalanced force because the molecules in the gaseous phase are so widely dispersed. As a result, the molecules at the surface are under tension and form a thin, skin-like layer that adjusts to create a minimum surface area. The property of surface tension causes liquid droplets to assume a spherical shape.

With the PWB chemical processes, the volume of solution that clings to a panel depends partly on surface tension. The force of surface tension appears to be most significant at the bottom edge of the part as it passes through and leaves the process solution. This force and the resultant volume of drag-out appear to be greatly affected by the orientation of the panel relative to the surface of the liquid (ref. 43).

The third factor that influences drag-out volume is the temperature of the process solution. Temperature is interrelated with viscosity and surface tension. As the temperature of a process solution is increased, its viscosity, surface tension, and, therefore, drag-out volume are reduced. A possible exception is when panels are withdrawn too rapidly from a hot process solution, evaporation concentrates the film and impedes drainage. This problem, however, can be overcome by reducing withdrawal time and using a fog spray rinse on the panels as they emerge from the process solution (ref. 44).

4.4.2 Drag-Out Reduction Techniques

Devices and procedures exist to successfully reduce drag-out. These techniques usually are employed to alter viscosity, chemical concentration, surface tension, velocity of withdrawal, and temperature. Also used are drag-out tanks and similar equipment for capturing lost plating solution and for returning it to the bath (ref. 45). Exhibit 4-3 shows the PWB facility survey results for drag-out reduction methods. Also shown in Exhibit 4-3 are the results of a similar survey conducted for the metal finishing industry during 1993-1994 (ref. 3). A comparison of survey results shows that most drag-out reduction methods are more common to one industry segment or the other. Several methods are found with similar regularity in both sectors. Some key differences between the industry sectors that affect P2 choices are discussed in this section.

Most drag-out reduction methods are inexpensive to implement and are repaid promptly through savings in plating and other PWB processing chemicals. An additional saving many times the cost of the changes is realized through decreased operating costs of a pollution control system. The reduced drag-out will decrease the need for treatment chemicals and, subsequently, the volume of sludge produced.

For some process solutions, return of drag-out may be impractical. In the case of process baths that become steadily contaminated by use, the return of drag-out would simply increase the frequency of dumping (ref. 45).

Exhibit 4-3. Drag-Out Reduction and Recovery Methods Data — Survey Results

Drag-Out Reduction or Recovery Method	No. of PWB Respondents Using Method	% of PWB Respondents Using Method	% of Plating Shops Using Method*
Allow for long drip times over process tanks	29	76.3	60.4**
Have drip shields between process and rinse tanks	23	60.5	56.9
Practice slow rack withdrawal from process tanks	20	52.6	38.1**
Use drag-in/drag-out rinse tank arrangements	13	34.2	20.8**
Use drag-out tanks and return contents to process baths	13	34.2	61.0**
Use wetting agents to lower viscosity	12	31.6	32.4
Use air-knives to remove drag-out	10	26.3	2.2**
Use drip tanks and return contents to process baths	4	10.5	27.0**
Use fog or spray rinses over heated process baths	4	10.5	18.9**
Operate at lowest permissible chemical concentrations	3	7.9	34.6
Operate at highest permissible temperatures	2	5.2	17.9

*Results published in reference 1.
**Data are for manually operated methods, which are the predominant type for the plating operations surveyed during the NCMS/NAMF project.

4.4.2.1 Minimizing Drag-Out Formation

Drag-out of various processing baths into subsequent rinses is a significant source of pollution in a PWB shop. The amount of pollutants contributed by drag-out is a function of factors such as the design of the racks carrying the parts to be plated and plating procedures. As previously discussed, several interrelated parameters of the process solution, including the concentration of process chemicals, temperature, viscosity, and surface tension, also impact pollution levels.

Many devices and procedures can be used successfully to reduce drag-out. These techniques are usually employed to alter those important and interrelated process solution parameters.

Controlling Plating Solutions. As a rule, as the chemical content of a solution is increased, its viscosity increases. Increased viscosity contributes not only to a large volume of drag-out, but also to a higher chemical concentration of drag-out. The consequent need for more rinse water creates additional pollution control problems. Process baths can often be operated at significantly lower concentrations than those recommended by chemical manufacturers. This practice received the lowest response rate on the survey; only 8% reduce bath concentrations to lower drag-out rates.

For years wetting agents have been used in process solutions as an aid to drag-out reduction. Survey results indicate that wetting agents are used by 32% of the PWB survey respondents. A wetting agent, usually a surfactant, reduces the surface tension of a liquid causing it to spread more readily on a solid surface. A typical plating bath solution has a surface tension close to that of pure water at room temperature or about 0.0050 lb/ft. The addition of very small amounts of surfactants can reduce surface tension considerably--to as little as 0.0017 to 0.0024 lb/ft. (ref. 43). Further additions of the wetting agent will not lower the surface tension appreciably beyond this point (ref. 46).

Kushner (ref. 43) estimates that the use of wetting agents will reduce drag-out loss by as much as 50 percent, although no test data or other quantitative information are presented. For plating baths, he recommends the use of non-ionic wetting agents, which are not harmed by electrolysis. PWB facilities contemplating the use of a wetting agent for drag-out reduction should conduct experiments to determine their potential benefit before implementation. In addition, facilities should investigate the compatibility of a wetting agent with the bath chemistry before use. Some process baths can only tolerate certain products (ref. 49).

Workpiece Withdrawal. The velocity at which work is withdrawn from the process tank has a major effect on drag-out volume. The faster an item is pulled out of the tank, the thicker the drag-out layer will be, because viscosity forces do not have a chance to operate and a much larger volume of liquid will cling to the surface (ref. 46). For this reason, an automatic machine that performs smooth, gradual withdrawal will usually drag-out less solution per item racked than will manually operated equipment.

In a study by the U.S. EPA, slowing the rate of withdrawal significantly reduced the amount of drag-out. The drag-out on a microetch bath was reduced by 45 percent (12.1 ml/ft^2 to 6.7 ml/ft^2) by adjusting the withdraw rate of an automatic unit from 100 ft/min to 11 ft/min (see Exhibit 4-4). A 50 percent reduction was achieved on an electroless copper bath (6.0 ml/ft^2 to 3.0 ml/ft^2) by reducing the withdraw rate from 94 ft/min to 12 ft/min (see Exhibit 4-5) (ref. 48). Less drastic changes to the withdrawal rate can be implemented without sacrificing waste reduction by combining and optimizing the effects of reducing part withdraw rates and increasing the draining time over the tank. The additional processing time needed to achieve a substantial reduction in drag-out loss is typically small in comparison to the overall production time. For the case study, the additional 16 to 17 seconds of withdraw/drain time was considered negligible in comparison to the total production time of 60 min. through the sensitize line. Also, minor modifications to other parts of the process can usually be made to off-set any increases due to waste minimization changes.

Exhibit 4-4. Summary of Micro-Etch Results

Experimental Conditions	Withdraw Rate (ft/min.)	Time of Withdraw (sec.)	Drain Time (sec.)	Total Time (sec.)	Drag-Out (ml/ft^2)
Baseline	100	1.7	3.4	5.1	12.1
Modification 1 slower rate of withdraw	11	14.9	2.5	17.4	6.7
Modification 2 longer drain time with intermediate withdraw rate	40	4.3	12.1	16.4	7.1

Exhibit 4-5. Summary of Electroless Copper Results

Experimental Conditions	Withdraw Rate (ft/min.)	Time of Withdraw (sec.)	Drain Time (sec.)	Total Time (sec.)	Drag-Out (ml/ft^2)

Baseline	94	1.8	5.2	7.0	6.0
Modification 1 slower rate of withdraw	12	13.9	3.2	17.1	3.0
Modification 2 longer drain time with intermediate withdraw rate	40	4.3	11.9	16.3	2.9

The survey indicates that 20 facilities (or 52.6% of the respondents) practice a slow rack withdrawal to reduce drag-out formation.

Drag-out can also be reduced by altering the position of panels as they are withdrawn from a process solution. Panels racked with an angular orientation will drain much faster than those racked perpendicular to the solution.

4.4.2.2 Direct Drag-Out Return

Commercially available equipment for the recovery of plating bath chemicals includes types that apply such principles as ion exchange, reverse osmosis, electrodialysis, and evaporation. These devices usually are applied to a single operation, such as copper electroplating, where they concentrate the salts in the rinse water, return them to the plating bath, and recycle the purified water to rinse tanks (ref. 3).

Although effective, these recovery technologies are capital intensive. Before the purchase of such equipment, PWB manufacturers should evaluate use of simple methods of drag-out recovery that require much less capital and are simpler to operate. After implementing these methods and establishing new drag-out conditions, PWB facilities can consider the applicability of additional recovery through commercially available units (ref. 3). This section describes methods that directly return the drag-out to the process tank. In the following section (Section 4.3.2.3), methods are described to recover the drag-out in tanks and then return it to the process bath.

Draining/Rinsing Over the Plating Tank. After a rack or basket is removed from a process tank, the drag-out drains from the item and it returns directly to the bath, as long as the item is held over the tank. This simple method of direct drag-out return can be maximized on a hand-line by installing a bar over the process line on which the operator can hang a rack or hook. On automatic machines, the unit can be programmed to increase dwell time above the process tank. Dramatic results from this simple method of waste minimization have been documented (ref. 48). Allowing a longer time above the process tank for the solution to drip from the panels is used by 76% of the survey respondents. Simple and effective, it is the most commonly practiced drag-out reduction procedure cited by the survey respondents.

Allowing the drag-out to dry on the panel can cause staining, peeling, passivation, or it may prevent complete rinsing. To increase the drag-out removal rate over the process tank, rinsing with small amounts of water can be employed. The amount of water that can be used will depend on the water balance for a given process tank. The water balance is affected mostly by evaporation. Process solutions operated at temperatures greater than 120°F often have sufficient surface evaporation such that rinsing can be performed over the tank. However, using this method may reduce or eliminate the potential benefit from other drag-out recovery methods (e.g., use of a drag-out tank).

Rinsing over the tank can be performed by flood rinsing (e.g., hose), spray rinsing, or fog rinsing. The use of flood rinsing is not practical except for very high temperature baths with high drag-out rates. Spray rinsing uses less water than flood rinsing. With the proper selection of spray nozzles, this can be a very efficient method of direct drag-out return. Nozzle selection should consider flow rate, spray velocity, and spray pattern. Air-assisted sprays are also utilized, which are generally more efficient than plain water sprays. Sprays can be hand-held or mounted on the tank rim. For automatic plating machines, the sprays can be controlled to operate only when the part exits the bath by installing photosensitive cells that detect part movement.

Fog rinsing is used at exit stations of process tanks. A fine fog is sprayed on the work, diluting the drag-out film and causing a run-back into the process solution. Fog rinsing is applied when process operating temperatures, high enough to produce a high evaporation rate, allow replacement water to be added to the process in this manner. Fog rinsing prevents dry-on patterns by cooling the panels, but it may preclude the use of a drag-out tank as a recovery option. For fog rinsing to be effective, work must be withdrawn from the process tank at a slow rate. From the PWB facility survey, fog rinsing is used by only 10.5% of the respondents.

Fog/spray rinsing over the bath has potential drawbacks and problems. Fog/spray rinsing may be messy, or worse, may cause splashing on nearby workers. Nozzles require frequent maintenance (i.e., unplugging) and must be occasionally repositioned to point in the correct direction.

Other Methods of Direct Drag-Out Return. The following are miscellaneous methods of direct drag-out return that are not discussed elsewhere in the report.

A drain board or drip shield is a tilted surface placed between process and rinse tanks that catches the drips from racks or barrels as they are transferred between tanks, thus preventing the drag-out from falling to the floor. The solution on the drain board returns to its original tank by gravity flow. The drain surface can be plastic or metal. For acid solutions, the best materials are vinyl chloride, polypropylene, polyethylene, and Teflon®-lined steel. Stainless steel should be used for hot alkaline solutions. It is important that the drain surface be positioned at an angle that allows the process solution to return to the bath (i.e., rather than the subsequent rinse) (ref. 6). Drain boards or drip shields are used by 60.5% of the survey respondents and is the second most frequently used method of drag-out reduction or recovery.

Another direct drag-out return method, the air knife, is a device that blows an intensive air stream at a rack as it exits the bath causing the drag-out to be blown off. The use of air knives is limited due to the potential to dislodge parts from racks and the drying effect of the air stream, which may cause staining, passivation, etc. Concerning the second limitation, Altmayer suggests that if the air is humidified to near saturation, drying will not occur (ref. 49). Air knives are used by 26.3% of the facilities responding to the survey. In a PWB shop, air knives are commonly found at the end of conveyorized equipment where low pressure air is used to blow or dam excess fluid off of the surface of horizontally transported panels.

4.4.2.3 Drag-Out Recovery and Return

Drip Tank. A drip tank is an ordinary rinse tank that, instead of being filled with water, simply collects the drips from racked panels after chemical processing and before rinsing. The drip tank is useful with work that involves continuous dripping over a period of time. When a sizable volume of solution has been collected in the drip tank, it can be returned to the process bath. Because drag-out is not diluted with water when using a drip tank, this technique is especially applicable to lower temperature process solutions (ambient to 120°F).

Using a drip tank will restrict the use of an additional rinse tank, when floor space is limited. An additional rinse tank, used as a drag-out tank or in a counterflow arrangement, is usually much more beneficial than a drip tank since a drip tank only recovers the drag-out that freely flows off the part/rack. The determining factors are the volume of drag-out, part configuration (i.e., drainability), and the evaporation rate in the process tank. Drip tanks are used by 10.5% of the survey respondents.

Drag-Out Tank. The drag-out tank is a rinse tank that initially is filled with pure water. As the PWB chemical processing line is operated, the drag-out rinse tank remains stagnant and its chemical concentration increases as more work is processed. Air agitation is often used to aid the rinsing process because there is no water flow within the tank to cause turbulence. The presence of a wetting agent is also helpful, according to Kushner (ref. 43). After a period of operation, the solution in the drag-out tank can be used to replenish the losses to the process bath. If sufficient evaporation has taken place, a portion of the drag-out tank solution can be added directly to the process bath (e.g., using a transfer pump). Thirty-four percent (34%) of the survey respondents indicated that they use drag-out tanks.

As a rough estimate, drag-out recovery will reduce drag-out losses by 50 percent or more (ref. 3, 10). The efficiency of the drag-out tank arrangement can be increased significantly by adding a second drag-out tank. Use of a two-stage drag-out system usually reduces drag-out losses by 70 percent or more. In some cases, multiple drag-out tanks (e.g., three to five tanks) can be used to completely close the loop and return essentially 100 percent of drag-out (ref. 3).

The drag-out rate and evaporation rate are the key parameters that determine what percentage of the drag-out can be recycled back to the process tank. Various mathematical formula have been used to estimate the recovery rate (ref. 50, 51). Exhibit 4-6 presents estimates for common conditions that can be used in lieu of the more complex equations.

Exhibit 4-6. Drag-Out Tank Recovery Rates for a Range of Common Conditions

Number of drag-out tanks	Drag-out Recovery Rate, % Evaporation to drag-out ratio (1 to 5)				
	E/DO=1	E/DO=2	E/DO=3	E/DO=4	E/DO=5
1	50.0	66.7	75.0	80.0	83.3
2	66.7	85.7	92.3	95.2	96.8
3	75.0	93.3	97.5	98.8	99.4
4	80.0	96.8	99.2	99.7	99.9
5	83.3	98.4	99.7	99.9	100

The transfer of solution between drag-out tanks and the process tank and the addition of fresh make-up water to the system can be accomplished in several ways. Ryder (ref. 52) recommends that transfers to the plating tank be accomplished using a small pump (magnetic drive, seal-less types), which is activated by a "dead-man" switch. The dead-man switch only permits solution transfer while the switch is depressed. If the operator leaves, the solution transfer automatically stops, which prevents catastrophic tank overflows. For adding make-up water, Ryder suggests using a level-controlled valve (local float controlled) in the first rinse. When the solution level in the first rinse is lowered (i.e., after solution is transferred to the plating bath), the float switch is activated and fresh water is added to the final rinse. Ryder further suggests the use of a water control valve on the inlet water line for shut-off during non-operating periods.

The use of an automatic drag-out return system was described by Roy (ref. 53). In this system, chemical metering pumps were used to return drag-out from the rinse tank to a plating tank. The pumps were controlled by a level sensor in the plating tank.

With multiple rinse tank arrangements, the transfer of solution from rinse tank to rinse tank can be accomplished in the same manner as a flowing counterflow rinse system. These are discussed in Section 4.5.

It should be noted that although drag-out reduction can be a very effective means of pollution prevention, it may also present the PWB manufacturer with a new set of problems. In particular, reducing drag-out reduces the purging of bath contaminants. The contaminants are contributed to process baths mainly by a breakdown of process chemicals and low concentration constituents in the fresh water (e.g., hardness). Other sources include: cross contamination due to transporting dripping racks over tanks, corrosion of bus bars, racks, anodes, tanks, etc., and airborne contaminants. This contamination may also lead to another problem--staining of the panels after the drag-out rinse.

To minimize the impact of contaminants, platers must do one or both of the following: (1) treat the raw rinse water prior to use with ion exchange and/or reverse osmosis technologies, or (2) perform bath maintenance. Bath maintenance technologies are discussed in Section 5.

Drag-out tanks can be placed in series to completely recover process chemicals and rinse water, as suggested by the estimates in Exhibit 4-6. This is achieved by balancing the introduction of rinse water with the evaporation rate of water from the process tank. One author suggests that aqueous developer and stripper processes can be operated in a similar manner. In these cases, rinse water flow is balanced with developer/strip solution feed systems rather than with evaporative losses. The author suggests that two chemical supply tanks be used, one serving as a makeup tank and one as the on-line supply tank. The rinse water should be directed back to the makeup tank. Periodically, based on level, a concentrated carbonate or hydroxide solution can be added to convert the rinse water to develop or strip solution. The solution is mixed and transferred back to the supply tank. Conductivity controllers can be used to ensure proper concentrations (ref. 41).

It is interesting to note that drag-out tanks are used more frequently by metal finishing facilities than by PWB facilities (61% vs. 34%) (see Exhibit 4-3). A higher sensitivity to contaminant build-up may, in part, explain this disparity. In addition, PWB process lines are long and room considerations are often cited as a limiting factor for drag-out tanks. For example, a typical electroless copper line may include over 20 tanks (including counterflowing rinses) without any drag-out tanks at all. Nevertheless, several tanks in this line are excellent candidates for drag-out recovery, including the heated cleaner-conditioner and the copper-rich micro-etchant baths. The electroless copper bath itself is an example of a poor candidate for drag-out recovery. This bath accumulates contaminants from chemical decomposition and requires frequent additions, which are usually accommodated with bailouts.

Drag-out tanks can be combined with counterflow rinsing to provide both chemical recovery and flow reduction. Combinations of rinse configurations are discussed in Section 4.5.3.5.

Drag-In/Drag-Out Rinsing. Drag-in/drag-out rinsing (also referred to as double-dipping) involves rinsing in the same solution before and after plating. This can be achieved by using a single rinse tank or two hydraulically connected rinse tanks, usually located on opposite sides of the process tank. In the latter case, which is most applicable to automatic plating machines, the rinse water is recirculated between the two rinse tanks using a transfer pump to maintain equal concentrations of chemicals in the tanks.

The advantage of a drag-in/drag-out arrangement is that plating chemicals rather than pure rinse water are transferred into the process tank by incoming racks and panels. This increases the recovery efficiency of the recovery rinse.

The drag-in/drag-out system finds application with plating baths that have a low to moderate evaporation rate and especially with baths that tend to increase in volume (i.e., equivalent to a negative evaporation rate). This condition, referred to as "solution growth," occurs when the volume of drag-in (water from the preceding rinse) can be greater than the sum of drag-out and evaporation. The recycle ratio, which determines recovery efficiency, is calculated as the volume of recycled rinse plus the volume of drag-out divided by the volume of drag-out. The recycle ratio, therefore, is greater with a drag-in/drag-out system than a common recovery tank. If the evaporation rate is low, the difference between the recycle ratios for common recovery and drag-in/drag-out systems is significant. When evaporation ratios are high, the difference is less. Generally, the use of a drag-in/drag-out arrangement will increase the recovery rate by 25 to 40 percent (ref. 3). As with drag-out tanks, the drag-in/drag-out arrangement can result in bath contaminant buildup. It also creates an extra labor step and will lengthen the process time.

4.5 Rinse Water Use Reduction

Although the plating industry as a whole has significantly reduced water use during the past 10 to 15 years, many plating operations can further reduce water use by improving the efficiency of their rinsing operations. The advantages of reducing water use include:

- Lowering operating costs by reducing the size of water bills.
- Reducing the quantity of treatment chemicals used (treatment chemical use is mostly dependent on the mass of contaminants, but a portion of treatment chemical use is related to hydraulic loading; see Section 6 which covers end-of-pipe treatment.
- Potentially improving the removal efficiency of waste treatment systems.
- Reducing the needed size of future end-of-pipe treatment systems and certain types of recovery technologies.

A summary of the survey data relative to methods for reducing rinse water use is presented in Exhibit 4-7.

Exhibit 4-7. Rinse Water Use Reduction Methods Data

Drag-Out Reduction or Recovery Method	No. of PWB Respondents Using Method	% of PWB Respondents Using Method	% of Plating Shops Using Method
Use counterflow rinses	31	81.2	68.2
Use flow controllers	30	78.9	69.8
Use spray rinses	27	71.1	39.0
Track water use with flow meters	25	65.7	11.6
Reactive or cascade rinsing	20	52.6	23.9
Use rinse timers	19	50.0	11.3
Recycle or reuse rinse water	11	28.9	--
Use conductivity or pH controllers	10	26.3	16.0
Use part sensors to activate rinse*	4	10.5	--
Use squeeze rollers to remove water*	1	2.6	--
Use spring-loaded valves to activate rinse*	1	2.6	--

*Added by respondent under “Other.”

Central to the reduction of rinse water use is the required quality of water used in rinsing. Simply reducing the flow rate of water in a rinse system, without regard to water quality, may cause loss of product quality or appearance or it may cause the contamination of the next tank in the plating sequence. Various rinse water quality criteria are presented in the literature.

Various methods of water use reduction have been identified in the literature and throughout the survey. These methods have been categorized into three groups: (1) optimizing the rinse tank design; (2) controlling the rate of rinse water use; and (3) using alternative rinsing configurations. The following is a discussion of each group.

PWB facilities practiced all rinse water use reduction methods more frequently than plating shops. While counterflow rinses and flow controllers were common in both types of shops, rinse timers, spray rinsing, flow meters and reactive/cascading rinses were far more prevalent in PWB shops. One explanation could be the presence of conveyorized equipment in nearly all PWB facilities such as etchers and resist developers, both of which commonly employ spray rinsing chambers, and etchers, are commonly equipped with cascading rinse chambers. Such equipment may also be equipped with flow meters.

4.5.1 Optimal Rinse Tank Design

The key objectives with regard to optimal rinse tank design are to attain fast removal of drag-out from the part and complete dispersion of the drag-out throughout the rinse tank. When these objectives are achieved, the time necessary for rinsing is reduced and the concentration of contaminants on the part when it leaves the rinse tank are minimized for a given rinse water flow rate. The following are rinse tank design elements that help to achieve fast drag-out removal and complete mixing. These methods can be combined to develop an optimal rinse tank design for a given workload.

- Select the minimum size rinse tank in which the parts can be rinsed and use the same size for the entire process line.
- Locate the water inlet and discharge points of the tank at opposite positions in the tank to avoid short-circuiting.
- Use a flow distributor/sprayer to feed the rinse water evenly.
- Use air agitation, mechanical mixing, or other means of turbulence.
- Use spray rinsing.
- Use ultrasonics, where applicable.

4.5.2 Controlling the Flow Rate of Rinse Water Use

Water use reduction can be achieved by coordinating water use and water use requirements, regardless of the type of rinse tank arrangement employed (e.g., single overflow, counterflow). When these two factors are perfectly matched, the rinse water use for a given work load and tank arrangement is optimized. Four methods of coordinating water use and water requirements were identified during the survey and literature search. Each of these methods is discussed in the following subsections. Some methods are applicable to a range of chemical processing operations while others are more relevant to specific conditions (e.g., small manual operations, large automated machines). Some of the methods can be combined to optimize water use.

4.5.2.1 Flow Restrictors

Flow restrictors are inexpensive devices that are connected in-line with the tank's water inlet piping to regulate the flow of water through the pipe. They are typically an elastomer washer that flexes under pressure such that the higher the water pressure, the smaller the hole available for flow passage. Therefore, they maintain a relatively constant flow under variable water pressures. Flow restrictors are available in a wide range of sizes (0.1 gpm to more than 10 gpm). The smaller sized restrictors are most commonly used with multiple counterflow rinse tank arrangements and the larger ones are commonly used with single overflow rinses. Some restrictors aerate the water as it passes through, in a manner similar to a kitchen faucet (venturi effect).

Flow restrictors are applicable to nearly all rinse systems. A possible exception is a rinse tank equipped with a conductivity controller (see Section 4.5.2.3). With conductivity controllers, the instantaneous water flow rate is unimportant, since the controller stops water flow based on the low conductivity set point of the controller and the conductivity of the water in the rinse tank. Therefore, restricting the flow will only increase the time needed to dilute the rinse water to the conductivity set point and will not affect the total volume of water used.

Flow restrictors as a stand-alone method of rinse water control are only effective with plating lines that have constant production rates, such as automatic plating machines. Even in such cases, to use water efficiently, the plater must have a means of stopping water flow during non-production periods. With variable production rates, flow restrictors alone will not provide the necessary coordination of rinse water need and use. One method for improving this coordination is to install a timer rinse control (see Section 4.5.2.4).

Generally, the size of a flow restrictor is selected to provide adequate rinsing for all parts. This means that the maximum rinse water flow requirement is the governing factor and that on the average, the flow will be higher than necessary for good rinsing. This fact is a sufficient reason for supplementing the control provided by a flow restrictor.

Flow restrictors are widely used by the respondents to the survey (79%).

4.5.2.2 Manual Control of Water Flow

Manual control of water flow simply refers to manually opening and closing water valves to adjust flow or to turn the water flow on or off. This method of control is obviously dependent on the operator and usually results in inconsistent water use.

Combining manual control with flow restrictors reduces the variability of water flow; however, it does not address the problem of water use during idle production periods. Manual control can be improved by installing a main water valve for an entire plating line that stops water flow to all rinse tanks in that line.

4.5.2.3 Conductivity Controls

These units consist of a probe or sensor located in the rinse tank that senses the conductivity of the rinse water, a transformer box that houses the solid state circuitry that controls the system, and a solenoid valve that opens and closes in response to signals from the circuitry. In use, when drag-out is introduced to the rinse tank, the probe senses a rise in conductivity above a set-point, which is picked up by the circuitry, and the solenoid water valve is opened. The valve remains open until the probe senses a drop in conductivity below a set-point. The set-points are operator-adjustable to permit use over a range of desired water qualities.

Conductivity rinse controls have been effectively used to reduce rinse water use. However, in some cases, they have been removed from service due to maintenance problems (ref. 3). The results of the survey show a moderate level of usage for conductivity controllers (26%).

The use of conductivity controllers does have some problems. First, operators who object to the appearance of a controlled rinse, which may be less clear than a free-flowing rinse, have been known to override conductivity controllers. Operators often override the units by placing the probe into a process tank or a bucket of process solution (i.e., causes solenoid to remain open). This problem can be controlled by shortening the length of the probe's cable or by running the cable through a PVC pipe (if using the latter method, be certain the piping arrangement permits access to the probe for periodic cleaning). Second, the controllers do not sense non-ionic contaminants and rinse tanks may become contaminated with particulates such as dust. Third, the units require frequent preventive maintenance to remain operable.

A new electroless sensor controller (induction type) provides some advantages over the conventional type described above. Due to the design of the new units, they are less likely to foul than the conventional controllers. The hardware cost of the new units is substantially higher ($1,140 vs. $290 for the conventional type) (ref. 54).

4.5.2.4 Timer Rinse Controls

Timer rinse controls consist of a push-button switch and timer mechanism and a solenoid valve. These units operate in a manner similar to conductivity controllers; however, rather than regulating rinse water flow on the basis of rinse tank water quality, the timer controls simply turn water on and off based on a pre-set time period.

In operation, a plater lowers parts into the rinse tank and pushes a button (alternatively, a momentary or photoelectric switch could be used that is activated by lowering a rack). The button or switch activates a timer and opens the solenoid valve for a preset time period. After that time period has expired, the solenoid valve automatically closes.

The timer setting is selected through trial and error. It is best to select a time period that provides consistently clean rinse water, without excessive waste. Once set, the time period is not changed unless the general trend of production changes. Timers are being used by 50% of the survey respondents.

4.5.2.5 Flow Meters and Accumulators

These devices by themselves do not reduce water use. However, they make the PWB manufacturer aware of water use rates and are useful in identifying excessive water use.

Flow meters and accumulators are most useful when installed on fresh water lines feeding individual rinse tanks or, at a minimum, on pipes feeding individual process lines (e.g., electroless copper). Meter readings taken over an extended time period will show trends in water use. Using these data, facility management can identify specific locations where excessive water use occurs and can correct the problem before long-term wastage has resulted.

4.5.3 Rinsing Methods

4.5.3.1 Counterflow Rinsing

PWB facilities have long reduced water use by employing several rinse tanks connected in series. Fresh water flows into the rinse tank located farthest from the process tank and overflows, in turn, to the rinse tanks closer to the process tank. This technique is termed counterflow rinsing because the work piece and the rinse water move in opposite directions. Over time, the first rinse becomes contaminated with drag-out and reaches a stable concentration that is lower than the process solution. The second rinse stabilizes at an even lower concentration and uses less rinse water than if only one rinse tank was in place. The more counterflow rinse tanks (three-stage, four-stage, etc.), the lower the rinse rate needed for adequate removal of the process solution.

Counterflow rinsing systems are not without drawbacks. The negative aspects of counterflow rinsing include the cost of additional rinse tanks, loss of valuable production space, and an increase in production time/labor.

The rinse rate needed for adequate cleaning is governed by an exponential equation that depends on the concentration of process chemicals in the drag-out, the concentration of process chemicals that can be tolerated in the final rinse tank, and the number of counterflow rinse tanks. The mathematical rinsing models are based on complete rinsing (i.e., removal of all drag-out from the part/fixture) and complete mixing (i.e., homogeneous rinse water). These conditions are not achieved or even approached unless there is sufficient residence time and agitation in the rinse tank. More typically, each added rinse stage reduces rinse water use by 50 percent.

Eighty-one percent of the survey respondents employ counterflow rinsing. This is a greater percentage than for any other method of reducing rinse water usage.

4.5.3.2 Cascade, Reactive, and Dual Purpose Rinsing

Cascade rinsing refers to the practice of reusing rinse water multiple times in different rinse tanks for succeeding less critical rinsing. Reactive rinsing is similar, but it refers to cases where a chemical reaction takes place because of using the rinse water for multiple purposes. Various cascade rinsing schemes are employed in the PWB industry. Poskanzer provides an example for an electroless line that is described in Exhibit 4-8 (ref. 55, 56). In this example, there is a double counterflow rinse after each process step. In four cases, the discharge from a rinse tank is reused in another rinse system. The author suggests that this scheme will reduce water use by 40% to 50% for the electroless copper line.

Dual purpose rinsing refers to the practice of using the same rinse tank for rinsing following more than one process tank. It provides essentially the same results as cascade and reactive rinsing but uses a fewer number of rinse tanks. Often, the employment of dual purpose rinsing means transporting a dripping rack/part over a considerable distance. This can result in dripping onto floors and/or the accidental contamination of other tanks. An exhaustive evaluation of dual purpose rinsing is presented by Mohler (ref. 57). Mohler presents methods and guidelines for ascertaining the accumulated concentration of chemicals in counterflow, dual-purpose rinses in order to determine the feasibility and economics of this technique.

Use of any of these methods must closely consider the combined chemistry in the rinse tank to prevent undesirable reactions that may impact worker safety (e.g., harmful vapor) or work quality (e.g., precipitation of solids).

Reactive or cascade rinsing is used by 66% of the survey respondents to reduce water usage.

4.5.3.3 Chemical Rinsing

The technique of chemical rinsing has been used by the metal finishing industry for many years. Lancy and Pinner have described the application of chemical rinsing to plant effluent treatment, known in the industry as integrated waste treatment (ref. 3). Aside from the environmental benefits, this type of rinsing also prevents the majority of heavy metal solids formed in the chemical rinse from reaching the succeeding water rinses by removing these materials in an external settling vessel. Removal of these solids is accomplished by flowing the chemical rinse solution to a treatment reservoir. The overflow from the reservoir is pumped back to the rinse tanks, forming a complete closed-loop system. Integrated treatment gained some popularity in the 1970's, but is believed to be in little use today, mostly due to high maintenance requirements.

In general, the long pre-treatment process lines and the high sensitivity to contamination limit the opportunity for chemical rinsing in a PWB shop.

4.5.3.4 Spray Rinsing

Spray rinsing is employed in various manners to reduce drag-out losses and rinse water use. Spray rinsing over process tanks (Section 4.4.2.2) provides direct recovery of drag-out. Spray rinse tanks can be used as drag-out tanks, single rinses, or multiple rinses.

A common use of spray rinsing is to substitute a spray rinse tank for an overflow rinse tank. Depending on the racking configuration, spray rinsing generally uses from one-eighth to one-fourth the amount of water that would be used for equivalent dip rinsing (ref. 3).

Combined spray and dip rinse tank designs are employed where the bottom portion of a rinse tank acts as a dip tank and the upper portion a spray rinse. A weir is located at approximately the middle of the tank which maintains the solution level in the tank. In operation, the rack is lowered into the dip rinse, raised above the solution level, and sprayed with fresh water. This combination rinse can be nearly as effective as a counterflow rinse, but takes up the floor space of one tank.

The design of spray rinses must consider the size and shape of the part. Spray nozzles are available in many sizes and spray patterns, and should be selected appropriately. Usually, the pressure in the waterline is sufficient to operate an effective spray rinse; however, higher spray velocities can be obtained by pumping.

A special application of the spray rinse is a patented unit that contains five to seven progressively cleaner rinse solutions in separate compartments (ref. 58). The solutions are successively pumped (up to 20 gpm) to a spray rinse tank and drain back to the unit. During each cycle, only the water use in the first spray is discarded or processed for recovery. The subsequent sprays are collected for reuse in the following cycles. The advantage of this unit is that it provides the effect of multiple counterflow rinsing with use of a single rinse tank. The floor space requirement of the unit is 7.5 square feet (five stage rinse unit) or 11.0 square feet (seven stage rinse unit).

The survey indicates that 71% of the respondents are using spray rinsing, making it the third most frequently used method for reducing water use.

The prevalence of spray rinsing in PWB facilities is due in part to presence of conveyorized spray rinsing found in resist developers and etchers. For these machines, there is essentially no automated alternative to spray rinsing. Furthermore, in the case of resist development, the effects of relatively high pressure spray are required to adequately remove developer and resist residues from the surface of the copper panel.

Specific spray patterns are often required in PWB processes. Many systems use water pressure to produce the desired pattern. A more efficient and cost effective alternative is to use an off-line tank with a recirculating sump. A pump can create the pressure needed to establish the desired pattern, while using a fraction of the water for a conventional spray system.

Combined spray and immersion (i.e., overflow) rinse systems are employed at some PWB facilities to reduce water use. One facility uses a pulsed spray system in the first rinse tank following a process tank and a conventional overflow rinse arrangement in the second rinse tank. Flow from the second rinse tank is used as makeup in the first rinse tank. With this system, drag-out dwell times are set at 20 sec., the sprays at 20-30 sec. (with 5 sec. side to side activated pulse), and overflow rinse at 20 sec. to 2 min. This system has reduced water use on the affected lines by 70% from that used with simple overflow rinses (ref. 59).

4.5.3.5 Combined Drag-Out Loss/Rinse Water Reduction Rinsing Arrangements

Some PWB facilities combine drag-out tanks and overflow rinsing in the same rinse systems. For example, a four rinse system could consist of two drag-out tanks connected in series and two free-flowing rinses connected in series (counterflow). Alternatively, the system could consist of three drag-out tanks in series and a single overflow rinse or a drag-in/drag-out arrangement and two counterflow rinses. Various rinsing configurations can also be combined with chemical recovery technologies, as discussed in Section 5. The optimal rinse configuration will depend on numerous factors including:

- The evaporation rate in the process tank
- The drag-out rate
- The rinse water quality requirement (final rinse)
- Process chemical costs
- Alternative technology recovery costs
- Water costs
- Wastewater treatment/sludge disposal costs

In general, when more of the available rinse tanks are used as drag-out tanks, the process chemical and wastewater treatment operating costs are lowered and water use costs are increased. The reverse is true when more tanks are used for counterflow rinsing than for drag-out recovery tanks.

The optimal configuration can be determined through mathematical means, which must be supported by data collection (i.e., drag-out and evaporation measurements, production rates, etc.) for producing accurate results. As an alternative to using the rinsing equations to perform the calculations, a modeling program can be employed. A commercially available software program permits an analysis considering up to five rinse stations and the use of supplemental evaporative recovery (ref. 60). This program permits the user to add recovery rinses, change tank volumes, experiment with process chemistries, add evaporators, and change workload to find the combination that makes the most environmental and economic sense (ref. 61).

5.0 Process Solution Maintenance and Chemical Recovery Technologies

5.1 Introduction

This section describes technologies used in the PWB industry for maintaining process solutions in operable condition and recovering process chemicals from spent baths and rinse waters. The information contained in this section was compiled from the PWB facility survey results, a literature search, and through contacts with vendors.

Often, bath maintenance, chemical recovery, and waste treatment technologies are competing pollution control measures. For example, some process solutions can be used on a bleed-and-feed basis (fresh chemical solution is introduced into a process to replace a portion of used solution, thereby maintaining the process bath within an operable chemical range), with the bleed stream going to waste treatment. Alternatively, a continuous bath maintenance technology may exist that keeps the bath operating within tolerable limits by removing contaminants, or, a recovery technology may be applied to the bath after it exceeds tolerable limits to recover reusable components. The decision to select bath maintenance, recovery, or waste treatment is often clouded by a lack of technical and cost information. The purpose of this section is to organize and present the technology information that was collected during the project so that it can be used in the decision process.

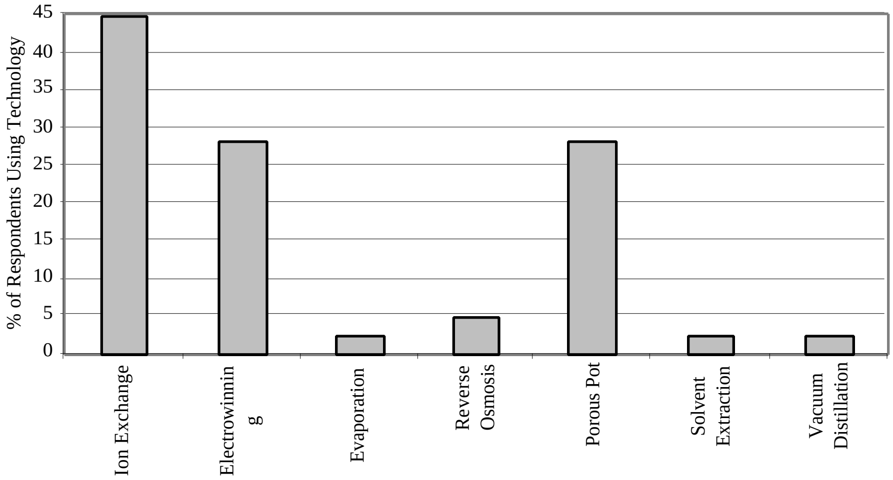
Survey data relative to recovery, recycle, and bath maintenance technologies are found in Appendix A. The data from the 1995 and 1997 surveys are contained in separate tables, because the number and wording of survey questions differed between the two surveys (i.e., in 1997, the scope of the survey was reduced in order to increase the response rate). Exhibit 5-1 is a summary of the two surveys. Shown are the percentage of respondents that use various recovery, recycle, and bath maintenance technologies.

Other information regarding recovery, recycle, and bath maintenance is contained in Exhibit 3-25. This exhibit indicates the specific types of wastes generated by the various processing steps of multilayer PWB manufacturing and the P2 technologies that can be applied.

The remainder of this section contains information on recovery, recycle, and bath maintenance technologies gathered from the survey, from literature, and through contacts with vendors. Due to the diversified nature of information collected during the project, some technologies receive greater attention than others. When available, the discussions include both technical and cost information.

Off-site recycling, which is not considered a pollution prevention method by EPA but is widely used by the PWB industry, is discussed in Section 5.4.

Exhibit 5-1. Recovery, Recycle, and Bath Maintenance Technologies Used



5.2 Solution Maintenance

Chemical solution maintenance includes a range of pollution prevention options that preserve or restore the chemical integrity of PWB process solutions, thereby extending their useful lives. The majority of PWB process solutions are used and then discarded. Some exceptions exist, such as etchants that are shipped off-site for recovery due to their economic value. However, due to rising costs for chemicals, energy, and treatment/disposal and increasingly more stringent environmental requirements, solution maintenance has become a greater priority to PWB facilities and the technologies they employ have increased in sophistication. Today, many firms are willing to expend significant amounts of capital and operating funds for equipment and methods that primarily reduce the disposal frequency of their baths.

In addition to extending bath lives, solution maintenance often improves the average operating efficiency and effectiveness of a process solution and, therefore, has a positive impact on PWB production rates and quality.

PWB process solutions are subject to a variety of forces that cause them to become unusable. The key contributing factors are: (1) depletion or chemical breakdown of bath chemicals; (2) etching of copper foil and plate; (3) contamination from impurities in make-up water, chemicals, anodes, etc.; (4) corrosion of racks, bussing, tanks, heating coils, etc.; (5) drag-in of non-compatible chemicals; and (7) errors in bath additions.

Solution maintenance replaces the practices of: (1) using a chemical solution until it is degraded and replacing it with fresh solution, or (2) decanting a portion of a degraded solution and replacing it with fresh solution (bleed and feed). In both cases, the spent solution is usually either batch treated, combined with other process wastes and treated in a central wastewater system, or transported to a recovery/treatment/disposal facility. On-site treatment is not always possible because concentrated wastes may upset treatment facilities designed primarily for treating dilute rinse waters. In some cases, facilities are able to reuse spent solution for either: (1) a less critical process application or (2) as a treatment reagent (e.g., spent acid cleaner used in place of sulfuric acid for pH adjustment). The former of these uses is regarded as a pollution prevention option by EPA. The latter method may reduce the overall use of chemicals at a shop, but because it involves treatment, it is not considered “pollution prevention” by EPA.

The remainder of Section 5.2 contains descriptions of PWB bath maintenance technologies that are either commonly in use or have been proven to work under certain production conditions.

5.2.1 Basic Bath Maintenance (Filtration, Carbon Treatment, and Electrolysis)

Basic bath maintenance methods were not specifically covered by the survey. However, some respondents indicated that they successfully employ methods such as filtration, carbon treatment, and electrolysis; therefore, a short discussion is included in this section.

Many process solutions, especially electroplating baths, can be maintained indefinitely by monitoring for organic and inorganic contaminants, making chemical adjustments when necessary, and utilizing filtration, carbon treatment, and electrolysis.

Filtration is the most commonly applied method of bath maintenance. It is used to remove suspended solids from plating and process solutions. Suspended solids in plating solutions may cause roughness and burning of deposits. Various equipment are used for filtration, with the most common being cartridge filters and precoat (diatomaceous earth) filters. Sand or multimedia filters are also employed. Cartridge filters are available with either in-tank or external configurations, with the former used mostly for small tanks and the latter for larger tanks. Most cartridges are disposable; however, washable and reusable filters have been recently commercialized.

Carbon treatment of plating baths is a common method of removing organic contaminants. The carbon adsorbs organic impurities that are present as a result of oil introduction or the breakdown of bath constituents. It is used on both a continuous and batch basis. Various application methods are available, including carbon filtration cartridges (contain up to 8 oz of carbon and are restricted to use on small applications), carbon canisters (up to 10 lbs of carbon), precoat filters, and bulk application/agitation/filtration (ref. 63).

Electrolysis, also referred to as dummy plating, is an electrolytic treatment process in which metallic contaminants in a metal finishing solution are either plated out (low current density electrolysis) or oxidized (high current density electrolysis).

Electrolysis is applied to a range of plating and other process solutions. The contaminant metals that are most frequently removed by dummy plating are copper, zinc, iron, and lead. Electrolysis is usually performed using a corrugated steel sheet cathode, with an anode to cathode spacing of approximately 4 in. The optimal current density will depend on the metal contaminants being removed. The normal range is 2 to 8 A/ft^2. The duration of treatment is typically 2 to 5 amp-hr/gal. Agitation is essential for speedy removal of contaminants, and air agitation should be used if the type of bath permits (ref. 64, 65, 66, 67).

Electrolysis can be performed on a batch or continuous basis, with batch treatment being the most common. Batch treatment is usually performed in the process tank and requires down-time. Continuous treatment is usually performed in a side-tank and cathodes are typically sized to permit 0.05 amp/gal of solution (ref. 65, 67). The solution is preferably returned to the process tank through a filter (ref. 68).

Basic bath maintenance recommendations for common plating solutions used in PWB facilities are presented in Exhibit 5-2.

Exhibit 5-2. Basic Bath Maintenance for Common Plating Solutions

Process Bath	Common Contaminates (tolerable levels)	Basic Bath Maintenance
Acid Copper Sulfate	Organic: residues from cleaners, resists. Inorganic: chloride (60-80 mg/l), chromium (25 mg/l), iron (500 mg/l), tin (300 mg/l), antimony (25 mg/l), nickel, lead, and arsenic.	Filtration: continuous (3-10 u filter, 4 turnovers per hour). Carbon treatment: needed approximately every 1,500 amp-hr per gal. Electrolysis: 10 A/ft^2 for 6 hr.
Copper Pyrophosphate	Organic: residues from cleaners, resists and oil. Inorganic: chloride (40 mg/l), sulfur (0 mg/l), iron (50 mg/l), nickel (50 mg/l), and lead (10 mg/l).	Filtration: continuous (3-5 u polypropylene filter, 4 turnovers per hour). Carbon treatment: minimum frequency of 6 mths. Electrolysis: 5 A/ ft^2 for 2-6 hr. once per week.
Solder Plate (tin-lead)	Organic: peptone or additive breakdown. Inorganic: chloride (2 mg/l), sulfate (2 mg/l), copper (15 mg/l), iron (400 mg/l), nickel (100 mg/l), and lead.	Filtration: continuous (3-10 u polypropylene filter, 4 turnovers per hour). Carbon treatment: frequency of 4-12 mths. Electrolysis: 3-5 A/ ft^2 for 2-4 hr. once per week for copper removal.
Acid Tin Sulfate	Organic: additive breakdown or resists. Inorganic: chloride (5 mg/l), copper (5-10 mg/l), iron (120 mg/l), nickel (50 mg/l), cadmium (50 mg/l), and zinc (50 mg/l).	Filtration: continuous (3-10 u polypropylene filter, 4 turnovers per hour). Carbon treatment: frequency of 4-12 mths.
Nickel Sulfamate	Organic: additive breakdown or resists. Inorganic: sulfates, copper (10 mg/l), chromium (20 mg/l), aluminum (60 mg/l), lead (3 mg/l), iron (250 mg/l), nickel (50 mg/l), cadmium (50 mg/l), tin (10 mg/l), calcium (0 mg/l), and zinc (10 mg/l).	Filtration: continuous (5-10 u polypropylene filter, 4 turnovers per hour). Carbon treatment: as needed, use 3-5 lb carbon per 100 gal. Electrolysis: 5 A/ ft^2 for 2-6 hr. once per week for copper removal.

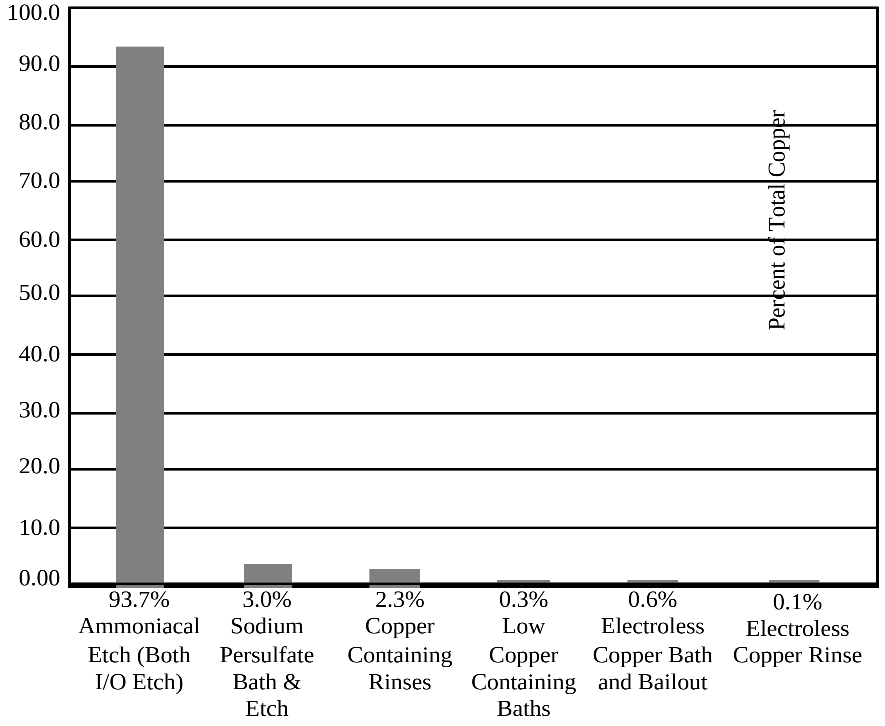
5.2.2 Etchant Regeneration

Spent etchant is the largest waste stream shipped off-site for most PWB shops. It also represents the most significant quantity of copper waste. Exhibit 5-3 shows a summary of copper waste source data for a particular PWB shop. For this facility, approximately 93% of the total amount of copper discharged was from the inner layer and outer layer etching processes.

Approximately 60% of the copper on the PWB is dissolved and removed by the etching process. When the copper content of the etchant increases beyond a certain level, the etchant cannot continue to effectively remove the copper from the board, and is considered spent. Spent etchant is stored in drums or a tank and is ultimately shipped off-site for reclamation.

Even in situations where the copper is recovered and the etchant is regenerated by the waste hauler, this waste stream may be an environmental hazard. Transportation of the spent etchant and its ultimate disposition may pose environmental risks and result in increased liability for the PWB facility. The costs of managing spent etchants and the danger they pose to the environment can be reduced dramatically with an on-site regeneration system. Recycling etchant onsite is an attractive alternative when considering the costs associated with shipping spent etchant, purchasing replacement fresh etchant, and the labor spent on manifesting and regulatory reporting. Recycling also permits the sale of recovered copper, reduces drum handling, and reduces the storage of hazardous waste.

Exhibit 5-3. Amount of Copper Wasted for Various Streams as a Percent of Total Discharge



Source: ref. 36.

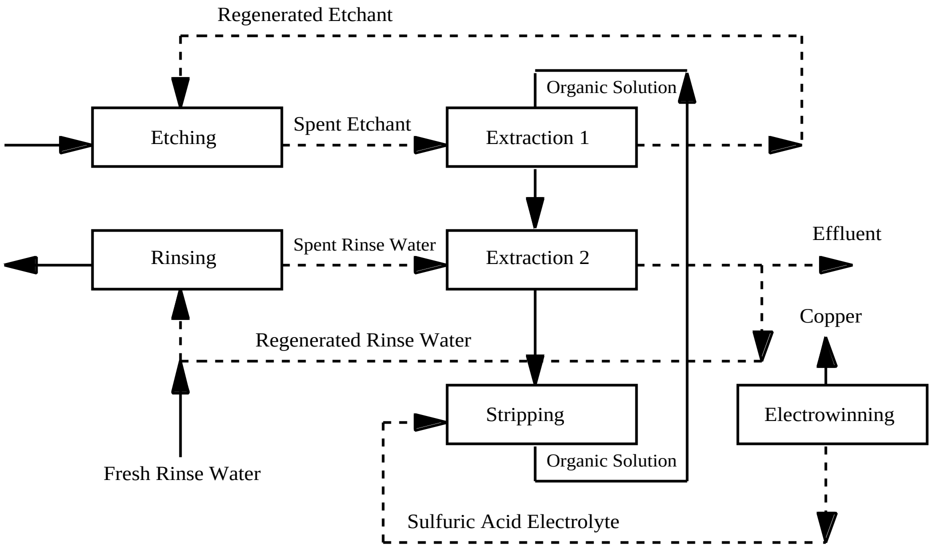
Ammoniacal etchants (ammonium chloride or ammonium sulfate) are the most commonly used in PWB facilities, followed by cupric chloride etchants. Some etchant regeneration systems may only work on one type, although, one system described below can process both etchants.

The following sections describe etchant regeneration systems. Most of the information in these sections is summarized from DfE case studies (ref. 69, 72, 74).

5.2.2.1 Ammoniacal Etchant Regeneration

The MECER System regenerates ammonium chloride, recycles rinse water, and recovers copper using a process of solvent extraction and electrowinning (Exhibit 5-4). The regeneration and recovery occurs in several stages: 1) a portion of the copper is removed from the spent etchant so that it can be used for further etching; 2) copper is removed from the rinse water so that it can also be reused; 3) copper is re-extracted and transferred to the electrolyte; and 4) in the electrowinning unit, copper is recovered from the now copper-enriched electrolyte to produce high quality, saleable copper metal sold for approximately $1.00/lb (or about 90% of the COMEX copper price) (ref. 69).

Exhibit 5-4. Ammoniacal Etchant Regeneration System



Units are sized based on the total throughput of the etching line, best estimated by a shop's current consumption rate of replenisher. Ten different size systems are available depending on the facility's annual replenisher volume, ranging from 14,300 gal/year to 380,000 gal/year (ref. 69).

One respondent to the survey uses this type of etchant regeneration system (ID# 946587). They purchased one unit in 1990 for regeneration of cupric chloride etchant (inner layer etching) and a second unit in 1994 for regeneration of ammoniacal etchant (outer layer etching). These were successful installations; however, the respondent indicates that: "We have invested extensive engineering resources to improve equipment process control." They indicate that the primary maintenance item is the replacement of anodes, cathodes, and membranes, which is done annually at this site for a cost of $10,000.

The Elo-chem Regeneration Module and Copper Recovery System by Atotech regenerates a proprietary ammonium sulfate etchant, which has a slower etch rate than ammonium chloride. The Elo-chem system consists of two separate regeneration circuits: an etchant recycling module and a copper recovery module. Etchant is regenerated utilizing atmospheric oxygen and ammonia to restore the copper in the spent etchant to the ionic form needed for etching. The regeneration occurs as a batch process. When a density meter indicates a high copper concentration, spent etchant is pumped to a tank with an electrolytic copper recovery cell. Etchant that has already been processed is reinjected with ammonia and oxygen before being sent back to the etcher. At the electrolytic cell, copper is deposited on the cathodes and is removed in sheets. This etchant has a 15-20% slower etch rate, and a proprietary rate accelerator is needed to keep the etch rate from falling any lower (ref. 69, 70).

The Elo-chem system is applicable to both large and small facilities. The same equipment is used for all size facilities, and multiple plating cells are added to accommodate facilities with larger production capacities. The average copper recovery capacity of the system is 5.4 lb/hour, with a maximum hourly capacity of 6.6 lb. One customer who runs a prototype board shop (using fewer than 10,000 gallons of etchant/year), describes this as the "ideal" system for their operation. They expect the system can eliminate the time and resources associated with shipping spent etchant off-site, reduce the space required for storage of fresh and spent etchant, decrease chemical purchase costs, eliminate safety issues associated with handling drums, and improve etching process control. Ammonia gas, a proprietary rate accelerator (added at 0.25 liter/plating hour), and small quantities of ammonium sulfate crystals (from an industrial chemical supplier) are needed to operate the system; actual quantities required depend on the carry-over losses. This system does not recycle or remove copper from rinse water (ref. 69).

5.2.2.2 Cupric Chloride Etchant Regeneration

The FSL Electrolytic Regeneration system from Finishing Services Limited regenerates etchant and plates out the copper. Users say their spent etchant has been reduced by 95%, and the volume of hydrochloric acid needed has dropped by 70-80%. Another saving is the elimination of oxidizer purchases (chlorine or peroxide). The copper plated out of the etchant can be sold as scrap. No changes are made to the rinse water stream.

The smallest FSL Regeneration system available is a module that removes 2.2 pounds of copper per hour; by joining these modules together, FSL can supply a system large enough to accommodate hundreds of pounds of copper per hour. As system capacity increases, however, so does the size of the system (ref. 69).

The payback from installation of the system is dependent on the operating parameters of each facility, such as throughput and current costs associated with off-site shipments of spent etchant. Savings include a reduction in the volume of hydrochloric acid used, elimination of oxidizer purchases (chlorine or peroxide), and savings associated with the reduction or elimination of spent etchant. Costs include capital investment for the equipment, electricity costs, minor costs from addition of chemicals to replace drag out, evaporation, and carry-over. Based on past experience, the manufacturer estimates a payback of 1.5 to 3 years. There is no change in the rinse water stream (ref. 69).

One of the survey respondents has installed an FSL unit (ID #946587) (see detailed data in Appendix A).

Membrane electrolysis can also be used for cupric chloride regeneration, although no U.S. commercial units were identified. With membrane electrolysis, an electrical current is passed through electrolytes that are separated by an ion specific membrane. Two reactions typically occur as the result of using membrane electrolysis: (1) ions of a given species are electrically driven across a selective membrane, and (2) chemical changes (e.g., oxidation/reduction) occur at the electrodes.

Cupric chloride regeneration using membrane electrolysis is accomplished by reoxidizing the cuprous chloride to cupric chloride, and by removing the dissolved copper. The etching solution is fed into an anode compartment and becomes the anolyte. A solution of 15 to 20% sulfuric acid is maintained in the catholyte compartment. An electrical current is passed through the electrolytes that are separated by a cation specific membrane that permits positively charged ions to pass from the anolyte to the catholyte. The oxidation of monovalent copper to bivalent copper occurs at the anode (ref.71). A commercialized system in Europe that that employs a PVC-based membrane was identified in the literature. A PWB facility in the UK reported a two-year pay-back from use of the technology (ref. 72).

5.2.2.3 Combined Cupric Chloride/Ammoniacal Etchant Regeneration

ARS Resource Recovery from ARS can handle both types of etchant. In addition, the system can simultaneously process acid copper plating baths, electroless copper dumps, and other copper bearing rinse water streams (ref. 73). Copper is recovered by liquid ion exchange in the form of copper sulfate. This can be sold as liquid copper sulfate, electrowon into copper metal, or crystallized into copper sulfate crystals (ref. 69).

ARS has recently installed its first integrated etchant regeneration and copper recovery system at one of the largest PWB manufacturing facilities in the country. At start-up, the system will allow this facility to process, on-site, its flows of cupric chloride spent etchant and ammoniacal spent etchant. In the future, the facility plans to use the system for recovery of copper from all copper dumps in the facility (ref. 69).

The initial system was designed for a large, high volume PWB manufacturer; however, ARS is currently developing the integrated regeneration technology to meet the needs of mid-sized companies. A payback period of about 2 years is estimated by the manufacturer, but depends on the facility-specific conditions (ref. 69).

5.2.2.4 Microetchant Regeneration

Microetching is a common process used as a preclean step in many stages of PWB manufacturing. Microetching removes anywhere from 10-70 microinches of copper to rid the panels of oxidation prior to the subsequent process, such as pattern plate, solder mask application, or hot-air-solder-leveling (ref. 74). Most facilities use a sulfuric-acid/hydrogen-peroxide solution as the microetchant, which can be maintained using electrowinning or crystallization.

Several approaches to using electrowinning for microetchant maintenance have been successfully employed. In one option, the working etch solution is continuously circulated through a separate electroplating cell where the dissolved copper is plated out on stainless steel cathodes or copper wire mesh. With this technique, the dissolved copper concentration can be maintained with a minimum amount of hydrogen peroxide breakdown. Additional proprietary stabilizers help to keep the peroxide decomposition to a minimum. For every 1 ampere hour of plating, approximately 1.0 to 1.3 milliliters of 50% hydrogen peroxide is consumed, in addition to the peroxide consumed in the etching process. One variation of this option that is under investigation is to employ a special cell with a membrane that separates the hydrogen peroxide from the plating cell. This may reduce the decomposition rate of the hydrogen peroxide.

Another facility reportedly uses a high surface area electrowinning system equipped with dimensionally stable anodes. This facility had been decanting 138 gallons of spent microetch solution per week from the electroless copper line and 35 gallons/week from the black oxide line. This spent solution was being sent off-site for recycling. In order to conserve sulfuric acid and prolong bath life, they installed the electrowinning unit (ref. 74). Their setup uses dimensionally stable anodes and cheap scrap laminate as the cathode onto which the copper is plated. The pumps are hard-piped for batch transfer from the microetch process bath to the electrolytic plate-out cell. The facility chose only the electroless copper and the black oxide lines for microetchant regeneration because other preclean processes do not have high copper concentrations, due to a high rate of copper drag-out.

Their continuous-batch plate-out system reportedly allows for better process control because the copper concentration remains more stable, which in turn provides for a more stable etching rate. In addition, the copper ion concentration in the microetch is lowered to 25 - 45 g/l, from an average of 45-80 g/l by the old decant method. The reduced copper concentration has the effect of decreasing the average amount of copper dragged into the subsequent rinse and then into waste treatment by about 50%. More importantly, the spent microetch is no longer decanted from these processes each week and sent off-site (ref. 74).

Several survey respondents use electrowinning for microetchant bath maintenance (ID #s 36930, 31838, 14, 34, and 53). Data relative to these installations can be found in Appendix A.

Additional information on electrowinning is presented in Section 5.3.2.

With the crystallization process, copper is recovered in the form of sulfate pentahydrate by cooling the solution to room temperature or below. The process can be carried out in batch or continuous modes. The former approach is more applicable to smaller shops that deal with lower volumes of solution. With the batch process, the copper laden solution is transferred to a separate tank and permitted to cool. When the copper sulfate crystallizes, it is decanted and returned to the operating tank and reused until the copper concentration reaches saturation. The crystallization process can be controlled by agitation and cooling rate. Larger operations use a two tank system with continuous transfer of solution into a highly agitated crystallization tank where it is cooled to 60 to 70°F, followed by crystallization in the second tank. Solution from the second tank flows continuously to the operating tank (ref. 75, 76, 77).

Facilities contemplating use of the crystallization maintenance method should investigate the availability of local markets for this material. It may be more difficult to find a recycler that accepts this material than the metallic copper recovered by electrowinning.

One survey respondent (ID#273701) has purchased and installed two crystallization units. Their first unit was purchased in 1988 and used on the final etching line. This unit processes 1,200 to 1,500 gal/day of solution that is fed to the unit at 50 g/l Cu. In 1993 they purchased a second unit that is used on the electroless copper line. The respondent is satisfied with the performance of both units. Additional details concerning these installations can be found in Appendix A.

5.2.2.5 Microetchant Reuse

Cascading reuse is another potential method of reducing the quantity of microetchant used in a PWB shop. With this method, microetchant is used in one process until its efficiency is reduced; it is then reused in another process that has a lower chemical requirement.

This concept was implemented by a company that had previously been using electrowinning to plate-out copper from spent sulfuric acid-potassium persulfate microetchant, then disposing of the solution. This particular chemistry could not be regenerated, due to the buildup of sulfates that resulted from the breakdown of the microetch components (a hydrogen peroxide-based microetchant, on the other hand, can be regenerated using this technology because the breakdown product is simply water). Therefore, in this case, electrolytic recovery served to remove copper before the solution goes to the wastewater treatment unit, but not to regenerate microetchant. The company was initially motivated to conserve microetch solution because their electrolytic plate-out unit frequently failed to meet capacity needs for processing spent solution. Excess waste had to be placed in drums until capacity was available.

Because the amount of copper that must be removed from the board varies among the different process lines, a microetch considered spent for the purposes of one process line may still be useful for microetching in a line requiring a lower etch rate. For example, at this facility the microetch step for an electroless copper line must remove 40 to 60 microinches of copper from the PWB, whereas the preclean step for pattern plating requires a microetch rate of 4 to 6 microinches. Using this process knowledge, they designed a continuous-flow system consisting of new plumbing and pumps to reuse microetch solution (ref. 78).

The reuse system is shown in Exhibit 5-5. The continuous-flow system begins with a single tank of microetch solution, prepared daily. This day tank is formulated to the specifications for the electroless copper line's preclean step, during which 40 to 60 microinches of copper must be removed from the panels. The microetchant is then used in the following sequence (ref. 78):

- **Microetch for Electroless Copper Plating.** A photocell provided by the electroless copper equipment vendor measures copper ion concentration in the microetch bath and automatically feeds fresh microetchant from the day tank to the bath when the copper concentration reaches a threshold of 10 g/l. Before this automated system was installed, the bath was dumped three times per week, the copper concentration in the bath ranged from 0 to 13 g/l, and the etch rate ranged from 14 to 60 microinches. The autofeed arrangement maintains copper concentration between 9 to 11 g/l, allowing for better process control and a more stable etch rate of 33 to 57 microinches. Although the flow of microetch could be triggered manually (i.e., without using a photocell), frequent analysis would be required to feed fresh solution into the microetch bath for electroless copper at the appropriate time. The benefits would not be as substantial (ref. 78).

- **Microetch for Pattern Plating.** As additions are made to the microetch tank for the electroless copper line, the excess overflows and is gravity-fed to the microetch prior to pattern plating. This preclean process needs to remove only 4 to 6 microinches of copper. Therefore, a weaker solution (one that has a higher copper concentration and less oxygen available) can be used. Because the etch rate is determined by temperature, concentration, and dwell time, the latter has been adjusted to achieve the desired etch rate based on the copper concentration of the incoming solution (ref. 78).

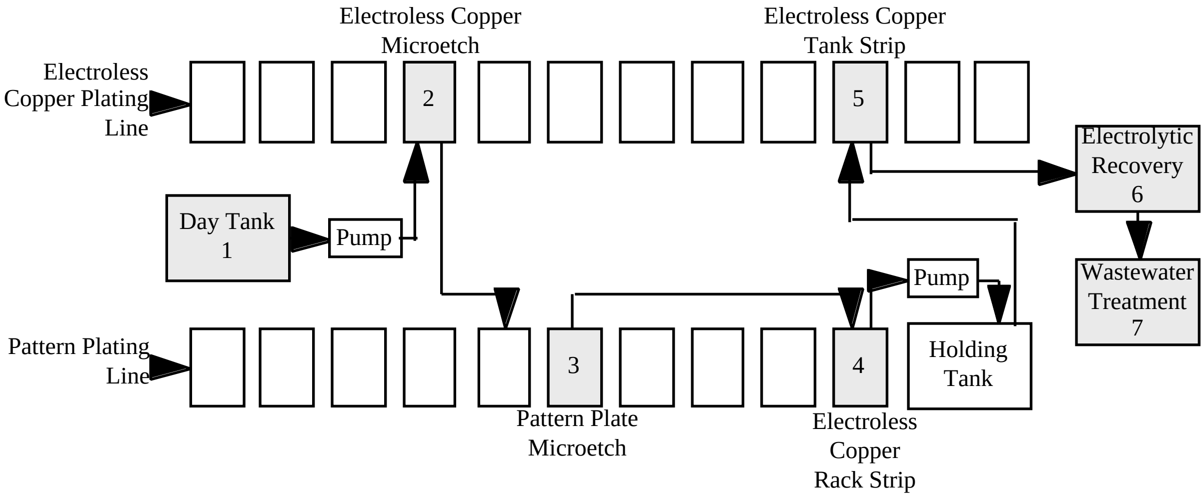
- **Electroless Copper Rack Strip.** The excess from the microetch bath for pattern plating flows, in turn, to a tank used for electroless copper rack stripping. During the electroless plating process, copper is deposited on the wire racks that hold parts to be plated, as well as on the inside of the plating tank. It is not necessary to use fresh microetch solution because etch rate is not a critical parameter in cleaning racks and tanks. Microetch solution can be reused from other processes to remove copper build-up (ref. 78).

- **Electroless Copper Tank Strip.** When the rack-strip tank is full, the microetchant is then pumped to a holding tank. Each weekend, the solution is pumped back into the electroless copper tank to remove copper build-up from its walls (ref. 78).

- **Electrolytic Recovery.** After cleaning the electroless copper tank, the microetchant is pumped to the electrolytic plate-out cell, where copper is plated out and sold to a recycler at $0.80/lb (ref. 78).

- **Wastewater Treatment**. The remaining spent microetchant, consisting of sulfates, sulfuric acid, residual copper, and water, is sent to wastewater treatment (ref. 78).

Exhibit 5-5. Continuous Flow Microetchant Reuse System



5.2.3 Permanganate Desmear Maintenance

Ion transfer is a relatively inexpensive and simple technology used for bath maintenance of permanganate desmear baths by 32% of the survey respondents. In the conventional permanganate process, the permanganate ion is reduced by heat and contact with PWBs, and is replaced by chemical addition. Also, during operation of this bath, by-products (including the manganate ion) accumulate in concentration, causing a sludge to form, and frequent disposal is necessary. The ion transfer technology (also referred to as porous pot) can be used to maintain a sufficiently low concentration of contaminants, and thereby reduce the frequency of disposal. One survey respondent indicated that use of the technology has resulted in up to a 90% reduction in chemical use for the applicable bath.

The common porous pot design consists of a rectifier, a ceramic pot that houses a cathode (protecting the cathode from direct contact with the process solution), and an anode, which surrounds the pot and is in direct contact with the bath. At startup, the pot is immersed into the bath (with the top remaining above the solution, preventing it from flowing into the cathode compartment) and filled with an electrolyte, usually sodium hydroxide. With the bath shielded from the cathode, the primary reaction that occurs is the anodic re-oxidation of the manganate ion back to permanganate. Using the porous pot, a bath-life extension of ten-fold or more can be realized.

Capital costs for this technology are low to moderate, and some respondents reported leasing the equipment from chemical vendors rather than purchasing it. Of those who did purchase the equipment, the price range was $2,500 to $14,000. The lease price ranged from $200/year to $900/year. Generally, the reported installation and operating costs were also low.

The survey data pertaining to this technology are shown in Exhibits 5-6 and 5-7. From the 1995 survey, ninety-two percent (92%) of the respondents who operate ion transfer units indicated they are satisfied with the technology. A somewhat lower percentage of respondents (67%) indicated that in the future they would buy the same technology from the same vendor if faced with a similar situation.

The 1997 survey data were similar. All installations were operating successfully and maintenance levels were as expected or lower.[5]

The porous pot technology is reported to be a relatively low maintenance item. The units require periodic cleaning, which one facility suggests should be done on a weekly basis (ID# 6710). Several respondents indicated that special attention should be given to cleaning the electrical contacts. The primary maintenance problem with this technology appears to be replacement of broken ceramic pots. One facility (ID# 3023) reported " porous pots are fragile and are broken frequently." Replacement pots cost approximately $100 each for certain models. One respondent also indicated that the metal frame of the unit corroded (ID#36930).

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[5] The 1995 and 1997 survey data are presented in separate exhibits because the survey questions were somewhat different.

Two facilities indicated that the concentrated caustic used in the pots presents a worker safety problem. One of those facilities (ID# 3023) indicated that handling of the pots has resulted in several worker accidents.

Exhibit 5-6. Porous Pot Technology Data (1995 Survey)

Resp. ID	Application	Year Purch.	Equip. Cost ($)	Install Cost ($)*	Labor (hr/yr)	Non-Labor ($/yr)	Use Code	Down Time %	Satisfied?	Future Decision
41739	Potassium Permanganate	1993	0	25	10	45	1	0	Yes	1
44486	Potassium Permanganate	1992	0	100	52	200	1	0	Yes	-
959951	Potassium Permanganate	1992	14000	5000	0	0	1	1	Yes	1
273701	Potassium Permanganate	1990	600	200	0	0	1	0	Yes	1
237900	Potassium Permanganate	-	0	0	0	0	1	2	Partially	3
6710	Potassium Permanganate	1989	750	125	20	875	1	0	Yes	4
955099	Potassium Permanganate	1990	0	0	550	0	1	1	Yes	1
953880	Potassium Permanganate	1992	0	100	8760	400	1	2	Yes	1
29710	Potassium Permanganate	1992	900	100	30	0	1	0	Yes	1
36930	Potassium Permanganate	1991	4000	200	100	1000	1	5	Yes	1
3023	Potassium Permanganate	1989	2500	1250	208	250	1	1	Yes	1
44657	Potassium Permanganate	1990	200	0	15	46	1	0	Yes	2

*The lower install costs are presumably annual lease costs.
Use codes: 1 = in use; 2 = not in use; 3 = not in use, future use expected
Future decision codes: (in response to survey question, “indicate a future course of action should you be required to fill a similar need”): 1 = buy the same technology from the same vendor; 2 = purchase same technology from different vendor; 3 = purchase different technology; 4 = do nothing.

Exhibit 5-7. Porous Pot Technology Data (1997 Survey)

Facility ID	Application	Reasons	Meet Need?	Maintenance	Overall Satisfy?	Future Decision
14	Potassium permanganate	1, 2, 3, 5, 6	Y	A	nr	S
23	Potassium permanganate	7	Y	A	5	S
42	Potassium permanganate	2, 3, 4, 5	Y	L	3	S
31	Potassium permanganate	2, 3, 5, 6, 7	Y	A	4	S
28	Potassium permanganate	1, 3, 5, 6	Y	A	3	D
37	Potassium permanganate	3, 5	Y	A	5	S
44	Potassium permanganate	1, 2, 5	Y	L	4	S
56	Potassium permanganate	4, 7	Y	A	5	S
45	Potassium permanganate	2, 5, 7	Y	A	5	S
50	Potassium permanganate	2, 3	Y	A	nr	S
35	Potassium permanganate bath on desmear line (has resulted in an 85-90% reduction in chemical use and treatment for that bath).	2, 3, 4, 7	Y	A	5	S
41	Potassium permanganate	2, 4	Y	A	nr	S

nr = no response

Reasons technology was purchased:
1 = to meet or help meet effluent limits
2 = to reduce process chemical purchases
3 = to reduce quantity of waste shipments off-site
4 = to increase production rate
5 = to reduce worker exposure to hazardous waste
6 = to recover a metal for resale
7 = to recover a chemical for reuse

Has the technology met the need for which it was purchased?
Y = yes
N = no
P = partially

Rate the level of maintenance required:
A = about what was expected
M = more than expected
L = less than expected

Overall satisfaction with the technology:
1 = very dissatisfied
5 = very satisfied

To fulfill a similar need in the future, which technology would you purchase?
S = same technology
D = different technology
S = none

5.2.4 Common Acid Regeneration

Several technologies are in use by industry to regenerate common acids, including sulfuric, hydrochloric, and nitric acids. Although these technologies are not commonly used by PWB shops, they are employed to a moderate extent by the metal finishing industry. The two most commonly used technologies, diffusion dialysis and acid sorption, are discussed in this section.

Recycling spent solution is not always as easy as hooking up a unit and adding fresh solution periodically. It may require extensive experimentation and teamwork. Understanding the chemistries involved in the process is the key to regenerating bath solutions successfully (ref. 74).

5.2.4.1 Diffusion Dialysis

Diffusion dialysis is an ion exchange membrane technology that competes directly with acid sorption (Section 5.2.4.2) as a purification/recovery method for acids that have become contaminated with metals (e.g., cleaning, stripping, and etching baths). This technology has been commercialized for less than 10 years, which is reflected by the fact that only one of the survey respondents indicated that they have employed diffusion dialysis.

The diffusion dialysis process separates acid from its metal contaminants via an acid concentration gradient between two solution compartments (contaminated acid and deionized water) that are divided by an anion exchange membrane. Acid is diffused across the membrane into the DI water whereas metals are blocked due to their charge and the selectivity of the membrane. A key difference between diffusion dialysis and other membrane technologies, such as electrodialysis or reverse osmosis, is that diffusion dialysis does not employ an electrical potential or pressure across the membrane. Rather, the transport of acid is caused by the difference in acid concentration on either side of the membrane. As such, the energy requirements for this technology are low.

The process uses ion exchange membranes that are assembled in a membrane stack. The membrane separates two liquids: (1) acid contaminated with metal, and (2) deionized water. The physical laws of diffusion and electroneutrality cause material in high concentration, to move to an area of low concentration without an imbalance of electrical charge. Because of the presence of the anion membrane, the metals in the concentrated solution are unable to pass from the concentrate to the DI water. However, anions in the concentrate (e.g., chlorides, sulfates, nitrates, phosphates) are permitted passage. Also, hydrogen ions, although positively charged, diffuse along with the disassociated acid (anions). The passage of hydrogen, which is key to the success of this process, is due to the small size of the hydrogen molecules and their mobility. The passage of the positively charged hydrogen ions satisfies the law of electroneutrality, preventing an imbalance of ionic charge on either side of the membrane (ref. 79, 80).

Diffusion dialysis, like other membrane technologies, is not 100 percent efficient; not all of the acid will be recovered and some leakage of metal will occur. In the laboratory, the process has yielded acid recovery efficiencies as high as 99%, with 98% metal removal. In the manufacturing environment, the practical limits are 80% to 95% acid recovery, with 60% to 90% of the metal contaminants removed. Also, the recovered acid may be of insufficient concentration to permit direct reuse. In such cases, vacuum evaporation may be needed to increase its concentration (ref. 81), although the economics of a concentration step are questionable. One source indicates, based on 1.5 years of experience with diffusion dialysis, that it is more efficient and economical than acid sorption for certain applications (e.g., recovery of mixed acid pickling baths) (ref. 80).

The diffusion dialysis membrane material is relatively resistant to chemicals commonly used in the PWB shop. However, contact with solvents could cause swelling of the membrane, and strong oxidizing agents can deteriorate the membrane material (ref. 82). The process is tolerant of feed solution temperatures up to 50°C (ref. 82).

One survey respondent reported the use of this technology (ID #955099). Their unit is successfully used for maintenance of a solder strip solution. The unit was purchased for $10,000 in 1994, and requires approximately 50 man-hours per year to maintain. However, use of the technology in PWB facilities has been reported elsewhere (ref. D, F). One facility successfully applies diffusion dialysis to a methane sulfonic acid (MSA) solder electrostrip to continuously remove metals. As a surface finish, this facility uses solder-mask-over-bare-copper with hot-air-solder-leveling. This outer layer finish prevents copper oxidation and facilitates solderability during the assembly process. Before panels can then undergo nickel/gold tab plating (also called finger plating, connector plating, or microplating) for electrical conductivity and environmental resistance, the tin/lead solder must be stripped from the panel. In the stripping process they use methane sulfonic acid (MSA) and apply a reverse electrical current to dissolve tin and lead from the boards.

In the past, the facility changed the acid every 30,000 ends (one pass of a circuit panel), or approximately every 6 weeks, depending on production schedules. MSA is an expensive acid (~$21/gal.), and accounted for an average of $17,000/year in raw material costs. Spent solution was sent off-site for disposal at a cost of approximately $5,600/year. The facility recognized an opportunity to conserve acid, prevent hazardous waste generation, and lower employee exposure to corrosive materials using a relatively simple and efficient in-process recycling technology called diffusion dialysis.

At this shop, the diffusion dialysis recycling unit is hard-piped to the MSA tab stripping bath. The company first evaluated a 5 gallon/day recycling unit in an off-line pilot test. They assessed parameters such as acid recovery and metal rejection rates, as well as the stripping rate of the recovered acid. The facility then proceeded to evaluate the system on-line. After working with the vendor to fine-tune metal rejection and acid recovery rates, they were able to maintain a constant solution level in the stripping bath. Based on the projects costs and savings, the payback on the investment was approximately 6 to 7 months (ref. 74).

The same facility is investigating the use of diffusion dialysis for maintaining their nitric acid/ ferric nitrate tin/lead etch-resist strip solution. The nitric acid solution is used to strip the tin/lead layer, and the ferric nitrate component is necessary to remove the intermetallic layer that forms when the tin and copper diffuse into each other. These solutions also contain wetting agents, copper etching inhibitors, and anti-tarnishing agents (ref. 74).

The investigation involves the use of diffusion technology to separate the stripped metals from the stripping solution, rendering it reusable. This would be a continuous, on-line recycling system similar to that used for their MSA recovery. The major roadblock to this process is the presence of an iron component in the proprietary stripping solution. They anticipate that the diffusion dialysis process will reject from the spent solution all metals, including the iron, which is essential to the stripping process. However, the facility believes it may be possible to determine the rate of loss of iron from the diffusion dialysis process and replace the iron with a concentrated replenisher. The difficulties here include adjusting for the losses of the other components, since rejection of organics and non-metal inorganic materials varies, depending on the charge and size (ref. 74).

In order to make these determinations, the facility contacted its solder strip chemical vendor and arranged a meeting with the company's process engineers, representatives from its chemical vendors, and the diffusion dialysis equipment vendor. Together they designed an off-line pilot system to test the acid reclaim efficiencies and metal rejection rates at various ratios of virgin to spent solder strip. The facility is awaiting further test results from its chemical vendor on parameters such as solder stripping rates, intermetallic removal, copper etching inhibition, and anti-tarnish capability. Based on the findings, the chemical vendor will be able to determine the additive package of chemical constituents that would replace the components lost from the diffusion dialysis process (ref. 74).

5.2.4.2 Acid Sorption

Acid sorption is a purification technology applicable to dilute to moderately concentrated acid solutions, such as cleaning and stripping baths. The term sorption, which includes both adsorption and absorption, is a general expression for a process in which a component moves from one phase to another, where it is accumulated, particularly for cases in which the second phase is a solid (ref. 435). Acid sorption is not a widely used technology by the PWB industry, although it has been commercially available in North America for approximately 15 years. As an acid bath maintenance technology, acid sorption competes with diffusion dialysis (Section 5.2.4.1).

Acid sorption is one of several processes where resins are used to absorb chemicals present in surrounding solutions and the chemicals are subsequently desorbed with water. These reversible sorption processes include ion exclusion (cation resin), ion retardation (special resin), and acid retardation (anion resin). Of particular interest in PWB manufacturing is acid retardation. This is a separation process where an acid is separated from its salts by using a column containing a strongly basic anion exchange resin of a specific porosity and particle size. This separation occurs because at high concentration the acid crosses the Donnan potential barrier (Donnan invasion) and is taken up by the resin, whereas the salts are excluded from it. The acid is thus “retarded” and the salts pass through the resin. This is not an ion exchange process, because the acid is desorbed from the resin with plain water.

The acid sorption or retardation process is employed to remove dissolved metal contaminants from acid baths. It is most often applied to the purification of sulfuric acid anodizing baths, and sulfuric acid and hydrochloric acid pickling baths. When these solutions are contaminated with dissolved metal, the free acid concentration decreases and the anodizing or pickling efficiency drops. Additions of fresh acid are possible up to a point, but eventually, the bath must be either purified or dumped.

Diagrams of the acid sorption process are presented in Exhibits 5-8 and 5-9. These diagrams illustrate the equipment of a particular commercial acid sorption manufacturer. During the sorption step, the acid and metal salt mixture is fed up through the resin bed. Acid is sorbed into the resin, while the remaining dissolved metal salts are rejected as mildly acidic solution, leaving from the top of the bed. Depending on the metal salt, this solution may be waste-treated or diverted to an electrowinning cell for recovery of the metal. During the desorption step, water flows down through the resin bed. Acid is desorbed from the resin and displaced from the bottom of the bed. City water is typically adequate for this step. The resin is stable under normal operating conditions for many years, without the need for regular replacement or any special treatment.

Exhibit 5-8. Acid Sorption Operating Cycle

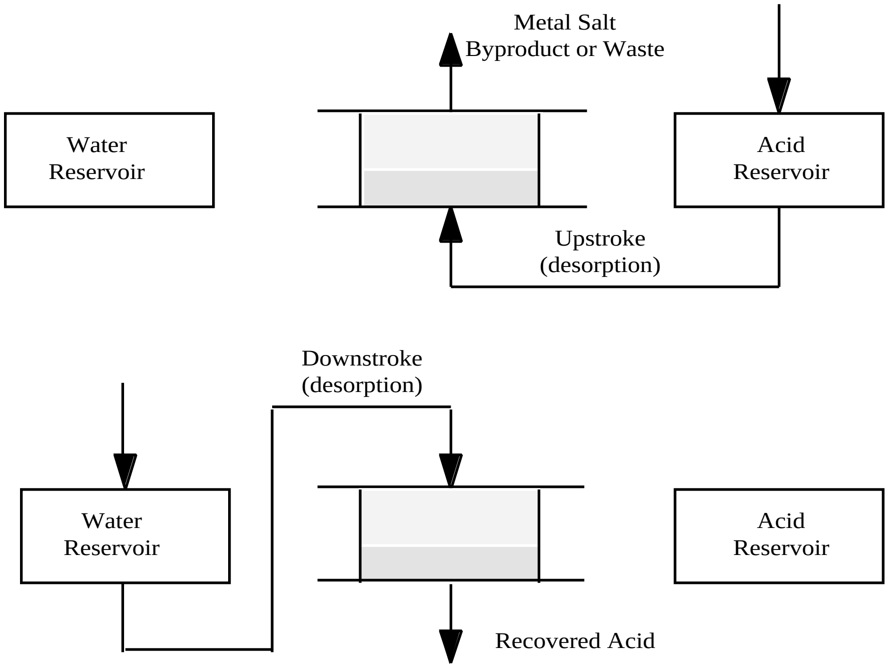
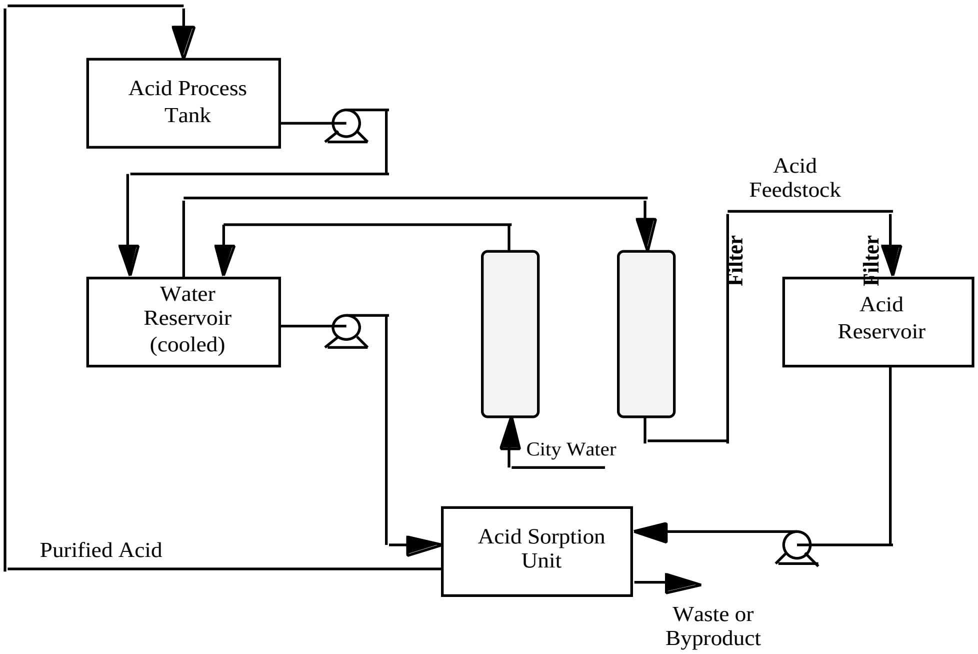


Exhibit 5-9. Acid Sorption Flow Diagram



Acid sorption does not recover all of the acid in a treated bath. Rather, it recovers only a percentage (typically 80% to 90%) of the "unused" or free acid (i.e., that acid which is not chemically bonded to the dissolved metal). Typically, 40% to 70% of the total acid is free acid. Therefore, if a shop's current method of operation involves dumping and treating spent acid baths and replacing the bath with fresh solution, then acid sorption can be expected to reduce their total acid usage by approximately 30% to 65% (ref. 83, 84).

In addition to reducing acid usage, there are several benefits from using acid sorption. These include: (1) reduces neutralization treatment reagent usage (e.g., caustic or lime); (2) reduces interruptions in production (i.e., when used on a continuous basis as opposed to batch purification); and (3) reduces process control variability caused by fluctuations in bath composition (i.e., when used on a continuous basis).

5.2.5 Electroless Copper Ethylenediamine-tetraacetic Acid (EDTA) Recovery

EDTA is the most widely used chelating agent with electroless copper. Its purpose is to keep the cupric ions in solution and prevent them from precipitating as copper hydroxide. It does present some problems downstream at the waste treatment level. While using precipitation to recover the copper is possible, the EDTA remains and will have an attraction to copper from other waste streams. If an ion exchange system is used, standard cation and chelating ion exchange resins cannot effectively remove dissolved copper with EDTA present. A method has been developed to recover the EDTA from spent electroless copper baths and solve these treatment problems.

EDTA is recovered by acidifying the solution and creating H_4EDTA, which is insoluble. Before this can be done, however, the copper must be removed. This is done through the introduction of HCHO and NaOH to the electroless solution, which causes the bath to become unstable, and the copper precipitates. The copper is then removed through filtration. The remaining filtrate contains sodium sulfate (or nitrate), sodium hydroxide, sodium formate, EDTA, formaldehyde, stabilizers, and additives. This is acidified with concentrated HCL or H_2SO_4 to reduce the pH to about 4. CO_2 gas is released, due to the presence of carbonate in the solution. After the gassing stops, more acid is added to bring the pH to 2.1 or below, and the EDTA is precipitated.

Although this H_4EDTA can be recycled to prepare a new electroless copper bath, this is not typically done. Electroless chemistry is usually supplied from the manufacturer with some of the components pre-mixed in the appropriate ratios. One of the components is EDTA (ref. 75).

5.2.6 Dry Film Stripping Solutions

Membrane filtration, including microfiltration and ultrafiltration, is a potentially viable technology for the recovery of developer solution associated with photoresists. Membrane filtration is a cross-flow filtration method as opposed to "dead-end" barrier filtration. With the latter method, all of the feed solution is forced through the membrane by an applied pressure. With a high solids-fed stream, the pores of a dead-end filtration device plug. With crossflow filtration, the fluid to be filtered is pumped across the membrane, parallel to its surface. By maintaining a high velocity across the membrane, the retained material is swept off the membrane surface. This mode of operation typically requires multiple passes and consumes a greater amount of energy than dead-end filtration. However, for high solids applications, crossflow filtration is the only practical method (ref. 3).

PWB facilities are interested in reducing the wastes from stripping processes because of the labor and cost of on-site treatment and/or preparing the materials for shipment off-site. A recent research project collected samples of waste developer, developer rinse, stripper, and stripper rinse (ref. 85). Tests of the spent stripper showed that it contained nearly the same concentration of ethanolamine (key stripper ingredient) as does fresh solution. Ultrafiltration was investigated as a means of generating a reusable product from the spent stripper. Earlier tests by other researchers were unsuccessful due to the use of antifoam in stripper, which tends to coat and foul the ultrafiltration surface. The current tests were performed on spent stripper containing no antifoam. The ultrafiltration unit successfully separated the spent stripper into a reusable product that represented 80% of original waste volume and 74% of the active ingredients in virgin stripper. The remaining 20% waste contained 100% of the solids, 83% of the copper, and 50-70% of the organics and dissolved solids. In a parallel board facility test, recycled stripper was used in a production situation (74% ultrafiltration filtrate and 26% virgin stripper) and proved to have the same stripping speed of purely virgin solution. Future test will focus on determining the number of times that stripper can be recycled.

The survey did not specifically request information on filtration of dry film stripping solutions. Therefore, the extent of use of this technology was not determined.

5.3 Chemical Recovery Technologies

Various technologies are used by PWB facilities to recover chemicals from spent baths and rinse waters. In most cases, the recovered chemicals are sent off-site for reclamation, rather than reused in the PWB shop. The two most common recover technologies are ion exchange and electrowinning. These technologies are often used in combination where ion exchange separates and concentrates the dissolved copper from rinse waters and electrowinning is used to recover the copper in metallic form from the concentrated solution. Due to the prolific use of these technologies, they are covered in greater detail in this report than other chemical recovery technologies.

5.3.1 Ion Exchange

5.3.1.1 Technology Description

Ion exchange is a chemical reaction wherein an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle (i.e., ion exchange resin). Ion exchange reactions are stoichiometric (i.e., predictable based on chemical relationships) and reversible. The resins are normally contained in vessels referred to as columns. Solutions are passed through the columns and the exchange occurs. Subsequently, when the capacity of the resins is reached, the ions of interest, which are attached to the resin, are removed during a regeneration step where a strong solution containing the ions originally attached to the resin is passed over the bed.

The strategy employed in using this technology is to exchange somewhat harmless ions (e.g., hydrogen and hydroxyl ions), located on the resin, for ions of interest in the solution (e.g., copper). In the most basic sense, ion exchange materials are classified as either cationic or anionic. Cation resins exchange hydrogen ions for positively charged ions such as copper, nickel, and sodium. Anion resins exchange hydroxyl ions for negatively charged ions such as sulfates, chromates, and cyanide.

The basic ion exchange column consists of a resin bed that is retained in the column with inlet and outlet screens, and service and regeneration flow distributors. Piping and valves are required to direct flow, and instrumentation is required to control regeneration timing. The systems are typically operated in cycles consisting of the following steps (ref. 3):

1. **Service (exhaustion)** – Water solution containing ions is passed through the ion exchange column or bed until the exchange sites are exhausted.
2. **Backwash** – The bed is washed (generally with water) in the reverse direction of the service cycle in order to expand and resettle the resin bed.
3. **Regeneration** – The exchanger is regenerated by passing a concentrated solution of the ion originally associated with it through the resin bed; usually a strong mineral acid or base.
4. **Rinse** – Excess regenerant is removed from the exchanger; usually by passing water through it.

The ion exchange process has been commercially available for many years, but early use was primarily for water deionization or softening. Use of the process for PWB pollution prevention and control is a more recent application, and widespread interest in it has grown rapidly over the past 10 years.

5.3.1.2 PWB Manufacturing Applications

Ion exchange is common in PWB facilities for several reasons. Among them are:

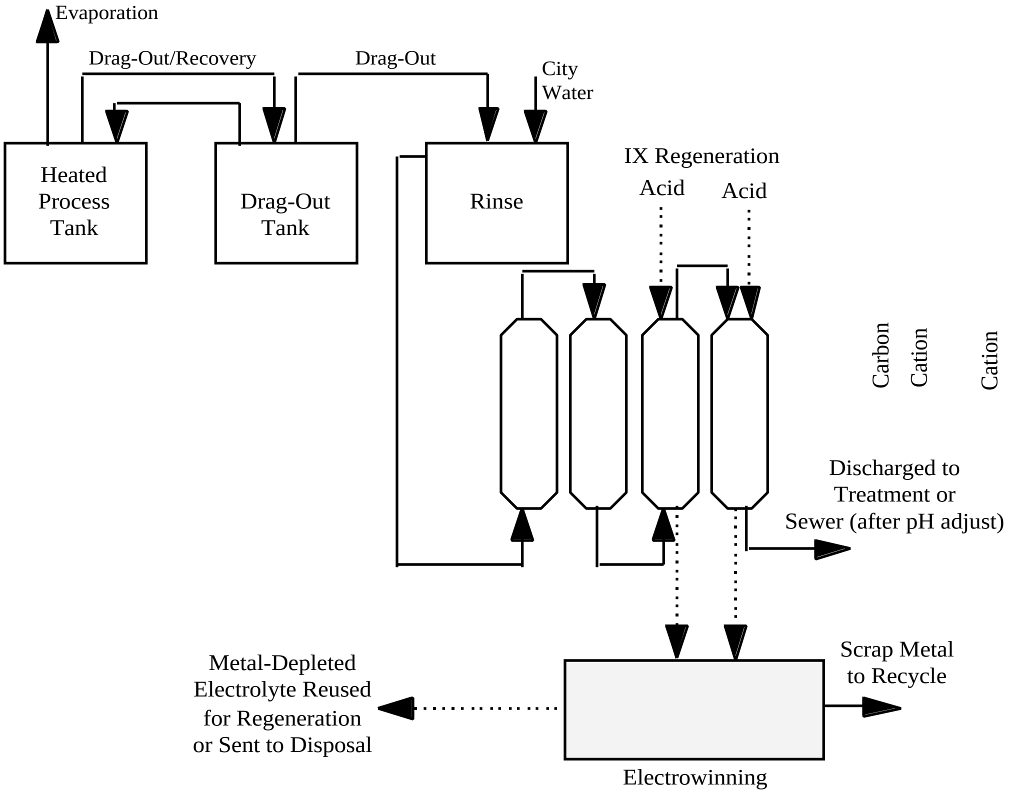
- Several PWB rinse water streams are readily compatible with ion exchange. Simple copper-bearing, low-organic streams from micro-etchant, acid dip, and copper electroplating rinses can usually be sent directly to ion exchange with no pretreatment. With carbon filtration and pH control of the incoming stream, additional rinse streams become ion exchange candidates.
- The preponderance of copper as the contaminating metal allows facilities to take advantage of the powerful ion exchange/electrowinning combination. Together, these two technologies combine to separate, concentrate, and recover copper from rinse streams.
- Ion exchange offers facilities the ability to close-loop some rinses and reduce the need for downstream treatment.
- Due to the large number of rinses potentially amenable to ion exchange and the ability of ion exchange to produce compliant effluent, some shops (particularly small ones) can employ metal-scavenging ion exchange as a primary end-of-pipe system.
- Reducing the quantity of copper entering the waste treatment system greatly reduces the quantity of wastewater treatment sludge generated, which is typically shipped off-site as hazardous waste.

Generally, ion exchange is limited to dilute rinse water streams, although scavenging resins can be used to treat more concentrated wastes under certain circumstances. As concentrations increase, ion exchange becomes impractical due to the increasing frequency of regenerations and the declining difference between the concentration of the regenerant, which is a constant (typically 5-10 grams/liter), and the concentration of the stream being treated.

Drag-out recovery tanks are used in conjunction with ion exchange systems, whenever feasible, to reduce the load on the ion exchange system. In operation, the drag-out tanks return the bulk of the plating chemicals directly to the plating bath, and an ion exchange unit connected to a subsequent flowing rinse captures only the residual chemicals. The needed size of the ion exchange unit and its regeneration frequency are therefore reduced.

Metal Scavenging Applications. When the sole objective of using ion exchange is to remove metal from a wastestream, a metal scavenging configuration is employed (Exhibit 5-10). This system uses only one type of ion exchange resin, either selective anion or cation, depending on the charge of metal or metal complex being targeted for removal (e.g., a cation-type resin is used for most copper removal applications). Because this system does not have both cation and anion resins, the rinse water will not be fully "deionized" and cannot be reused as rinse water for common rinsing purposes. The primary advantage of metal scavenging is the large capacity (in terms of rinse water treated) vs. a deionizing configuration, since only divalent cations are exchanged, and common monovalent cations such as sodium and potassium are bumped off the resin and passed. Thus, regeneration cycles are longer, lowering chemical and other operating costs.

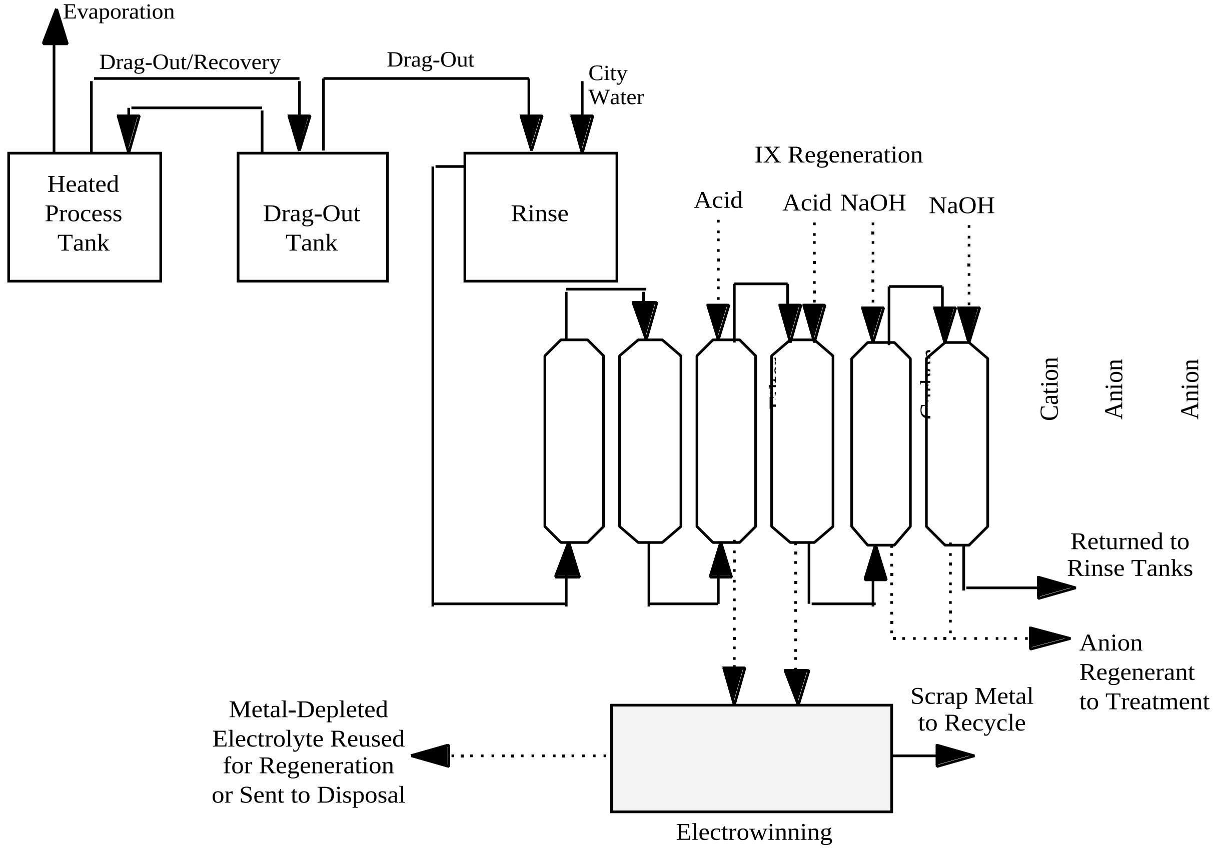
Exhibit 5-10. Ion Exchange Recovery-Metal Scavenging Configuration



Certain PWB wastestreams are commonly treated with the metal scavenging configuration. Most common are copper, tin-lead, and gold rinse systems. Various copper rinses are commonly processed with this technology, including etch, microetch, and copper electroplating. Resins are regenerated using sulfuric acid. In the case of tin-lead, ion exchange scavenging is employed to remove lead from rinse water, which is then often discharged. Regeneration may be performed on-site with methane sulfonic acid (MSA), or the resin, when exhausted, can be shipped off-site for processing/disposal. Point source ion exchange treatment of tin-lead rinses may be performed to protect downstream units from lead-bearing streams. Ion exchange may also outperform the primary waste treatment system, and this configuration may cost-effectively maintain compliance where lead discharge limits are more stringent than copper limits. Gold rinses are often ion exchanged for the purpose of gold recovery. When exhausted, gold-bearing resin is usually processed offsite to ensure efficient recover of the gold.

Deionization. When the objective is to recover metal and recycle rinse water (i.e., closed-loop), a deionization configuration is employed. This configuration uses a combination of cation and anion exchange columns in series to remove all ions from the rinse water (Exhibit 5-11). This strategy may be employed when continuous discharge is impractical due to stringent limits, or where the benefits of water reuse outweigh the cost of installing and operating a water recycling ion exchange unit.

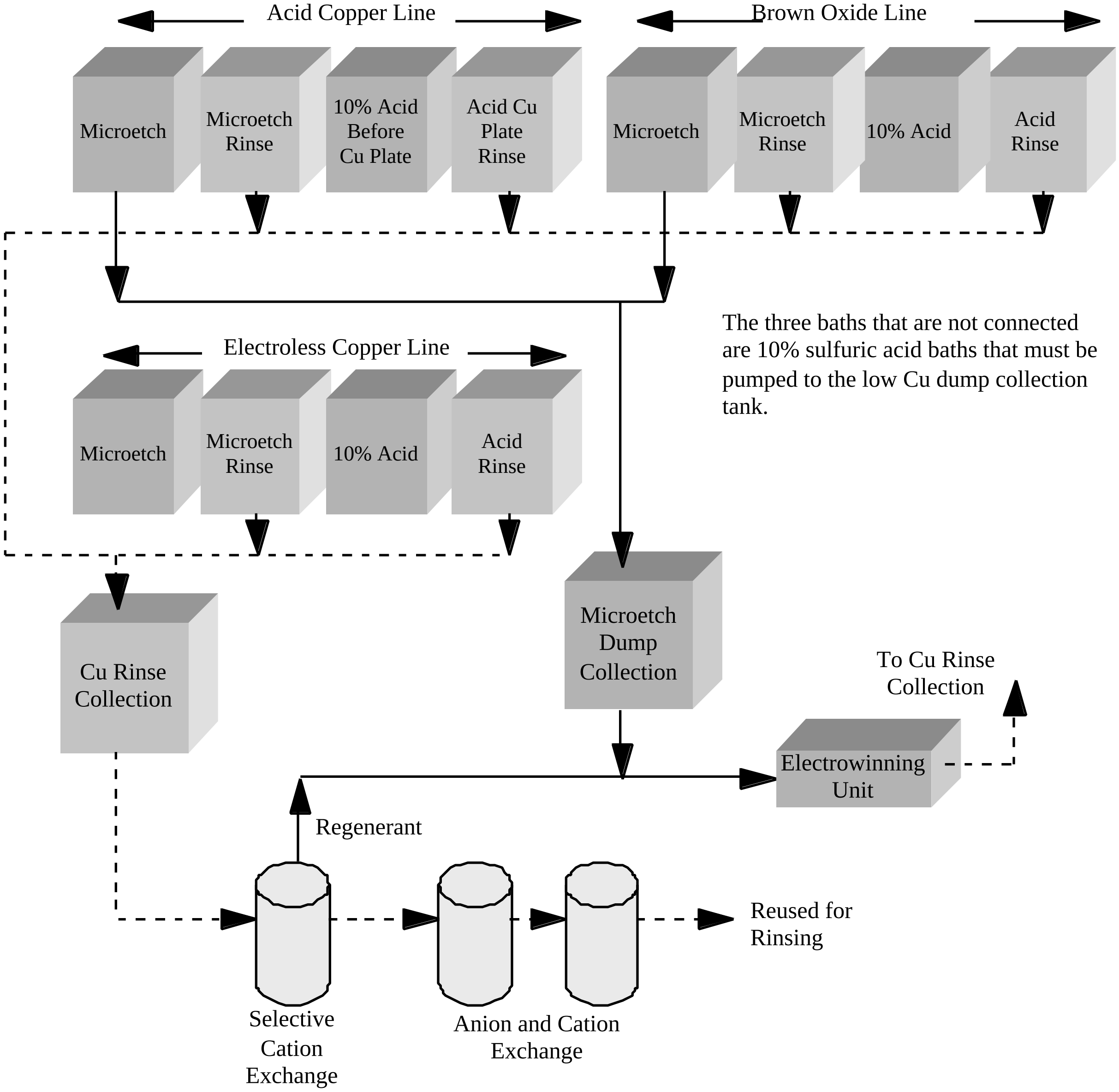
Exhibit 5-11. Ion Exchange Recovery-Metal Recovery/Deionized Water Cycle



A good candidate for deionization is the electroplating copper rinse system. With this application, rinse water containing copper is sent to the cation and anion exchange columns, and deionized water is returned as fresh rinse water to the rinse system. The anion regenerant, usually NaOH, can usually be pH treated and discharged. The cation regenerant stream is interesting due to its similarity to the plating bath make-up--sulfuric acid and copper sulfate. While it is possible to return the regenerant to the plating bath, thereby closing the loop for most of the process, this is generally not done for two important reasons: (1) the performance of the PWB through-hole plating in various stress tests is quite sensitive to small variations in bath chemistry, making additions of regenerant inadvisable, and (2) the copper sulfate plating bath is operated at too low of a temperature to create sufficient evaporative headroom for the regenerant additions. The regenerant is an ideal electrowinning candidate, and this is the most common treatment option.

Deionization or metal scavenging can be accomplished using "point-of-source" ion exchange as shown in Exhibits 5-10 and 5-11, or by using a central system similar to that shown in Exhibit 5-12. With this system, rinses are first processed through a selective resin for cation removal, and subsequently processed through anion and cation resins for complete deionization. They are then returned to the rinse system (ref. 36).

Exhibit 5-12. Central Copper Recovery System Utilizing Ion Exchange and Electrowinning



Process Residuals. The primary residuals from ion exchange recovery processes are the regenerants and backwash solutions. The regenerants are concentrated wastes and the backwash is dilute. Both solutions are either caustic or acidic, depending on the resin type and application. High metal-bearing regenerates (typically cation resin) are sometimes reused directly in the bath, further processed to recover the metal (e.g., electrowinning), waste treated, or sent to an off-site recovery facility. Low metal-bearing regenerants (typically anion resin) and backwash solutions are typically treated on-site. Waste treatment processes generate sludge that is an EPA listed hazardous waste (F006).

The volume of regenerant produced will depend on the regeneration requirement (e.g., lbs of acid per ft^3 of resin) and the concentration of acid used (typically 1 to 5%). The regeneration requirement will depend on the resin type, application (metal or complex being recovered) and the configuration (cocurrent vs counterflow). Typical volumes of regenerant are 20 to 50 gal/ft^3 of resin. The volume of regenerant waste is sometimes reduced by reusing the last portion of the regenerant, which will be less contaminated with metal and contains free acid. Backwash volumes depend mostly on the equipment design and the application. Typically, backwashing generates 25 to 75 gal/ft^3. The backwash is partly reused by some equipment vendors as make-up water for regenerant, in an effort to reduce the total waste volume generated. Because backwash contains only dilute concentrations of pollutants it is typically not a major concern and is treated on-site and discharged. However, for facilities working toward zero discharge, the backwash volume could present a significant problem. Both backwash and regenerant can be processed by evaporation to reduce the volume requiring disposal. However, this increases the capital and operating costs of the system. Also, evaporation of hazardous wastes is sometimes regulated as a RCRA technology and may require a permit to operate.

5.3.1.3 Survey Results

The survey results pertaining to ion exchange recovery are presented in Exhibits 5-13 and 5-14. Of the PWB facilities responding to the survey, 44% are using ion exchange for chemical recovery. Some of the recovery systems also serve as the primary end-of-pipe treatment. The latter mostly include central systems that recover copper using ion exchange and electrowinning, but do not recycle water.

Exhibit 5-13. Ion Exchange Technology Data (1995 Survey)

Resp. ID	Application	Year Purch.	Equip. Cost ($)	Install Cost ($)	Labor (hr/yr)	Non-Labor ($/yr)	Use Code	Down Time %	Satisfied?	Future Decision
T1	Various Rinses	1991	90000	0	800	6300	1	0	Yes	-
502100	Plating, cleaning, etching	1985	100000	20000	1500	2000	1	0	Yes	3
955703	Various rinses	1990	75000	25000	7488	25000	1	0	Yes	1
36930A	Copper rinses	1989	5000	5000	50	1000	1	0	Yes	1
36930	Copper rinses	1989	15000	5000	250	2000	1	0	Yes	1
37817	Various rinses	1989	50000	0	500	1500	1	0	Partially	3
25503	Copper rinses (etch, plate, cupric chloride)	1991	45000	3000	2200	3600	1	1	Yes	1
3470	Various rinses	1984	100000	200000	3000	35000	1	0	Yes	1
31838	Various rinses	1994	24000	4000	100	2000	2	0	Yes	-
358000	Mixed Cu rinses. Also serves as EOP treatment	1993	15000	5000	2500	1500	1	10	Yes	1
43694	Cu bearing rinses (etch, microetch, plate)	1990	60000	0	4000	50000	1	1	Yes	1

Use codes: 1 = in use; 2 = not in use; 3 = not in use, future use expected
Future decision codes: (in response to survey question, “indicate a future course of action should you be required to fill a similar need”):
1 = buy the same technology from the same vendor; 2 = purchase same technology from different vendor; 3 = purchase different technology; 4 = do nothing.

Exhibit 5-14. Ion Exchange Technology Data (1997 Survey)

Shop ID	Technology	Application	Reasons	Meet Need?	Maint.	Overall Satisfy?	Future Decision
14	Ion Exchange	Point source metal bearing rinses	1, 2, 3, 5, 6,	Y	A	nr	S
22	Ion Exchange	All copper rinse waters and process bath dumps less than 2g/l copper and little or no tin, lead or iron	1, 3, 4, 5, 6,	Y	A	5	S
43	Ion Exchange	(IX application not defined)			A	nr	
19	Ion Exchange	(not defined)	1	Y	A	4	S
21	Ion Exchange	Etch rinse and micro etch rinses	1, 3	Y	A	5	S
55	Ion Exchange	(not defined)	1	Y	L	4	S
34	Ion Exchange	Rinses after etchants, copper plate, and tin strip	1, 2, 3, 4, 5	Y	M	3	S
49	Ion Exchange	Rinse waters	1, 3, 6	Y	A	4	S
29	Ion Exchange	Pattern solder copper, electroless Cu, ammoniacal Cu, solder strip, acid Cu, Ni sulfate, Au, and Ag	1, 2, 3, 5	Y	L	5	S
54	Ion Exchange	Horizontal etcher & chem clean line rinses (total 9 gpm)	1, 6	Y	L	5	S
54	Ion Exchange	All copper bearing rinses with >60 ppb copper content, except the three still rinses in previous system (60 gpm)	1, 6	Y	M	4	S
30	Ion Exchange	Small systems used for closed loop rinse after gold plating	6	Y	A	4	S
44	Ion exchange	Copper plating/etching rinses.	1, 2, 3, 5, 6	Y	A	5	S
52	Ion Exchange	All metal bearing rinses	1, 3, 6	Y	A	4	S
38	Ion Exchange	(IX application not defined)	1, 2, 3, 4, 5	P	A	3	S
32	Ion Exchange	Rinse water from the etcher. The cleaned water is then recycled to the rinse tank of the etcher. "We are generating more hazardous waste than without IX unit."	3, 4, 5, 7	P	M	3	S
53	Ion Exchange	Sulfuric acid rinses	1, 3, 5, 6	Y	A	2	S
45	Ion exchange	Various rinses in the electroless and oxide lines	2, 3, 6, 7	Y	A	5	S
47	Ion Exchange	Acid cleaners, metal-bearing rinses	1, 3, 4	Y	M	4	S
36	Ion Exchange	Plating rinses, plating bath, developer rinses, board cleaning, general water rinses	1, 3	Y	A	4	S
20	Ion Exchange	Copper Plating Bath rinses Cupric Chloride etch rinses	1, 2, 3, 5, 6	Y	L	4	S
26	Ion Exchange	Used to remove copper from rinse waters from microetch and precleaner rinses on our oxide, Cu, etch, nickel, and gold plating lines	1	Y	M	3	S
46	Ion Exchange	Nickel drag-out, gold drag-out, microetch, and spent shadow conditioner/cleaner.	1, 6	Y	A	3.5	S
39	Ion Exchange	Nickel bearing rinse waters	1	Y	A	4	S
13	Ion Exchange	System just being installed	1, 4		A	nr	D

Reasons technology was purchased:
1 = to meet or help meet effluent limits
2 = to reduce process chemical purchases
3 = to reduce quantity of waste shipments off-site
4 = to increase production rate
5 = to reduce worker exposure to hazardous waste
6 = to recover a metal for resale
7 = to recover a chemical for reuse

Has the technology met the need for which it was purchased?
Y = yes
N = no
P = partially

Rate the level of maintenance required:
A = about what was expected
M = more than expected
L = less than expected

Overall satisfaction with the technology:
1 = very dissatisfied
5 = very satisfied

To fulfill a similar need in the future, which technology would you purchase?
S = same technology
D = different technology
S = none

Based on the survey results, it appears that most installations of ion exchange by PWB facilities are successful. The 1995 survey results indicate that 90% of the facilities that use ion exchange as a recovery technology are satisfied with its performance. Similarly, facilities responding to the 1997 survey that employ ion exchange rated the technology a 4.0 on a scale of 1 to 5 (five being the best). In a similar survey conducted with the metal finishing industry, ion exchange received an overall rating of only 3.2. The lower rating by the metal finishers may be due to difficulties associated with using this technology with metals other than copper. For example, the metal finishers using ion exchange for cadmium and zinc recovery rated the technology 2.0 and 2.6, respectively.

Equipment prices for ion exchange systems purchased by the survey respondents vary widely ($10,000 to $120,000 installed costs), due to major differences in system capacities (some larger systems are used to process nearly all rinses waters generated) and levels of automation. Operating and maintenance requirements appear to be moderate to high.

5.3.2 Electrowinning

Electrowinning is employed in PWB facilities to remove metallic ions from concentrated rinse water, spent process solutions, and ion exchange regenerant. An electrowinning unit consists of a rectifier and a reaction chamber that houses anodes and cathodes. In the simplest design, a set of cathodes and anodes are set in the reaction chamber containing the electrolyte. When the unit is energized, metal ions are reduced onto the cathode. The rate at which metal can be recovered (i.e., plated onto the cathode) from solutions depends on several factors, including the concentration of metal in the electrolyte, the size of the unit in terms of current and cathode area, and the species of metal being recovered.

Electrowinning is different from other recovery technologies (e.g., evaporation, ion exchange) in that an elemental metal is recovered rather than a metal bearing solution. The recovered metal is usually not pure enough to be used as anode material in plating processes. More often, it is sold as scrap metal.

Electrowinning is particularly applicable for removing metal from solutions containing a moderate to high concentration of metal ions (>3,000 mg/l). Below 1,000 to 2,000 mg/l of metal, the conventional electrowinning process becomes very inefficient. Therefore, it is not thought of as a "compliance" technology (i.e., a technology that will meet wastewater discharge standards). Rather its benefit is in recovering valuable metals that would otherwise be converted to metal hydroxide sludge by the wastewater treatment system.

High surface area (HSA) electrowinning, developed during the 1970s and commercialized in the 1980s with the reticulate cathode design, extends the applicability of this technology to low concentration solutions and in some cases HAS electrowinning may serve as a compliance technology for specific wastestreams. HAS units employing reticulate cathodes are designed as flow though tanks where the electrolyte passes through a series of cathodes. Each reticulate cathode is made up of thread-like material that is woven into a sheet and given a metallized surface. During use, the ions plate onto the surface of the cathode (up to 5 to 10 lbs./ft^2). The cathodes are subsequently removed and sold as scrap.

Commercial units employ a variety of strategies designed to increase plating efficiency at the relatively low metal concentrations found in typical electrolytes available for electrowinning. This is usually accomplished by design innovations that focus on causing motion of the electrolyte across the surface of the cathode or increasing the surface area of the cathode (e.g., HAS). Solution movement reduces the effect of concentration polarization, a condition where the thin film of electrolyte surrounding the cathode is depleted of metal ions. A high cathode surface area permits efficient operation at low metal concentrations.

Electrowinning is applied to a wide variety of chemical solutions found in the PWB industry. Metals that are most commonly recovered by electrowinning are copper, gold, and silver. For practical purposes, the degree to which a metal can be recovered by electrowinning depends on its position in the electromotive series. In general, metals that have more positive standard electrode potentials plate more easily than the ones with less positive potentials. As an illustration, the more noble metals, such as silver and gold, can be removed from solution to less than 1 mg/l using flat plate cathodes, whereas with copper and tin, a concentration in the range of 0.5 to 1 g/L or more is required for a homogeneous metal deposit.

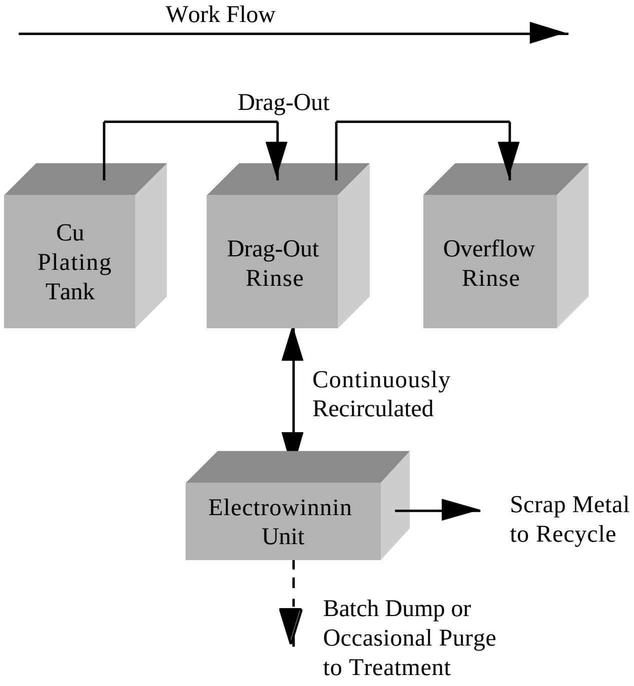
5.3.2.2 Applications

Ion Exchange Cation Spent Regenerant. Ion exchange is employed in a variety of configurations in PWB shops, ranging from closed-loop treatment of single rinse systems to a major component (particularly in small shops) of the waste treatment system handling combined rinse streams from a majority of the wet processes. The metal-rich spent cation regenerant is an ideal and logical candidate for electrowinning. For most PWB ion exchange installations, sulfuric acid is the cation regenerant of choice, which is a particularly favorable electrowinning electrolyte.

The ion exchange-electrowinning combination (Exhibit 5-10) is most efficient with copper-bearing rinses that may be combined from several sources (Exhibit 5-12) or accomplished at the location of a single process. Although ion exchange may also be employed on tin-lead and gold rinse systems, cation resins primarily employed to remove lead or gold are not usually regenerated on-site, due to the difficulty of the cycle or the expense of the required regenerant.

Drag-out Tanks. Since the efficiency of electrowinning falls off as the concentration of metal falls, electrowinning of rinse water is, in general, less efficient that that of ion-exchange regenerant where ion exchange serves to concentrate metal. Nevertheless, electrowinning is quite effective at greatly reducing the introduction of metal into flowing rinses ultimately treated by the facilities main waste treatment system when employed on drag-out rinses (Exhibit 5-15).

Exhibit 5-15. Electrowinning Technology Applied to a Drag-Out Tank



Drag-out tanks are rinse tanks, initially filled with water. Parts are first rinsed in this tank; then proceed to the flowing rinse system. In the most efficient configuration, a drag-out rinse is placed after a heated process tank, and the contents of the drag-out tank are returned (recovered) to the process tank as evaporative loss make-up. The level of the drag-out tank is made-up with fresh water, thereby maintaining the overall concentration of the drag-out tank below that of the process tank. This simple arrangement is quite effective at reducing the mass of metal entering the flowing rinses, but the efficiency of the drag-out tank is a function of the temperature (evaporation rate) of the process fluid. Cool process fluids create little evaporative headroom, and little drag-out fluid can be returned.

A major source of copper-bearing drag-out in the PWB facility is the copper electroplating tanks. Today, the overwhelming electrolyte of choice for PWB copper electroplating is copper sulfate. This bath is generally maintained at 80°F or below making it less than an ideal candidate for conventional drag-out recovery rinsing. Some facilities have opted for a closed loop ion-exchange/electrowinning system to handle the flowing rinses of the copper electroplating process. A second effective alternative is to employ a drag-out rinse tank connected to an electrowinner, through which the drag-out tank solution is continuously circulated. In this configuration, the metal concentration of the drag-out tank is maintained at a low level (determined by the introduction rate due to drag-in, the metal removal rate of the electrowinner, particularly at low concentration levels, which can be greatly enhanced by the use of high-surface-area cathodes), thereby reducing the drag-out of metal to the flowing rinse. A properly sized electrowinning unit can maintain the drag-out tank metal concentration well below 100 mg/L, compared to the 14-25 g/L copper concentration contained in the process fluid. The effect being, with the drag-out and electrowinning configuration, the introduction of copper into flowing rinses will be reduced by two orders of magnitude when compared to a standard flowing or counterflowing rinse system.

In the copper sulfate example, the drag-out tank gradually accumulates sulfuric acid, which is not an unfavorable environment for PWBs and, therefore, only rarely will the tank need to be dumped. When applied to other plating or preparation processes, the build-up of constituents (the electrowinning is only removing metal) from the process fluid may require more frequent dumping of the drag-out tanks, lowering the overall efficiency of the system.

The drag-out electrowinning configuration can also be employed after tin-lead, nickel, and gold plating, with good to excellent results. Recovery of gold from drag-out tanks is common for obvious economic reasons, although many facilities also opt for ion exchange of gold rinse water, which is another effective method of gold recovery. Nickel recovery from dragout tanks following nickel electrolytic plating is less common. Nickel plating baths are generally heated to above 120°F, making conventional drag-out recovery effective. Also, many facilities only plate nickel on connector edges (only a small portion of the PWB is immersed and the drag-out is much lower compared to copper electroplating), and a significant percentage of PWBs may receive no nickel plating at all, making an investment in nickel drag-out recovery less attractive. On the other hand, the value of nickel is 3 to 4 times that of copper, making nickel recovery more economically attractive to facilities that do full panel nickel plating or otherwise generate above-average nickel drag-out.

Tin-lead plating, like copper sulfate, is generally performed at low temperature, making the drag-out, electrowinning configuration attractive. The move in the industry away from tin-lead to tin-only plating and the competition from ion exchange of tin-lead flowing rinses has limited the use of electrowinning. Although the drag-out with electrowinning configuration will perform nearly as effectively with tin lead as with copper, a few factors combine to make the overall system somewhat more expensive and less attractive strategically. The tin-lead plating operation is basically the only source of lead in the rinsewater of a PWB facility (other sources may contribute minute amounts). Cation exchange essentially can remove nearly all lead from the rinses from this operation, thereby preventing any lead from reaching the conventional waste treatment system. Elimination of lead from rinsewater available from ion exchange may be viewed favorably to the reduction of lead achieved by electrowinning. Also, the common electrolyte for tin-lead plating is flouboric acid, which necessitates the use of expensive, precious-metals-coated anodes.

Tin is not usually recovered (as it is usually not regulated), except incidentally along with lead in ion exchange or electrowinning systems.

Spent Process Fluids. It is possible to electrowin several spent process fluids to recover metal and/or to reduce the burden on the general waste treatment system. While there are several spent process fluids found that are easily electrowinned, it is not an extremely common practice due mainly to a combination of competing technologies or treatment methods, and the cost of handling irregularly timed or one-time dumps of potential electrowinning candidates.

A large process fluid waste stream that can be electrowinned is spent micro-etchant. The currently favored micro-etchant chemistries are sulfuric-persulfate or sulfuric-peroxide. These baths contain 20-40 or more g/L of copper when spent. Both are strong oxidizing solutions, and the spent bath is usually reduced with sodium meta-bisulfite or other reducing agent before electrowinning. With very high copper concentrations and the favorable sulfuric acid-based electrolyte, electrowinning proceeds at very high efficiencies, near copper’s theoretical maximum plating rate of 1.19 g/amp-hour. A unit capable of delivering 500 amps can easily plate a pound of copper out of such solutions in a single hour, the proceeds from which can easily cover energy costs and, depending on the level of automation and the amount of labor involved in the handling and preparation of the electrolyte, may also cover the operating costs.

A study at one circuit board facility involving copper recovery from microetchant demonstrated that an 80 to 90% electrowinning efficiency could be achieved, while reducing metal content to 1 mg/l in the waste stream (ref. 7). Two types of cathodes were used in an air-sparged electrolytic recovery cell during a two-step operation. Flat reusable stainless-steel sheet cathodes were first used to reduce the copper concentrations of the solution from 20 grams per liter down to 500 milligrams per liter. The cathodes are removed and the copper is peeled off (up to 2 lbs.

of copper per cathode). The second step employs disposable high-surface-area cathodes that collect up to 3 lbs. of copper per cathode and reduce the copper concentration of the solution below 1 mg/l. After two years, the original stainless-steel cathodes were still in use and nearly 1,000 lbs. of copper has been collected. The process reportedly reduced hazardous waste generation by more than 35 tons. Another benefit is a reported 50% reduction in the cost of operating the wastewater treatment system.

Electrowinning of micro-etchant competes with common and simple treatment methods. In the case of sulfuric-peroxide, chilling is very effective. Both sulfuric-peroxide and sulfuric-persulfate spent baths can be shipped off-site for copper recovery. This option is often attractive to small shops that produce only a hundred gallons of spent micro-etchant/year.

Another large process waste stream is spent sulfuric acid dips. These, too, are readily electrowinned. However, the concentration of copper in these spent bath, however, is low, usually 1 g/L or less. While electrowinning can reduce the copper concentration much lower, efficiency at this concentration is reduced and plating times per unit of copper recovered much higher.

Spent electroless copper is also an electrowinning candidate, but more effective, easier methods are available. Spent electroless copper is produced steadily by bail-out (to make room for frequent additions), and the bath itself is relatively short-lived. Most facilities prefer to treat the bailout by passing it through activated foam canisters that cause copper to plate-out on the media surface. The effluent from these cartridges is nearly metal-free.

Spent gold baths are commonly electrowinned, although credits for gold content can also be obtained by shipping the spent bath for off-site recovery.

Other spent electroplating fluids (tin, tin-lead, copper, nickel) are not produced in large quantities. Copper sulfate baths may last for several years, and the timing of the dump is based solely on analysis. Similar bath lives are common for nickel and tin-lead, making an electrowinning recovery strategy for these baths uncommon.

Restrictions. Solutions containing hydrochloric acid, or the chlorine ion in general, are usually not processed using electrowinning, since electrolysis of these fluids can result in the evolution of chlorine gas. Fluoboric acid electrolytes, such as tin-lead fluoborate, generally require platinized anodes, affecting the cost-effectiveness of electrowinning such solutions. Solutions containing chelated metals, reducing agents, and stabilizers are more difficult for direct application of electrowinning.

Nickel recovery using electrowinning is possible, but it requires close control of pH and is therefore performed less frequently than for metals such as copper and gold.

Exhibit 5-16. Electrowinning Technology Data (1995 Survey)

Resp. ID	Application	Year Purch.	Equip. Cost ($)	Install Cost ($)	Labor (hr/yr)	Non-Labor ($/yr)	Use Code	Down Time %	Satisfied?	Future Decision
959951	Lead-bearing rinses from resist strip and solder drag-out	1986	21000	0	2080	0	1	5	Yes	1
955099	Microetch on electroless	1990	0	0	0	0	1	1	Yes	1
965874	Gold rinse	-	0	0	0	0	1	2	Yes	1
42751	Microetch	1992	15000	2000	500	0	2	20	No	3
44657	Photo fixer	1994	800	30	24	12.56	1	0	Yes	1
36930	Black oxide line microetch bath	1992	20000	1000	60	1000	1	0	Yes	1
37817	All baths high in cu conc.	1989	6000	200	250	1000	1	2	Yes	3

Exhibit 5-17. Electrowinning Technology Data (1997 Survey)

Shop ID	Application	Reasons	Meet Need?	Maint.	Overall Satisfy?	Future Decision
14	Copper peroxide etchants	1, 2, 3, 5, 6	Y	A	no response	S
22	Recovers the copper from ion exchange regenerant	3, 5, 6	Y	A	5	S
22	Recover Copper from bath dumps and other sources that do not go to ion exchange	1, 3, 5, 6	Y	A	5	S
34	Microetches, rack stripper, ion exchange regenerant	1, 3, 5, 6	Y	L	5	S
29	Cu IX regenerate, Pb IX regenerate, chelated Cu regenerate, persulfate etches, and Ni sulfates.	1, 3, 5	Y	L	5	S
37	Spent cleaner\conditioner baths	1, 3, 6	Y	A	5	S
54	All spent copper laden baths	1, 6	Y	M	5	S
44	Drag out rinses following copper plate	1, 3, 6	Y	A	4	S
53	Sulfuric acid rinses, some micro-etches	1, 3, 5, 6	Y	A	2	S
56	Concentrated wastes from gold plating and silver artwork developing	1, 5, 6	Y	A	4	S
45	All copper bearing drag-out and spent baths are processed down to a low Cu conc. Using EW and then go through a copper specific resin for polishing to less than 2 mg/l Cu. Adjusted then sent to the local POTW. The technology is sound, but our system needs a few enhancements to make it more productive.	1, 3, 6	P	A	4	S
51	Spent copper baths, spent fixer baths	1, 3, 6	Y	A	3	S
36	Plating baths. Cost of running is greater than benefits much of the time.	1, 3	P	M	2	D
46	Ion exchange regenerant	1, 6	P	M	3	S

Use codes: 1 = in use; 2 = not in use; 3 = not in use, future use expected
Future decision codes: (in response to survey question, "indicate a future course of action should you be required to fill a similar need"): 1 = buy the same technology from the same vendor; 2 = purchase same technology from different vendor; 3 = purchase different technology; 4 = do nothing.

Reasons technology was purchased:
1 = to meet or help meet effluent limits
2 = to reduce process chemical purchases
3 = to reduce quantity of waste shipments off-site
4 = to increase production rate
5 = to reduce worker exposure to hazardous waste
6 = to recover a metal for resale
7 = to recover a chemical for reuse

Has the technology met the need for which it was purchased?
Y = yes
N = no
P = partially

Rate the level of maintenance required:
A = about what was expected
M = more than expected
L = less than expected

Overall satisfaction with the technology:
1 = very dissatisfied
5 = very satisfied

To fulfill a similar need in the future, which technology would you purchase?
S = same technology
D = different technology
S = none

5.3.3 Evaporation

Evaporators are commonly used in the metal finishing industry for the recovery of plating solutions. However, this technology is not widely applied by the PWB industry. Only 3.5% of the survey respondents indicated that they use evaporative equipment. One respondent uses evaporative recovery to recover drag-out of their electroplating copper solution (ID #133000). One respondent uses evaporation to reduce their volume of wastewater and achieve zero discharge (ID #36). However, there is no recovery of chemicals or water. Another respondent uses evaporative distillation to recover gamma butyrolactone (solvent) on their solder mask line.

There are two primary types of evaporators: atmospheric and vacuum evaporators. Both are employed to concentrate dissolved chemicals into a smaller volume by removing water. The concentrated dissolved chemicals are either recovered or discarded off-site. An atmospheric evaporator is a relatively simple device that evaporates water at atmospheric pressure and releases the moisture to the environment. A vacuum evaporator is a distilling device that vaporizes water at low temperatures when placed under a vacuum. Vaporized waters are typically condensed and reused. Additional details of the two types of evaporators are presented in this section.

5.3.3.1 Atmospheric Evaporators

Most commercial atmospheric evaporator units consist of a pump to move the solution, a blower to move the air, a heat source, an evaporation chamber, and a mist eliminator. The evaporation chamber is where the solution and air are mixed and is usually filled with packing material or finned panels to increase the air to water interface. The mist eliminator removes any entrained liquid from the exit air stream. In operation, the temperature of the solution being evaporated is elevated, and the heated solution is introduced into the evaporation compartment. Air from the room is then blown through the compartment, where it accepts the water vapor and is then vented out of the chamber.

Commercial units are advertised to have evaporation rates of 10 to 90 gph, depending on the size of the unit and operating conditions (e.g. solution temperature). Often actual evaporation rates are considerably less because the atmospheric conditions within PWB manufacturing facilities do not match the ideal conditions under which the manufacturers rate their systems. To meet higher evaporative requirements, it is feasible to utilize multiple atmospheric evaporators in series. However, the use of atmospheric evaporators is generally limited by energy costs to applications where the required evaporation rate is 50 gph or less.

Most commercial atmospheric evaporator units have the same principals of operation. To achieve chemical recovery, solution from a heated plating tank is fed to and concentrated by the evaporator and returned to the plating tank. This approach reduces the volume of solution in the plating tank, thereby "making room" for the recovery rinse water/drag-out to be added to the plating bath. Often two or more recovery rinse stations are used to minimize the overall rinse water requirements of the process and increase the recovery rate of plating chemicals. Less frequently, atmospheric evaporation is applied to ambient or low temperature baths. In this case, the recovery rinse water may be fed to the evaporator from a heated transfer tank, which increases the overall evaporative capacity of the system. The latter application is often restricted by the maximum temperature that can be applied to the solution, since heat sensitive components of the bath could be destroyed.

5.3.3.2 Vacuum Evaporators

Vacuum evaporators are applied to the recovery of a wide range of process solutions within the metal finishing industry, but are not widely used by PWB manufacturers. They are especially applicable in situations where atmospheric evaporators are either technically or economically impractical. This includes: (1) the recovery of heat sensitive chemicals (e.g., cyanide plating baths); (2) the recovery of chemicals that are sensitive to air oxidation (e.g., cyanide plating baths or the stannous tin bath); (3) low or ambient temperature plating solutions where there is no appreciable surface evaporation; (4) the recovery of solutions that contain volatile components; and/or (5) where high evaporation rates (e.g., >20 to 40 gph) are necessary to achieve recovery, and atmospheric evaporators become too expensive (i.e., energy cost) to operate (ref. 299).

Vacuum evaporators depend on the fact that water, when introduced into a vacuum, tends to boil off, or vaporize. The rate of vaporization is directly related to the level of the vacuum and the temperature of the solution. In operation, heated solution is introduced into the vacuum chamber, the boiling point of the solution is reduced by the vacuum and the resultant vapor (distilled water) is removed from the chamber. The vapor can be either discharged or condensed for return to the process (e.g., as rinse water).

5.3.4 Other Recovery Processes

5.3.4.1 Silver Recovery from Photoplotting Film

Silver is used as the light-sensitive material that forms the image on photoplotting film. For the ordinary circuit, almost 80% of the silver emulsion is developed into the chemistry and can be recovered by one of two methods. With metallic replacement, the solution can be passed through a steel wool cartridge, where the iron in the steel reacts with the silver and replaces it. A silver sludge settles to the bottom of the cartridge.

The scrap film has the remaining amount of silver that is not developed. This film can be collected in bins and sent out to a commercial reclamation facility. This process is not done on-site because of the complexity of the process.

5.3.4.2 Removal of Copper from Electroless Copper Baths

Copper contained in the spent electroless copper plating solution is difficult to recover using electrowinning, but can be recovered for off-site recycle using a proprietary deposition technology or sodium borohydride reduction. With the deposition technology, the copper solution is passed through canisters or modules that contain a sponge-like material deposited with copper and palladium (ref. 36). The copper in the spent solution is autocatalytically reduced and retained in the unit. One survey respondent indicted that they use this technology (ID #993585) and that they were very satisfied with its performance.

With sodium borohydride reduction, a 0.5 to 1% by volume $NaBH_4$ solution is added to a tank containing the spent electroless copper bath. This causes the copper to precipitate and it can be removed by decanting. This process generates a significant quantity of flammable hydrogen gas and therefore must be conducted under controlled conditions (e.g., ventilated tank) (ref. 36).

5.4 Off-Site Recycling

Off-site recycling is a commonly used alternative for PWB manufacturers as a means of managing spent etchant solutions and wastewater treatment sludges. Widespread implementation of this option reduces the quantity of wastes being disposed of in landfills. The PWB survey gathered information regarding the types of wastes sent to off-site recycling firms, quantities, destinations, and associated costs. These data are presented and discussed in this section.

A summary of data related to off-site recycling of spent process solutions, including etchants, is presented in Exhibit 5-18. Nearly all respondents reported using off-site recycling for disposing of spent process baths. A summary of data related to off-site recycling and disposal of wastewater treatment sludges is presented in Exhibit 5-19. Nearly ninety percent (90%) of those who provided data concerning the destination of their sludges indicated that they ship the sludges to recycling facilities rather than landfills.

5.4.1 Off-site Recycling of Spent Process Baths

By far, the most commonly reported spent process fluid that is sent off-site for recycling is spent etchant, particularly spent ammoniacal etchant. Spent ammoniacal etchant is created at a rate of roughly 1 gallon per 30 surface square feet of inner- and outer-layer panels. On-site regeneration of ammoniacal etchant is not widespread. One respondent reported installing solvent extraction technology for the purpose of on-site regeneration of ammoniacal etchant and copper recovery. The reason that spent etchant is a popular waste for off-site recycling is due mostly to its high copper concentration, which is typically 150 g/l Cu (i.e., 15% Cu). Etchant that is sent off-site is processed to recover the copper and regenerate the etchant for reuse. Eighty-three percent (83%) of the respondents who completed the off-site recycling section of the survey reported that they send spent ammoniacal etchant off-site for recycling. Costs associated with ammoniacal etchant recycling were provided in several different types of units and varied widely, but in general, it was clear that etchant recycling represented a major portion of overall recycling costs. One respondent (ID# 462800) reported an income from off-site recycling of their spent cupric chloride etchant ($26,000 annually).

Waste products other than etchant are less frequently sent off-site for recycling by the survey respondents. The next most commonly shipped waste product is tin and/or tin-lead stripping solutions. These solutions are listed by 20% of the respondents who completed this section of the survey form. Like etchant, spent stripping solutions have a high metal concentration that makes them viable candidates for recycling. Also, stripping solutions are generated in relatively high volumes, furthering the economics of off-site recycling. For example, ID# 44486 reported shipping 49,911 lb of tin strip and ID# T2 reported shipping 9,000 lb of tin stripper. In comparison, these quantities are equivalent to approximately 20% to 30% of their etchant volume sent off-site.

Flux, solder dross from the hot-air-solder-level process, and other lead-bearing solutions are shipped off-site for recycling by 20% of the respondents. However, the quantities of these materials that are shipped are relatively small. One exception was ID# 41739, who reported shipping 20,000 pounds of solder bath to an off-site recovery facility. Tin-lead plating baths generally have a long life-span (several years) and disposal of the solution is an unusual event. For this reason, it is believed that with this particular case, shipment was a one-time event. For example, the facility may have replaced their tin-lead plating bath with a tin-only solution or needed to dispose of a bath due to irreversible contamination.

Micro-etchants are shipped off-site for recovery by only 8% of the respondents. Spent micro-etchants typically contain copper concentrations of 15 to 30 g/l Cu (i.e., 1.5 to 3.0% Cu). Other respondents reported electrowinning these solutions on-site, or treating them with conventional precipitation.

Gold- and silver-bearing wastes are sent off-site by 15% of the respondents. Gold electroplating baths (usually gold cyanide) have a long life-span, and not surprisingly, the reported volumes were all 100 gallons or less. Solutions containing gold may include spent gold electroplating bath, or the contents of drip or drag-out tanks on the gold plating line. Silver is present in film developing fluids that may be reclaimed on-site (electrowinned), shipped off-site for metal reclamation, or combined with other waste streams and treated conventionally.

Ten percent (10%) of the respondents indicated that spent rack stripping solution is shipped off-site. Plating racks are typically coated with a non-conductive substance to prevent electroplating from occurring on the rack surface itself. Due to use, this coating may degrade and plating can accumulate on the rack, especially near the clamps and contact points. This unwanted copper deposit is removed in a stripping solution such as dilute nitric acid. The volume of spent stripping solution can be significant. Respondent T3 shipped 1,000 gallons of nitric acid rack stripper off-site at a cost of more than $5 per gallon. By comparison, this volume is equivalent to 12.5% of the etch volume shipped by the same respondent.

5.4.2 Wastewater Treatment Sludge

A very high percentage of respondents (88% of those providing data) indicated that they send their wastewater treatment sludge to off-site disposal facilities rather than to landfills. This percentage appears to be particularly high when compared to the 31% of plating facilities that use this method for disposal (based on results presented in ref. 3).

The average and median unit costs for off-site recovery of sludge are $0.48/lb and $0.21/lb, respectively. In general, the lower costs experienced by some respondents compared to others were due to larger-size shipments and shorter distances to the recycling sites, both of which reduce transportation costs. However, in some cases, differences in unit costs may be the result of other factors. For example, ID#'s 133000 and 953880 ship similar quantities of sludge the same distance to the same recycling company.[6] The unit cost of the off-site recycling for the two PWB manufacturers varies significantly ($0.17/lb vs $0.40/lb). One difference between the sludges shipped by these respondents is the percent solids. ID# 133000 is shipping a much dryer sludge (60% solids compared to 35% solids for ID# 953880). The dryer sludge will have a greater recovery value. By drying sludges PWB manufacturers can also reduce transportation costs, since drying reduces the volume of the sludge. The sludge drying technology and its impact on sludge volume are discussed in reference 1. One facility reported a reduction of sludge quantity from 418,441 lbs/yr to 110,116 lb./yr by installing a sludge dryer (ref. A).

A discussion of off-site recycling, including descriptions of processes used by recycling companies, is presented in reference 1.

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[6] This particular recycling company operates recycling facilities in both Arizona and Pennsylvania. Due to the confidentiality procedures employed during this project, it is not known if the two PWB manufacturers discussed send their waste to the same site.

Exhibit 5-18. Off-Site Recycling of Spent Process Fluids

Resp. ID	Waste Description	Source	Quantity (per year)	Available Cost Data	Name of Recycle Company	Distance to Recycle Company (miles)
279	cupric chloride	etch	11,000 gal	5.54 $/gal	Phibro Tech	40
279	cupric chloride	etch rinses	6,000 gal	5.55 $/gal	Phibro Tech	40
3023	ammoniacal	etch	199,450 gal	0.50 $/gal	Macdermid	75
3470	ammonia etch	etch	18,000 gal	nr	nr	nr
3470	gold plate bath	plate	60 gal	nr	nr	nr
6710	D001/D002	sulfuric/peroxide	440 gal	1.96 $/gal	US Filter Rec.	40
6710	D002	ammoniacal etch	8,000 gal	1.52 $/gal	Phibro Tech	350
25503	cupric chloride	etch	2,000 gal	0.25 $/gal	Old Bridge	3,300
29710	D002/D004	etch	98,000 lb	nr	Macdermid	768
29710	F005/D001	paint	1,536 lb	nr	Safety-Kleen	100
29710	D001	solder wave	2,721 lb	nr	Safety-Kleen	100
29710	D001	HASL	1,482 lb	nr	Safety-Kleen	100
32482	gold plating	gold plate	100 gal	nr	Advanced Chem	120
33089	ammoniacal etchant	etch	60,000 lb	0.29 $/lb.	US Filter Rec.	225
33089	tin/lead	solder strip	6,000 lb	0.40 $/lb.	US Filter Rec.	225
36930	etchant	etch	60,000 gal	4,000 $/yr	Phibro Tech	400
36930	microetch	etching/cleaning	6,000 gal	9,600 $/yr	nr	nr
37817	flux	hot air leveler	200 gal	230 $/drum	Entech Managt.	150
37817	etchant	etch	23,000 gal	nr	Dexter	nr
37817	resins	cadines	15 ft^3	160 $/drum	Entech Managt.	150
37817	acid sludge	waste catch drains	200 gal	230 $/drum	Entech Managt.	150
41739	D002	ammoniacal etch	17,000 gal	18,060 $/yr	Phibro Tech	400
41739	F007	gold bath	25 gal	3,000 $/yr	Technic	800
41739	D008	solder bath	20,000 lb	nr	Alpha Metals	800
42692	ammoniacal etchant	etch	52,883 gal	nr	Old Bridge	400
42751	cupric chloride	inner layer etch	83,700 gal	nr	Norris Environ.	1,000
42751	ammoniacal etchant	outer layer etch	32,050 gal	nr	Phibro Tech	1,200
43694	ammoniacal etchant	etch	35,000 gal	nr	S. Cal Chem	30
43841	D002	etch	13,700 gal	38,000 $/yr	Phibro Tech	500
43841	D001	oil/glycol	220 gal	2,000 $/yr	Safety Kleen	1,500
43841	class 55	board scrap	38,000 lb	7,000 $/yr	SIMCO	1,000
44486	NH etchant	Cu etch	255,370 lb	nr	Phibro Tech	200
44486	peroxide/sulfuric	tin strip	49,911 lb	18,135 $/yr	Phibro Tech	200
44486	flux	HASL	32,292 lb	16,000 $/yr	Hydrite	90
44486	acid Ni	Ni plate	195 lb	683 $/yr	PhibroTech	200
44657	D002/D008	etch	6,300 gal	nr	Hubbard Hall	nr
133000	etchant	etch	40,000 gal	0.20 $/gal	Macdermid	150
237900	ammoniacal etchant	etch	50,000 gal	0.10 $/gal	S. Cal Chem	370
237900	acid	nitric solder strip	2,000 gal	4.60 $/gal	Norris	370
237900	acid	solder strip	1,000 gal	5.00 $/gal	Norris	370
237900	acid	plating	1,400 gal	4.80 $/gal	Norris	370
358000	etchant	etch	70,000 gal	0.11 $/gal	Old Bridge, NJ	600
358000	tin stripper	tin stripper	1,800 gal	3.18 $/gal	Republic	200
462800	spent copper	etch	1,419,393 lb	26,000 $/yr[1]	Phibro Tech	40
462800	acid rinse water	etch	349,020 lb	0.05 $/lb	Envirite	30
462800	copper sludge	etch/microetch	12,854 lb	0.00 $/lb	Phibro Tech	40
462800	spent flux	hot air leveling	4,400 lb	0.91 $/lb	AKA Industrial	55
502100	sludge	etch	1,000 gal	nr	nr	nr

946587	D002	Cu sulfate plating	7,500 gal	0.12 $/lb	Learonal	980
947745	etchant	etching	3,960 gal	0.06 $/lb	Phibro Tech	250
947745	stripper	rack strip	1,200 lb	0.29 $/lb	Encycle	250
953880	D002	etch	15,000 gal	nr	Phibro Tech	600
955099	etchant	ammoniacal etch	65,000 gal	nr	Macdermid	280
955099	CuSO4	plating	12,000 gal	2.00 $/lb	Phibro Tech	400
955099	solder	HASL	22,000 lb	1.10 $/lb[1]	Dexter	50
955703	etchant	etch	45,000 gal	0.18 $/lb	Phibro Tech	25
955703	solder oil	HASL	1,300 gal	0.40 $/lb	DK	20
955703	tin strip	tin strip	5,000 gal	0.37 $/lb	Phibro Tech	25
955703	flux	HASL	800 gal	0.40 $/lb	Romic	70
959951	gold	tab plate	50 gal	nr	Electrochemicals	nr
959951	silver	film processor	250 gal	nr	Electrochemicals	nr
959951	ammonia	etch	15,840 gal	nr	Phibro Tech	nr
965874	etchant	etch	15,800 gal	0.30 $/gal	Phibro Tech	600
36930A	etchant	etching	4,200 gal	nr	Phibro Tech	400
T1	gold	deep gold	nr	nr	Learonal	nr
T1	ammoniacal etch	inner/outer etch	nr	nr	Phibro Tech	nr
T2	etchant	Cu chloride etch	18,500 gal	3.68 $/gal	Phibro Tech	7
T2	etchant	ammoniacal etch	33,000 gal	nr	Phibro Tech	7
T2	tin strip	tin strip	9,000 gal	3.45 $/gal	Encycle, TX	450
T2	nitric acid	rack strip	660 gal	4.09 $/gal	Encycle, TX	450
T3	etchant	etch	8,000 gal	nr	S. Cal Chemical	10
T3	nitric acid	rack strip	1,000 gal	5.46 $/gal	Great West. Chem	10

[1] Income from recycled process fluid.
nr = no response

Exhibit 5-19. Off-Site Recycling/Disposal of Wastewater Treatment Sludge

Resp. ID	Quantity (lbs)	Percent Solids (%)	Recycle or Dispose	Cost ($/yr)[2]	Cost ($/lb)[2]	Company	Distance to Site (miles)
279	nr	nr	nr	nr	nr	nr	nr
29710	nr	nr	nr	nr	nr	nr	nr
31838	nr	nr	nr	nr	nr	nr	nr
36930	nr	nr	nr	nr	nr	nr	nr
43694	nr	nr	nr	nr	nr	nr	nr
237900	nr	nr	nr	nr	nr	nr	nr
358000	nr	nr	nr	nr	nr	nr	nr
955703	nr	nr	nr	nr	nr	nr	nr
3470	10,000	75	nr	nr	nr	nr	nr
965874	5,000	15	nr	nr	nr	nr	nr
25503	1,200	95	unknown	720	0.60	Norris Env	30
42692	200,000	40	unknown	85,000	0.43	S. Water Treat. Co	300
273701	300	50	D	200	0.67	US Filter Rec.	nr
36930A	18[1]	50	D	nr	nr	US Filter Rec.	30
33089	80,000	35	D	48,000	0.60	US Filter Rec.	225
502100	3,000	75	R	nr	nr	nr	nr
959951	33,190	50	R	nr	nr	Cyprus Miami	nr
T2	58,000	25	R	nr	nr	Encycle, TX	450
44486	nr	nr	R	nr	nr	Foreman Metals	20
462800	12,854	98	R	0	0	Phibro Tech	40
T1	260,000	80	R	35,000	0.13	Encycle, TX	1,500
41739	42,000	65	R	6,000	0.14	Encycle, TX	600
107300	400,000	60	R	60,000	0.15	WRC	222
740500	1,700,000	36	R	275,000	0.16	WRC	1,500
55595	140,000	40	R	22,880	0.16	Envirite	400
42751	250,000	48	R	39,375	0.16	WRC	nr
133000	160,000	60	R	27,000	0.17	WRC	300
947745	9,600	80	R	1,875	0.20	Encycle, TX	250
3023	320,000	41	R	68,000	0.21	WRC	375
946587	308,000	53	R	63,150	0.21	WRC	1,000
955099	220,000	48	R	50,000	0.23	WRC	500
32482	14,000	65	R	4,000	0.29	WRC	nr
44657	8,200	30	R	3,000	0.37	WRC	750
953880	120,000	35	R	48,000	0.40	WRC	300
43841	10,000	26	R	7,800	0.78	WRC	500
6710	18,000	nr	R	25,000	1.39	WRC	850
37817	1,000	95	R	1,500	1.50	NE Chemical Co	400
T3	10,000	80	R	20,000	2.00	Encycle, TX	1,800

[1] Unit is ft^3

[2] Some variation in costs among respondents may be due to inclusion or omission of analytical fees (sometimes referred to as material profile fees).

nr = no response

6.0 End-of-Pipe Treatment

6.1 General

End-of-pipe treatment is, by definition, not pollution prevention. However, it is an important aspect of pollution control and it sometimes competes financially with pollution prevention options when facilities are developing pollution control strategies. To make informed decisions about implementing pollution prevention alternatives that include consideration of all applicable costs and potential savings requires accurate data. Therefore, the topic of waste treatment was included in the PWB survey project so that the true costs of treatment could be examined. The applicable portion of the survey form requested respondents to describe the type of waste treatment system currently in use at their facilities and to provide operating and cost data. These data are summarized and discussed in this section.

6.2 Wastewater Characterization

Data that characterize the respondent's raw wastewater from their PWB processes are presented in Exhibit 6-1. The data indicate that copper and lead are the most abundant of the regulated metals. Copper was reported to be present by all respondents. Copper concentrations in the raw wastewaters ranged from 0.4 mg/l to greater than 100 mg/l. Factors affecting the copper concentration of raw wastewater may include: the effectiveness of rinse water controls (which will determine the level of dilution); whether or not process solutions that have relatively high copper concentrations (e.g., spent acids and micro-etches) are commingled directly with rinse water; the effectiveness of drag-out reduction and recovery; and the presence of upstream recovery/recycle technologies, such as ion exchange and electrowinning.

Sixty-two percent (62%) of the facilities that provided raw wastewater data reported the presence of lead. Concentrations of lead ranged from less than 1 mg/l to 20 mg/l. The primary sources of lead in a PWB manufacturing process are drag-out from the tin-lead electroplating and stripping operations. Lead may also be introduced in small quantities from reflow or solder-leveling operations. Respondents not reporting lead in their raw wastewater may remove lead with a recovery/recycle technology (e.g., ion exchange) upstream, or may not perform lead plating (or, therefore, stripping). Also, possibly due to a higher sensitivity to lead discharges than some other metals, more aggressive drag-out reduction and recovery methods may be practiced for lead sources.

Forty-eight percent (48%) of the facilities that provided raw wastewater data reported the presence of nickel. Nickel concentrations ranged from less than 1 mg/l to 7.5 mg/l. The most common source of nickel in the raw wastewater is nickel electroplating or electroless nickel plating, which serve as an undercoat for gold. Another common process is the electrolytic nickel-gold plating of the connector edge ("tab plating") of certain PWBs (e.g., PC expansion cards). Wastewater flows generated from these operations may be small in comparison to copper or tin-lead plating operations, and drag-out from typical nickel-gold tab electroplating process baths is generally low. Not all PWBs require tab nickel-gold plating, and few require full nickel-gold. For tab plating, a small portion of the board is actually immersed in the bath, thereby limiting dragout. Respondents not reporting nickel in their wastestream may perform little or no nickel plating, or they may aggressively recover nickel drag-out.

Sixteen percent (16%) of the facilities that provided raw wastewater data reported the presence of silver. Only one respondent reported silver in concentrations greater than 1 mg/l. Silver is present in the photographic developer and fix solutions (and associated rinses) required to create film images. Silver is also used at some PWB facilities for electroplating, but less commonly than for photographic purposes.

Exhibit 6-1. Discharge Limitations and Compliance Difficulties

Respondent ID	Cu max mg/l	Cu avg mg/l	Pb max mg/l	Pb avg mg/l	Ni max mg/l	Ni avg mg/l	Ag max mg/l	Ag avg mg/l	CN max mg/l	CN avg mg/l	TTO max mg/l	TTO avg mg/l
40 CFR 413	4.5	2.7	0.6	0.4	4.1	2.6	1.2	0.7	1.9	1.0	2.13	-
40 CFR 433	3.38	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	0.65	2.13	-
6710	4.50	0.37	0.60	0.10	4.10	0.09	1.20	0.01	1.90	0.01	2.13	-
36930A	2.59	1.59	0.53	0.33	3.05	1.83	0.33	0.18	0.92	0.50	1.63	-
36930	4.34	2.60	0.58	0.39	3.95	2.91	1.16	0.67	1.83	0.96	2.05	-
273701	3.38	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	-	-	-
358000	**2.00**	**1.50**	-	-	-	-	-	-	-	-	-	-
955703	3.00	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	0.65	0.58	-
33089	3.38	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	0.65	2.13	-
107300	2.00	1.00	0.30	0.10	1.30	1.00	-	-	-	-	2.13	-
502100	1.00	1.50	-	-	-	-	-	-	-	-	-	-
44657	3.00	2.07	0.60	0.40	2.20	-	0.43	0.24	1.20	0.65	2.13	-
43694	3.00	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	0.65	0.58	-
29710	0.49	0.41	0.43	0.27	2.50	1.50	0.02	0.02	0.76	0.41	1.34	-
T3	2.70	2.70	0.40	0.40	2.60	2.60	0.70	0.70	1.00	-	2.13	-
T1	1.00	0.03	0.20	0.05	1.00	0.04	0.50	0.01	-	-	2.35	1.00
955099	1.50	-	0.20	-	1.00	-	2.00	-	1.00	-	5.00	-
37817	5.00	3.50	1.00	0.25	-	-	-	-	-	-	-	-
959951	3.22	0.45	0.60	0.11	2.91	0.43	0.85	0.12	1.90	0.17	2.13	-
947745	3.38	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	0.65	2.13	-
95880	0.25	-	0.19	-	0.60	-	0.13	-	0.74	-	0.74	-
42751	3.00	2.07	0.69	0.43	2.50	2.38	1.00	-	1.20	0.65	2.13	-
32482	3.38	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	0.65	-	-
44486	4.50	2.70	0.60	0.40	4.10	2.60	5.80	-	1.90	1.00	1.30	-
42692	4.50	2.70	0.60	0.40	4.10	2.60	-	1.90	1.00	-	2.13	2.13
41739	4.00	0.40	**0.60**	**0.30**	4.00	0.50	1.00	-	1.00	0.01	-	-
43841	4.30	2.60	0.57	0.38	0.72	0.23	0.03	0.01	1.82	0.96	2.13	-
T2	2.20	2.07	0.69	0.43	3.00	2.38	0.43	0.24	1.00	0.65	2.13	-
3470	1.50	2.07	0.20	0.23	1.00	2.38	0.43	0.24	0.50	0.65	2.13	-
740500	3.38	1.70	0.69	0.40	3.98	1.60	0.43	0.24	1.20	0.65	2.13	-
279	3.00	2.02	-	-	-	-	-	-	-	-	-	-
3023	1.50	-	**0.20**	-	1.00	-	2.00	-	0.50	-	1.00	-
237900	**2.70**	**1.00**	**0.40**	**0.40**	2.60	0.25	0.70	0.70	0.50	0.50	2.13	-
133000	1.50	-	0.34	-	4.10	-	0.23	-	0.60	-	2.13	-
25503	3.00	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	0.65	0.58	-
946587	3.40	-	0.50	-	2.20	-	0.80	-	0.40	-	-	-
462800	2.90	1.91	0.39	0.26	2.64	1.69	-	-	1.23	0.65	1.40	-
31838	3.00	1.50	0.69	0.43	3.00	1.50	0.43	0.24	0.80	0.40	2.13	-
55595	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr
965874	3.38	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	0.65	2.13	-

Bold type indicates compliance difficulty with discharge parameter.
nr = no response
40 CFR 413 maximum is based on a 4 day average concentration.
40 CFR 433 maximum is based on a monthly average concentration.

Total toxic organics (TTO) were reported in raw wastewater by 20% of the respondents. The primary sources of toxic organics are solder mask ink solvents and screen cleaners, certain film strippers, phototool cleaners, and tape residue removing solvents.

6.3 Types of Processes/Systems Employed

Exhibit 6-2 summarizes the respondents' wastewater treatment equipment purchase data. The primary purpose of the wastewater treatment systems employed is the removal of dissolved metals. This is accomplished by the respondents through installation of conventional metals precipitation systems,[7] ion exchange-based metals removal systems, combined precipitation/ion exchange systems, and aluminum chip reactor systems. The most common type is conventional metals precipitation systems, which includes precipitation units followed by either clarifiers or membrane filters for solids separation. Fifty-eight percent (58%) of the respondents reported having conventional metals precipitation systems installed. Polishing filters are also commonly employed following precipitation/solids separation. The use of clarifiers is the predominant method for separation of precipitated solids from the wastewater (only 12.1% of the respondents with conventional precipitation technology reported using membrane filters). Several respondents use reverse osmosis to further process the wastewater and a portion of the treated water is reused for rinsing.

Thirty percent (30%) of the respondents reported using ion exchange as their basic waste treatment technology and another 6% used ion exchange in conjunction with conventional metals precipitation units. Thirty-six percent (36%) of the ion exchange systems included electrowinning. The use of ion exchange as a waste treatment technology is more widespread in the PWB industry than in the plating industry, where it is found in approximately 6% of plating shops (ref. 1). One reason ion exchange is more common as an end-of-pipe technology for PWB facilities is the limited number of regulated ionic species present in PWB wastewater. For most shops, copper, lead, and nickel are the only metal ions present in significant concentrations, all of which are amenable to ion exchange. Furthermore, these metals are also easily electrowinned from ion exchange regeneration solutions, which makes the ion exchange/electrowinning combination an effective metal recovery system for PWB shops. Facilities using ion exchange tend to be small- to medium-size with the median sales level being $7.5 million, compared to $14.5 million for all respondents.

Six percent of the respondents employ an aluminum bed reactor system as their primary end-of-pipe treatment. With this technology, the wastewater pH is lowered to approximately pH 3.2 and it flows through an aluminum chip bed. Copper present in the wastewater is exchanged for aluminum on the surface of the chips. Eventually, the chips are removed and sent off-site for disposal or recovery. This technology does not effectively remove chelated copper or other regulated metals such as nickel or lead.

Column 8 of Exhibit 6-2 shows the satisfaction ratings given by the respondents for their treatment system or system component. The ratings are based on a scale of 1 to 5, with 1 being a low level of satisfaction and 5 being a high level of satisfaction.

Column 9 of Exhibit 6-2 indicates if the respondent reported that a failure, malfunction, or other event associated with the end-of-pipe system resulted in a permit exceedance. Thirty-two percent (32%) of the respondents indicated that they did experience a permit exceedance due to their system. Some respondents reported the nature of the permit exceedance; these included: pH (7.9% of all respondents), Pb (10.5% of all respondents), Cu (10.5% of all respondents), and Ag (2.6% of all respondents).

Exhibit 6-2. Wastewater Treatment Equipment Data

Resp. ID	System	Type of System	Flow (gpm)	Year Pur-chased	Cost ($)	Manufacturer	Rating[1]	Permit Exceed Yes or No[2]
3023	Initial System	(not in use)	100	1984	250,000	Chemtronics	3	Y
3023	Upgrade 1	ion exchange	40	1992	553,000	Memtek	4	-
3023	Upgrade 2	precipitation/membrane	54	1994	125,000	Memtek	4	-
3023	Upgrade 3	resist strip treatment	-	1995	60,000	JCL Associates	4	-
3470	Initial System	ion exchange	0.5	1993	25,000	none	3	Y
6710	Initial System	precipitation/clarifier	22	1987	50,000	JWI	4	N
25503	Initial System	ion exchange	9	1991	45,000	Remco	4	N
29710	Initial System	unknown	120	nr	nr	Baker Bros	4	Y
29710	Upgrade 1	ion exchange-copper	12	1991	70,000	Bio Recovery	5	-
29710	Upgrade 2	ion exchange-nickel	3	1992	46,000	Bio Recovery	5	-
29710	Upgrade 3	ion exchange-copper	50	1993	237,000	Kinetco	4	-
32482	Initial System	precipitation/clarifier	2	1986	120,000	Lancy	4	N
33089	Initial System	precipitation/clarifier	9	1987	4,000	various	2	Y

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[7] Conventional treatment is a series of unit operations that is commonly installed for metals removal by facilities in the metal finishing and PWB manufacturing industry sectors. Metals removal is accomplished using hydroxide precipitation followed by separation of the precipitated metals.

33089	Upgrade 1	filter press	-	1989	12,000	JWI	4	-
33089	Upgrade 2	new tanks, repipe	-	1994	6,000	various	5	-
37817	Initial System	ion exchange	10	1989	50,000	Eastern Ind Wtr	3	N
37817	Upgrade 1	electrowinning	-	1989	6,000	Retec	4	-
41739	Initial System	precipitation/membrane	50	1989	300,000	Memtek	4	Y
41739	Upgrade 1	pre/post-treat upgrade	-	1993	250,000	Gabel Contracting	5	-
42692	Initial System	ion exchange	70	1987	250,000	NCA	3	N
42751	Initial System	precipitation/clarifier	100	1986	nr	Napco	4	N
42751	Upgrade 1	polishing filter	-	1994	16,000	Conrec	3	-
42751	Upgrade 2	filter press	-	1994	24,000	JWI	4	-
43694	Initial System	ion exchange	20	1990	60,000	Remco	4	N
43841	Initial System	precipitation/filtration	55	1983	65,000	DMP	1	Y
43841	Upgrade 1	filter press	-	1985	13,000	JWI	5	-
43841	Upgrade 2	equalization pit	-	1991	400,000	Generic	3	-
43841	Upgrade 3	filter bags	-	1993	1,000	Generic	3	-
44486	Initial System	precipitation	nr	1990	25,000	unknown	5	N
44657	Initial System	precipitation/clarifier	6	1986	200,000	Andco	3	N
55595	Initial System	precipitation/filter press	15	1976	1,200,000	in house	4	N
107300	Initial System	precipitation/clarifier	250	1980	nr	Durion/Chemtronics	5	N
107300	Upgrade 1	sludge dryer	-	1992	83,000	Fenton	3	-
107300	Upgrade 2	equalization tank	-	1993	43,000	Fedco	5	-
133000	Initial System	precipitation	175	1984	362,000	Manchester	4	N
133000	Upgrade 1	sludge dryer	-	1993	40,000	JWI	5	-
133000	Upgrade 2	clarifier	-	1993	40,000	Graver Water	4	-
133000	Upgrade 3	rinse water pump	-	1990	4,500	Durco	5	-
237900	Initial System	precipitation/clarifier	73	1984	300,000	Stranglo	2	N
273701	Initial System	ion exchange/electrowin	10	1994	40,000	self	5	N
358000	Initial System	ion exchange	30	1991	nr	Lisle-Metrix Ltd	4	N
462800	Initial System	ion exchange/ precipitation	103	1990	240,000	Kisco	4	N
740500	Initial System	precipitation/clarifier	300	1981	20,000	various	4	N
946587	Initial System	precipitation	60	1987	250,000	Memtek	2	Y
946587	Upgrade 1	clarifier	-	1994	50,000	Parkson	3	-
947747	Initial System	precipitation	30	nr	nr	nr	nr	Y
947745	Upgrade 1	clarifier	-	1989	30,000	Atlantes	5	-
953880	Initial System	precipitation/filtration	30	1984	125,000	Memtek	4	N
955099	Initial System	precipitation/clarifier	83	1981	nr	-	3	N
955099	Upgrade 1	polishing system	-	1990	nr	Serfilco	3	-
955703	Initial System	electrowinning	-	1989	nr	Baker Bros	5	N
955703	Upgrade 1	ion exchange	70	1990	nr	Remco	5	-
965874	Initial System	ion exchange/electrowin	20	1993	65,000	Smith Engineering	3	Y
36930A	Initial System	ion exchange	40	1989	201,000	nr	3	N
T1	Initial System	precipitation/clarifier	135	1980	1,200,000	Dickson	1	N
T1	Upgrade 1	sludge dryer	-	1990	60,000	OSI	2	-
T1	Upgrade 2	chemical tester	-	1992	7,000	Acrison	4	-
T2	Initial System	precipitation/clarifier	40	1989	25,000	Atlantes	3	Y
T2	Upgrade 1	sludge dryer	-	1993	20,000	Leatherwood	3	-
T2	Upgrade 2	air scrubber	-	1994	11,000	Fenton	4	-
T3	Initial System	precipitation/membrane	30	1984	75,000	Memtek	4	Y
T3	Upgrade 1	nr	-	1987	25,000	Memtek	5	-
T3	Upgrade 2	nr	-	1991	10,000	in-house	5	-

[1] Satisfaction rating is based on a scale of 1 to 5, with 1=lowest and 5=highest.
[2] Indicates if a failure, malfunction, or other event associated with the end-of-pipe system resulted in a permit exceedance (Y = yes, N = no).
nr = no response

6.4 End-of-Pipe Treatment Capital Costs

End-of-pipe wastewater treatment capital costs are included in Exhibit 6-2. Capital costs ranged from $1.2 million (purchased in 1980 for a flow of 135 gpm) to $4,000 (purchased in 1987 for a 9 gpm flow). For ion exchange systems, costs ranged from $250,000 (purchased in 1987 for a 70 gpm flow) to $40,000 (purchased in 1994 for a 10 gpm flow).

6.5 End-of-Pipe Treatment Operation Costs

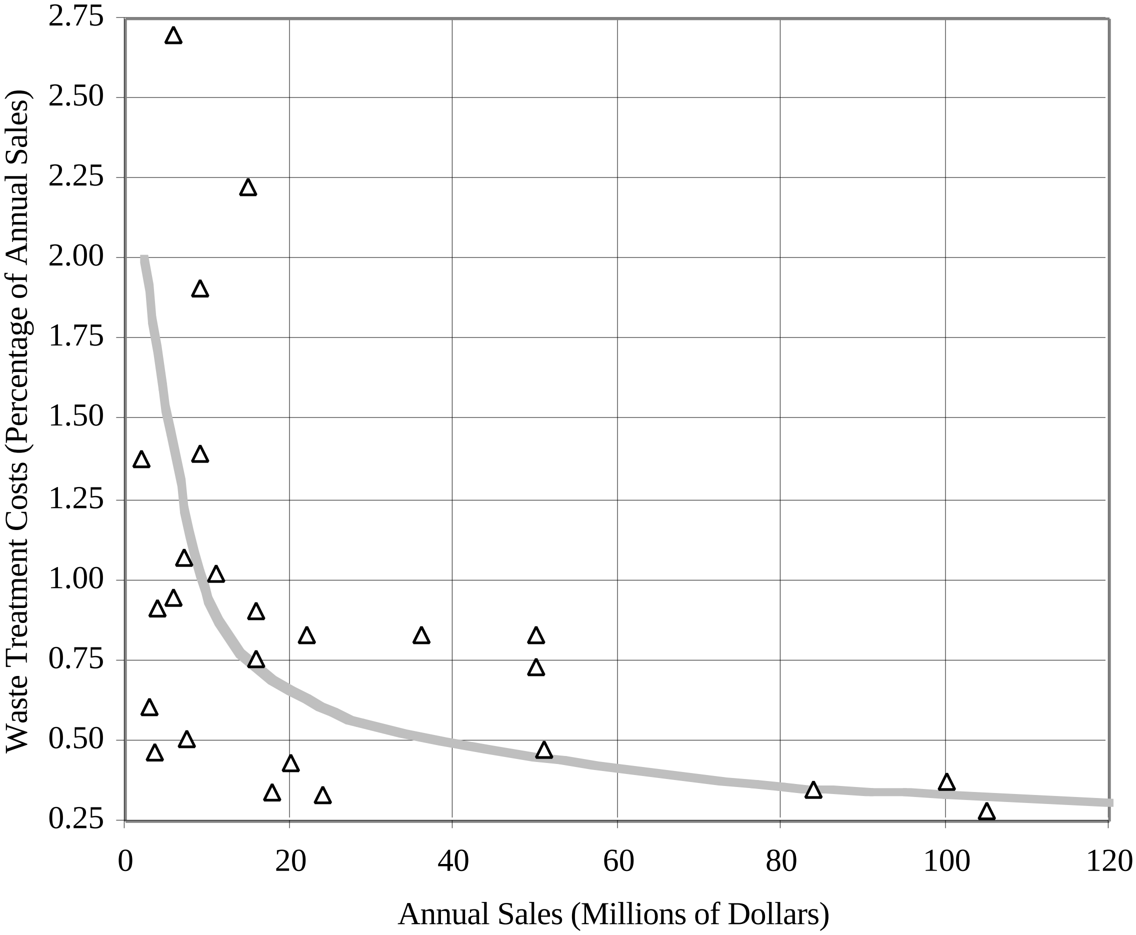
Exhibit 6-3 displays the major operating costs associated with end-of-pipe wastewater treatment. For the three largest facilities (in terms of sales) that provided data, these costs represent 0.29%, 0.37% and 0.35% of sales. The data indicate that waste treatment operating costs, as a percentage of annual sales, are higher for small shops than for large shops. Fourteen percent (14%) of the facilities reporting had costs in excess of 2% of sales with the highest being 3.1%. All of these facilities had sales near or below the median sales level for all respondents. The median cost for waste treatment as a percentage of annual sales was 0.83%, and the average was 1.02%. A plot of waste treatment operating costs as a percentage of sales volume for all respondents is presented is Exhibit 6-4.

Exhibit 6-3. Wastewater Treatment Operating Costs

Respondent ID	Production (board ft2 per year)	Average Wastewater Flow (gpd)	Chemical Costs ($/yr)	Chemical Costs ($/Kgal of Flow)	Sludge Costs ($/yr)	Routine O&M (hrs/yr)	Repair Time (hrs/yr)	Costs ($/Kgal of Flow)
36930A	nr	27,000	1,600	0.23	0	100	40	0.53
955099	nr	120,000	141,000	4.52	50,000	20,000	300	15.88
55595	nr	20,000	nr	-	nr	nr	nr	-
44486	nr	100,000	nr	-	nr	nr	nr	-
955703	nr	98,000	15,500	0.61	nr	7,000	30	4.75
6710	15,000	10,560	6,768	2.47	25,000	1,040	30	17.42
947745	40,000	13,000	13,212	3.91	1,875	780	50	8.15
44657	42,358	6,000	6,460	4.14	3,000	550	30	11.64
29710	57,000	74,000	37,444	1.95	nr	3,552	nr	4.72
502100	60,000	nr	nr	-	nr	1,200	100	-
32482	75,000	31,000	40,492	5.02	4,000	2,200	100	9.80
25503	90,000	5,000	2,200	1.69	720	2,200	40	28.09
36930	96,000	nr	13,100	-	nr	800	50	-
965874	175,000	21,000	10,456	1.92	nr	10,000	100	29.66
953880	180,000	35,000	96,092	10.56	48,000	1,760	100	18.90
T3	200,000	16,000	24,185	5.81	20,000	600	240	13.65
33089	200,000	20,000	13,320	2.56	48,000	2,000	100	17.85
3470	240,000	20,000	4,755	0.91	0	2,000	200	7.26
43841	250,000	38,000	26,674	2.70	7,800	5,100	100	11.38
279	250,000	5,200	nr	-	nr	nr	nr	-
237900	273,000	105,000	87,012	3.19	nr	6,000	425	6.72
273701	280,000	25,000	11,800	1.82	200	3,500	700	11.54
41739	300,000	57,125	71,374	4.81	6,000	3,120	100	8.46
959951	320,000	20,000	48,561	9.32	nr	nr	nr	-
42692	360,000	100,000	172,429	6.63	85,000	4,992	100	12.84
43694	500,000	9,000	20,320	8.68	nr	4,000	40	34.58
358000	500,000	30,000	20,624	2.64	nr	2,500	250	7.93
42751	540,000	6,000	nr	-	39,375	10,000	2,500	-
37817	540,000	140,000	6,320	0.17	1,500	550	45	0.46
T2	600,000	48,000	96,250	7.71	nr	3,000	250	11.62
133000	600,000	160,000	167,000	4.01	27,000	6,500	500	7.19
T1	936,000	160,000	167,764	4.03	35,000	2,080	500	5.80
740500	1,800,000	400,000	98,000	0.94	275,000	nr	nr	3.59
946587	1,900,000	200,000	108,840	2.09	63,150	8,050	208	5.69
3023	2,300,000	145,000	124,029	3.29	68,000	6,834	342	7.95
31838	3,000,000	280,000	nr	-	nr	nr	nr	-
462800	3,750,000	26,000	23,875	3.53	0	4,000	150	12.74
107300	5,000,000	250,000	143,850	2.21	60,000	9,275	1,571	5.64
Median:				3.24				9.13
Mean:				5.00				11.41

nr = no response

Exhibit 6-4. Waste Treatment System Operational Costs as a Percentage of Annual Sales



6.6 Sludge Generation and Disposal

Wastewater treatment sludge data were presented previously (Exhibit 5-19) and discussed in Section 5.4.2.5. The three largest facilities (in terms of production) that provided data generated sludge solids at a rate of 0.048, 0.003, and 0.057 lb/ft^2 of production. The variation evidently comes, in part, from product mix. The facility generating only 0.003 lb/ft^2 is exclusively a single-sided PWB manufacturer, whereas the other two have a product mix of double-sided and multilayer PWBs, for which additional process steps increase waste generation, including sludge production. Eighty-eight percent (88%) of those responding indicated they recycle their wastewater treatment sludge. Costs associated with the disposition of sludge ranged from $2.00/lb to $0.13/lb. Annual costs and unit costs are given in Exhibit 5-19.

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Appendix A – Survey Data

Data for Exhibits 1-1, 1-2, 1-3, 1-4, 1-5, 1-6

Respondent ID	Facility Size	Employees	Ft^2 Production	Sales
6,710	nr	51	15,000	4,683,453
29,710	nr	500	57,000	45,916,206
33,089	15,000	30	200,000	1,500,000
947,745	9,000	28	40,000	2,000,000
279	15,000	40	250,000	2,500,000
32,482	26,500	35	75,000	2,800,000
36930A	18,000	38	nr	3,000,000
44,657	22,000	40	42,358	3,038,042
37,817	14,000	45	540,000	3,600,000
25,503	25,000	40	90,000	4,000,000
502,100	37,000	65	60,000	4,500,000
T3	24,000	50	200,000	6,000,000
965,874	38,000	105	175,000	6,000,000
273,701	22,500	80	280,000	7,000,000
959,951	54,000	85	320,000	7,000,000
3,470	30,000	100	240,000	7,500,000
953,880	30,000	100	180,000	9,000,000
41,739	31,800	130	300,000	9,000,000
43,841	56,000	115	250,000	11,000,000
44,486	36,000	150	nr	14,000,000
42,692	50,000	150	360,000	15,000,000
T2	30,000	175	600,000	16,000,000
955,703	112,500	150	nr	16,000,000
955,099	100,000	250	nr	16,000,000
36,930	nr	200	96,000	17,000,000
358,000	36,000	0	500,000	18,000,000
462,800	55,000	210	3,750,000	20,000,000
237,900	300,000	178	273,000	22,000,000
43,694	42,000	450	500,000	24,000,000
133,000	125,000	366	600,000	36,000,000
42,751	50,000	380	540,000	40,000,000
31,838	300,000	480	3,000,000	45,000,000
107,300	200,000	350	5,000,000	50,000,000
55,595	109,000	420	nr	50,000,000
T1	70,000	550	936,000	51,000,000
946,587	120,000	500	1,900,000	84,000,000
740,500	600,000	1,000	1,800,000	100,000,000
3,023	190,000	830	2,300,000	105,000,000
10	36,000	125		10,000,000
11	20,000	55		4,000,000
12	16,788	37	50,000	
13				
14	250,000	450	800,000	58,000,000
15	4,000	40	350,000	4,500,000
16	36,000	350	792,000	
17	17,000	65		6,000,000
18	30,000	120	78,000	12,000,000
19	17,500	450	2,800,000	67,000,000
20	25,000	55	50,000	4,000,000
21	55,000	215	3,660,560	20,000,000
22	15,000	36		3,500,000
23	45,000	158	337,500	19,000,000

24	45,000	158	337,500	19,000,000
25	75,000	237	750,000	23,000,000
26	28,500	80	225,000	6,000,000
27	26,480	83		6,000,000
28	18,000	55	227,500	3,800,000
29	75,000	216	1,200	26,000,000
30	250,000	1,200	2,321,203	130,000,000
31	29,500	240	52,000	24,000,000
32	71,064	195	1,611,578	61,000,000
33	30,000	125	260,000	8,000,000
34	33,000	150	17,000	19,000,000
35	25,000	103	500,000	12,000,000
36	10,000	35	240,000	3,000,000
37		15	20,000	1,000,000
38	6,800	12		900,000
39	25,000	140	900,000	20,000,000
40	30,000	300	215,900	32,000,000
41	12,000	750	3,200,000	72,000,000
42	22,000	37		2,500,000
43	40,000	65	145,000	6,000,000
44	35,625	85	78,000	10,000,000
45	22,500	150	120,000	18,000,000
46	44,000	180	248,400	20,000,000
47	18,000	106	1,100	6,250,000
48	16,000	32	1,300,000	2,500,000
49	120,000	200		
50	35,000	115	193,700	8,000,000
51	11,000	25	104,000	2,000,000
52	18,000	49		7,700,000
53	70,000	110		
54	10,625	33	70,000	
55	64,500	180	719,468	17,000,000
56	69,000	170	720,000	17,000,000
57	15,000	4	2,000,000	6,000,000

Data for Exhibits 1-7, 1-8

Resp. ID	Rigid	Flex	Combination	Single	Double	4-6	8-12	14-20	More than 20
36930A	1	60	40	1	60	20	18	2	1
955,099	100	1	1	5	40	30	24	1	1
55,595	100	1	1	5	60	30	5	1	1
44,486	100	1	1	1	30	60	10	1	1
955,703	100	1	1	1	10	65	20	5	1
10	10	1	1	1	30	48	20	1	1
11	10	1	1	1	28	25	39	7	1
13	1	1	1	1	1	1	1	1	1
17	10	1	1	10	53	25	12	1	1
22	10	1	1	20	50	25	5	1	1
27	1	60	40	5	10	80	5	1	1
38	10	1	1	10	90	1	1	1	1
42	10	1	1	10	30	20	40	1	1
49	1	1	1	60	40	1	1	1	1
52	90	5	5	1	10	28	50	10	2
53	10	1	1	5	45	45	5	1	1
8	90	5	5	10	40	10	10	10	20
47	10	1	1	1	5	42	42	10	1

29	10	1	1	1	1	1	40	40	20
6,710	100	1	1	1	5	1	15	80	1
34	10	1	1	2	10	40	45	3	1
37	10	1	1	5	89	5	1	1	1
947,745	100	1	1	5	65	28	2	1	1
44,657	100	1	1	5	50	25	18	2	1
12	10	1	1	10	80	10	1	1	1
20	1	95	5	75	20	2	2	1	1
31	10	1	1	1	5	23	60	10	2
29,710	100	1	1	1	60	30	10	1	1
502,100	1	95	5	50	45	1	5	1	1
54	10	1	1	1	55	30	15	1	1
32,482	90	10	1	5	70	20	5	1	1
18	10	1	1	10	15	22	51	1	1
44	95	5	1	5	50	45	1	1	1
25,503	5	85	10	70	20	3	2	1	1
36,930	100	1	1	1	3	70	25	2	1
51	10	1	1	13	84	3	1	1	1
45	10	1	1	1	12	70	14	4	1
43	10	1	1	1	65	27	7	1	1
965,874	100	1	1	15	85	1	1	1	1
953,880	100	1	1	5	55	30	10	1	1
50	10	1	1	3	48	34	15	1	1
33,089	100	1	1	20	80	1	1	1	1
T3	98	1	1	10	30	50	10	1	1
40	10	1	1	1	5	60	32	2	1
26	10	1	1	10	73	17	1	1	1
28	10	1	1	8	82	10	1	1	1
3,470	100	1	1	5	83	11	1	1	1
36	85	3	12	13	51	22	13	1	1
46	10	1	1	1	20	60	10	9	1
43,841	100	1	1	10	50	24	15	1	1
279	100	1	1	75	25	1	1	1	1
33	10	1	1	3	97	1	1	1	1
237,900	100	1	1	1	5	65	29	1	1
273,701	98	2	1	5	70	25	1	1	1
41,739	100	1	1	32	50	27	1	1	1
959,951	100	1	1	8	80	12	1	1	1
23	10	1	1	1	40	39	20	1	1
24	10	1	1	1	40	39	20	1	1
15	1	10	1	30	70	1	1	1	1
42,692	100	1	1	3	62	35	1	1	1
358,000	100	1	1	1	30	50	15	5	1
43,694	1	100	1	74	23	3	1	1	1
35	99	1	1	5	50	30	13	2	1
37,817	100	1	1	80	20	1	1	1	1
42,751	100	1	1	1	10	20	50	20	1
T2	100	1	1	1	40	43	12	5	1
133,000	1	60	40	4	60	5	25	5	1
55	10	1	1	1	49	49	1	1	1
56	10	1	1	1	40	50	10	1	1
25	10	1	1	1	3	17	60	20	1
16	10	1	1	1	2	35	45	10	2
14	10	1	1	1	1	10	60	28	2
39	10	1	1	1	10	40	40	10	1
T1	100	1	1	1	10	28	50	10	1
48	10	1	1	10	90	1	1	1	1
32	1	1	1	1	1	1	1	1	1

740,500	100	1	1	1	1	80	20	1	1
946,587	100	1	1	1	10	65	20	5	1
57	10	1	1	10	1	1	1	1	1
3,023	100	1	1	1	1	70	15	15	1
30	10	1	1	1	10	30	50	9	1
19	10	1	1	1	1	82	14	3	1
31,838	100	1	1	1	1	30	40	30	1
41	10	1	1	1	1	50	42	8	1
21	10	1	1	10	1	1	1	1	1
462,800	100	1	1	100	1	1	1	1	1
107,300	100	1	1	10	85	5	1	1	1

Data for Exhibit 1-9

Respondent ID	Feet	Electroless	Palladium-only	Carbon-based	Graphite-based	Electroless Ni	Other
36930A	0	100	0	0	0	0	0
955099	0	100	0	0	0	0	0
55595	0	100	0	0	0	0	0
44486	0	100	0	0	0	0	0
955703	0	100	0	0	0	0	0
13	0	100					
37	0					100	
15	4000				100		
38	6800			100			
36	10000	100					
54	10625	100					
51	11000		100				
41	12000	100					
6710	15,000	100	0	0	0	0	0
22	15000		100				
48	16000	100					
12	16788	100					
17	17000	100					
19	17500	100					
28	18000	100					
47	18000	100					
52	18000	100					
11	20000	100					
42	22000	100					
45	22500	100					
20	25000		100				
35	25000	100					
39	25000			100			
27	26480	100					
26	28500			100			
31	29500	100					
18	30000	100					
33	30000				100		
40	30000	100					
34	33000	100					
50	35000				100		
44	35625	100					
10	36000	100					
16	36000	100					
947745	40,000	100	0	0	0	0	0
43	40000	100					

44657	42,358	100	0	0	0	0	0
46	44000			100			
23	45000	100					
24	45000	100					
29710	57,000	0	100	0	0	0	0
502100	60,000	100	0	0	0	0	0
55	64500	100					
56	69000			100			
53	70000	100					
32482	75,000	99	0	0	1	0	0
25	75000	100					
29	75000	100					
25503	90,000	97	3	0	0	0	0
36930	96,000	100	0	0	0	0	0
49	120000				100		
965874	175,000	100	0	0	0	0	0
953880	180,000	100	0	0	0	0	0
33089	200,000	100	0	0	0	0	0
T3	200,000	100	0	0	0	0	0
3470	240,000	100	0	0	0	0	0
43841	250,000	0	0	0	100	0	0
279	250,000	0	100	0	0	0	0
30	250000	100					
237900	273,000	100	0	0	0	0	0
273701	280,000	100	0	0	0	0	0
41739	300,000	100	0	0	0	0	0
959951	320,000	100	0	0	0	0	0
42692	360,000	100	0	0	0	0	0
358000	500,000	100	0	0	0	0	0
43694	500,000	0	100	0	0	0	0
37817	540,000	0	100	0	0	0	0
42751	540,000	100	0	0	0	0	0
T2	600,000	100	0	0	0	0	0
133000	600,000	100	0	0	0	0	0
T1	936,000	99	0	0	0	1	0
946587	1,900,000	100	0	0	0	0	0
3023	2,300,000	100	0	0	0	0	0
31838	3,000,000	100	0	0	0	0	0
462800	3,750,000	0	0	0	0	0	2
107300	5,000,000	100	0	0	0	0	0

Data for Exhibits 1-10, 1-11

Respondent ID	**Feet**	**Tin**	**Tin-Lead**	**Dry Film**	**Nickel Gold**	**Other**
36930A	0	0	95	0	5	0
955099	0	33	67	0	0	0
55595	0	0	0	0	0	0
44486	0	100	0	0	0	0
955703	0	0	0	100	0	0
13	0	40	5	50	5	
37	0	100				
15	4000	80		20		
38	6800	90		10		
36	10000		95	2	2	
54	10625			10		
51	11000	84		16		
41	12000	82			18	

6710	15,000	0	100	0	0	0
22	15000		100			
57	15000					100
48	16000		95	5		
12	16788		90	7	3	
17	17000		60	40		
19	17500	80	10	5	5	
28	18000		100			
47	18000	97	3			
52	18000		85		15	
11	20000		81		19	
42	22000	10	80		10	
45	22500			100		
20	25000			100		
35	25000	20		80		
39	25000	100				
27	26480			100		
26	28500	90		8	2	
31	29500		95		5	
18	30000		10	15	75	
33	30000	88	10	1	1	
40	30000	97			3	
34	33000	98		2		
50	35000	100				
44	35625	93	5			2
10	36000	40	5	50	5	
947745	40,000	0	95	2	3	0
43	40000		10			
44657	42,358	0	95	0	5	0
46	44000		99	1		
23	45000	85			15	
24	45000	85			15	
21	55000					100
29710	57,000	100	0	0	0	0
502100	60,000	0	5	95	0	0
55	64500	99	1			
56	69000	98			2	
53	70000	90	10			
32482	75,000	90	5	0	5	0
25	75000	90			10	
29	75000		90		10	
25503	90,000	1	2	96	1	0
36930	96,000	96	2	0	2	0
49	120000	78		20	2	
965874	175,000	85	0	15	0	0
953880	180,000	0	100	0	0	0
33089	200,000	0	95	5	0	0
T3	200,000	0	80	10	10	0
3470	240,000	75	10	10	5	0
43841	250,000	0	85	10	5	0
279	250,000	0	0	65	0	35
30	250000	75	20		5	
237900	273,000	0	100	0	0	0
273701	280,000	50	45	0	5	0
41739	300,000	0	0	100	0	0
959951	320,000	65	35	0	0	0
42692	360,000	95	5	0	0	0
358000	500,000	98	0	0	2	0

43694	500,000	0	0	100	0	0
37817	540,000	0	0	2	0	98
42751	540,000	80	0	0	20	0
T2	600,000	100	0	0	0	0
133000	600,000	0	95	0	5	0
T1	936,000	0	99	0	1	0
740500	1,800,000	0	0	100	0	0
946587	1,900,000	94	1	0	5	0
3023	2,300,000	0	100	0	0	0
462800	3,750,000	0	0	0	0	100
107300	5,000,000	98	0	0	2	0

Data for Exhibit 1-12

Respondent ID	Inner Cupric	Inner Ammoniacal	Inner Other	Outer Cupric	Outer Ammoniacal	Outer Other
36930A	0	100	0	0	100	0
955099	0	100	0	0	100	0
55595	0	0	0	0	0	0
44486	0	100	0	0	100	0
955703	0	100	0	0	100	0
13		100			100	
37		100			100	
15		100			100	
38					100	
36		100			100	
54		100			100	
51		100			100	
41		100			100	
6710	0	100	0	0	100	0
22		100			100	
57					100	
48					100	
12		100			100	
17		100			100	
19	100				100	
28						100
47		100			100	
52		100			100	
11		100			100	
42		100			100	
45	100			100		
20	100			100		
35		100			100	
39					100	
27	100			100		
26		100			100	
31		100			100	
18		100			100	
33					100	
40		100			100	
34		100			100	
50		100			100	
44		100			100	
10		100			100	
16		100			100	
947745	0	100	0	0	100	0

43		100			100	
44657	0	100	0	0	100	0
46	100				100	
23		100			100	
24		100			100	
21				100		
29710	0	100	0	0	100	0
502100	100	0	0	95	5	0
55		100			100	
56		100			100	
53		100			100	
32		100				
32482	0	0	100	0	0	100
25		100			100	
29		100			100	
25503	100	0	0	97	3	0
36930	0	100	0	0	100	0
49	100			20	80	
965874	0	0	0	0	100	0
953880	0	100	0	0	100	0
33089	0	0	0	0	100	0
T3	0	100	0	0	100	0
3470	0	100	0	0	100	0
43841	0	100	0	0	100	0
279	0	0	0	100	0	0
14					100	
30		100			100	
237900	0	100	0	0	100	0
273701	0	0	100	0	0	100
41739	0	100	0	0	100	0
959951	0	100	0	0	100	0
42692	0	100	0	0	100	0
358000	0	100	0	0	100	0
43694	0	100	0	0	100	0
37817	0	0	0	0	100	0
42751	100	0	0	0	100	0
T2	100	0	0	0	100	0
133000	0	100	0	0	100	0
T1	0	100	0	0	100	0
740500	100	0	0	100	0	0
946587	100	0	0	0	100	0
3023	0	100	0	0	100	0
31838	0	100	0	0	100	0
462800	0	0	0	100	0	0
107300	50	50	0	0	100	0

Data for Exhibits 1-13, 1-14

Respondent ID	Direct Discharge	Indirect Discharge	Zero Discharge	Average Flow (gal/day)	Maximum Flow (gal/day)	Cost of Water ($/gal)	Cost of Sewer ($/gal)
36930A		X		27,000	0	0.95	1.45
955099		X		120,000	140,000	3.10	9.30
55595	X			20,000	22,500	1.00	24.40
44486		X		100,000	130,000	1.62	0.79
955703		X		98,000	108,000	1.70	0.55
13	X			30000	33000		

37		X		10000	12000	2	1
15	X			13500	17000		
38	X			3000	4000	5	3
36			X	400	800	0	0
54	X			80000	120000		
51	X			9500	11700	2	1
41		X		230000	275000	1	1
6710		X		10,560	21,120	1.50	3.50
22		X		10000	18000		
57		X		40000	50000	2	3
48		X		12000	30000	1	2
12		X		17000	24000	3	
17		X		18000	21000		
19		X		275000	310000	1	3
28		X		40000	51000	2	3
47	X			25000	32000	3	1
52	X			21000	32000		
11		X		32500	52000	2	3
42		X		25000	40000		
45		X		25000	30000	1	
20		X		3500	5000		
35		X		31000	39000	3	4
39	X			95000	115000	1	0
27	X			25000	28000		
26		X		77000	80000	2	0
31		X		60000	90000	1	1
18		X		40000	42000	1	2
33	X			45000	70000	5	0
40		X		60000	90000		
34		X		70000	85000	1	0
50		X		39000	50000	0	0
44		X		35000	40000	2	2
10	X			30000	33000		
16		X		200000		1	0
947745		X		13,000	18,000	1.50	1.50
43	X			51628	72288	1	0
44657		X		6,000	180,000	1.98	2.29
46		X		45000	60000		
23		X		130000		2	1
24		X		130000		2	1
21		X		113000	175000	3	1
29710	X			74,000	124,000	nr	nr
502100		X		35	45	nr	nr
55	X			168900	168900	1	3
56		X		50000	65000	1	0
53	X			35000	40000	0	0
32		X		215	300	2	3
32482		X		31,000	54,000	1.94	nr
25		X		110000	130000	1	1
29	X			34000	150000		3
25503		X		5,000	6,500	nr	nr
36930		X		0	0	nr	nr
49	X			64000	85000		
965874		X		21,000	27,000	1.72	1.03
953880		X		35,000	45,000	1.33	2.60
33089		X		16,000	25,000	1.32	2.28
T3		X		20,000	30,000	nr	4.00
3470		X		20,000	30,000	0.00	0.06

43841		X	38,000	50,000	3.54	2.57
279	X		5,200	5,500	7.56	5.82
14						
30	X					2
237900		X	105,000	125,000	1.43	0.61
273701		X	25,000	30,000	1.41	1.35
41739	X		57,125	65,000	0.80	1.60
959951		X	20,000	30,000	nr	nr
42692	X		100,000	125,000	0.03	nr
358000		X	9,000	12,000	nr	nr
43694		X	30,000	40,000	1.00	0.78
37817		X	6,000	11,000	1.20	0.21
42751		X	140,000	160,000	1.60	3.10
T2		X	48,000	62,400	1.61	2.70
133000		X	160,000	200,000	2.73	2.33
T1	X		160,000	185,000	1.63	2.92
740500		X	400,000	1,000,000	2.22	3.08
946587		X	200,000	250,000	0.58	0.73
3023		X	145,000	160,000	3.78	5.24
31838		X	280,000	420,000	1.85	1.90
462800		X	26,000	31,000	13.80	3.40
107300	X		250,000	300,000	1.50	1.96

Discharge Limitations and Compliance Difficulties
Data Discussed in Section 1.4.5

Respondent ID	Cu max mg/l	Cu avg mg/l	Pb max mg/l	Pb avg mg/l	Ni max mg/l	Ni avg mg/l	Ag max mg/l	Ag avg mg/l	CN max mg/l	CN avg mg/l	TTO max mg/l	TTO avg mg/l
40 CFR 413	4.5	2.7	0.6	0.4	4.1	2.6	1.2	0.7	1.9	1.0	2.13	-
40 CFR 433	3.38	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	0.65	2.13	-
6710	4.50	0.37	0.60	0.10	4.10	0.09	1.20	0.01	1.90	0.01	2.13	-
36930A	2.59	1.59	0.53	0.33	3.05	1.83	0.33	0.18	0.92	0.50	1.63	-
36930	4.34	2.60	0.58	0.39	3.95	2.91	1.16	0.67	1.83	0.96	2.05	-
273701	3.38	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	-	-	-
358000	**2.00**	**1.50**	-	-	-	-	-	-	-	-	-	-
955703	3.00	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	0.65	0.58	-
33089	3.38	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	0.65	2.13	-
107300	2.00	1.00	0.30	0.10	1.30	1.00	-	-	-	-	2.13	-
502100	1.00	1.50	-	-	-	-	-	-	-	-	-	-
44657	3.00	2.07	0.60	0.40	2.20	-	0.43	0.24	1.20	0.65	2.13	-
43694	3.00	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	0.65	0.58	-
29710	0.49	0.41	0.43	0.27	2.50	1.50	0.02	0.02	0.76	0.41	1.34	-
T3	2.70	2.70	0.40	0.40	2.60	2.60	0.70	0.70	1.00	-	2.13	-
T1	1.00	0.03	0.20	0.05	1.00	0.04	0.50	0.01	-	-	2.35	1.00
955099	1.50	-	0.20	-	1.00	-	2.00	-	1.00	-	5.00	-
37817	5.00	3.50	1.00	0.25	-	-	-	-	-	-	-	-
959951	3.22	0.45	0.60	0.11	2.91	0.43	0.85	0.12	1.90	0.17	2.13	-
947745	3.38	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	0.65	2.13	-
95880	0.25	-	0.19	-	0.60	-	0.13	-	0.74	-	0.74	-
42751	3.00	2.07	0.69	0.43	2.50	2.38	1.00	-	1.20	0.65	2.13	-
32482	3.38	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	0.65	-	-
44486	4.50	2.70	0.60	0.40	4.10	2.60	5.80	-	1.90	1.00	1.30	-
42692	4.50	2.70	0.60	0.40	4.10	2.60	-	1.90	1.00	-	2.13	2.13
41739	4.00	0.40	**0.60**	**0.30**	4.00	0.50	1.00	-	1.00	0.01	-	-
43841	**4.30**	**2.60**	**0.57**	**0.36**	0.72	0.23	**0.03**	**0.01**	1.82	0.96	2.13	-
T2	2.20	2.07	0.69	0.43	3.00	2.38	0.43	0.24	1.00	0.65	2.13	-

3470	1.50	2.07	0.20	0.23	1.00	2.38	0.43	0.24	0.50	0.65	2.13	-
740500	3.38	1.70	0.69	0.40	3.98	1.60	0.43	0.24	1.20	0.65	2.13	-
279	3.00	2.02	-	-	-	-	-	-	-	-	-	-
3023	1.50	-	**0.20**	-	1.00	-	2.00	-	0.50	-	1.00	-
237900	**2.70**	**1.00**	**0.40**	**0.40**	2.60	0.25	0.70	0.70	0.50	0.50	2.13	-
133000	1.50	-	0.34	-	4.10	-	0.23	-	0.60	-	2.13	-
25503	3.00	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	0.65	0.58	-
946587	3.40	-	0.50	-	2.20	-	0.80	-	0.40	-	-	-
462800	2.90	1.91	0.39	0.26	2.64	1.69	-	-	1.23	0.65	1.40	-
31838	3.00	1.50	0.69	0.43	3.00	1.50	0.43	0.24	0.80	0.40	2.13	-
55595	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr
965874	3.38	2.07	0.69	0.43	3.98	2.38	0.43	0.24	1.20	0.65	2.13	-

Bold type indicates compliance difficulty with discharge parameter.
nr = no response
40 CFR 413 maximum is based on a 4 day average concentration.
40 CFR 433 maximum is based on a monthly average concentration.

Data For Exhibit 1-16

Environmental and Occupational Health Challenges	% of PWB Survey Respondents Citing Challenge	% of Plating Survey Respondents Citing Challenge
Meeting air emission standards	23.3	23.2
Eliminating solvent use	32.5	23.8
Frequently changing regulations	55.8	54.5
Consistently meeting effluent and discharge limits	32.5	38.2
Increasing cost of compliance	68.6	72.4
Reducing worker exposure to chemicals	41.8	—
Inconsistent enforcement of regulations	29.1	—
Hazardous waste transportation liabilities	13.2	—
Lack of hazardous waste disposal sites	4.7	17.9
Management/worker acceptance*	1.2	—
Permit modification time*	1.2	—
Understanding local, state and federal regulations*	1.2	—

*Added by respondent under "other." This item may have been more frequently selected if it had been listed on the survey form.
— Indicates that item was not listed on the survey form.

Data For Exhibit 1-17

Items for Which Available Information is Insufficient	Percentage of PWB Survey Respondents Citing Information Need
Chemical recycling (such as etchant, developer)	41.9
Water recycling	33.7
Certified courses for pollution prevention	33.7
Fully or semi-additive process	30.2
Tin-lead alternatives	29.1
Smear removal alternatives	23.3
Direct imaging	15.1
Solder mask disposal*	1.1
In-house waste treatment*	1.1
Treatment for resist stripper*	1.1
Air quality issues*	1.1
Low cost chemical and water recycling*	1.1

*Added by respondent under "other." This item may have been more frequently selected if it had been listed on the survey form.

Data For Exhibit 1-18

Source of Information	% of PWB Survey Respondents Citing Source	% of Plating Survey Respondents Citing Source
Vendor	48.8	63.6
In-house engineer	50.0	20.0
Professional journals	39.5	66.1
Literature from trade organizations	32.6	-
In-house chemist	35.0	22.6
Books	35.0	51.1
Other shops, competitors	33.7	-
Conferences	24.4	53.6
Other in-house employees	27.9	4.4
Consultant	18.6	51.4
Internet*	1.1	-
From regulators-WWTP, OSHA, EPA*	1.1	-

*Added by respondent under “other.” This item may have been more frequently selected if it had been listed on the survey form.