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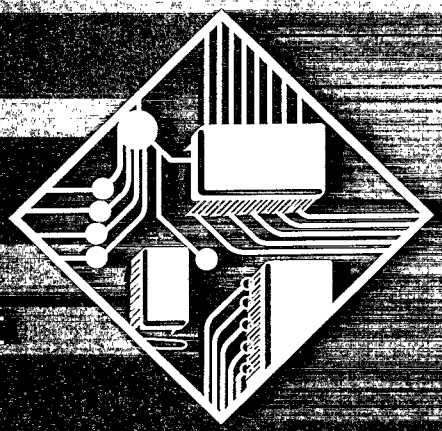
# Printed Wiring Board Cleaner Technologies Substitutes Assessment: Making Holes Conductive

## Volume 1



Design for the Environment
Printed Wiring Board Project

U.S. EPA

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# PWB Engineering Support Team

The PWB Engineering Support Team consisted of University of Tennessee faculty and graduate students who developed analytical models for the project and/or authored sections of this document. Members of the Team and the sections to which they contributed are listed below:

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# Disclaimer

Some information in this document was provided by individual technology vendors and has not been independently corroborated by EPA. The use of specific trade names or the identification of specific products or processes in this document are not intended to represent an endorsement by the EPA or the U.S. Government. Discussion of federal environmental statutes is intended for information purposes only; this is not an official guidance document, and should not be relied on by companies in the printed wiring board industry to determine applicable regulatory requirements.

# For More Information

To learn more about the Design for the Environment Printed Wiring Board Project, or to obtain other related materials, please contact:

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Or visit the Design for the Environment Printed Wiring Board Project Web site at:

http://www.ipc.org/html/ehstypes.htm#design

For more information about the Design for the Environment Program, visit the Design for the Environment Program Web site at:

http://www.epa.gov/dfe

The web site also contains the document, *Cleaner Technology Substitutes Assessment: A Methodology and Resources Guide*, which describes the basic methodology used in this assessment.

To learn more about the University of Tennessee Center for Clean Products and Clean Technologies, visit the Center's Web site at:

http://eerc.ra.utk.edu/clean/

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GCI, Inc.

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## ACRONYMS

| | |
|---|---|
| ABC | activity-based costing |
| ADD | average daily dose |
| AsF | assessment factor |
| AT | averaging time |
| ATSDR | Agency for Toxic Substances and Disease Registry |
| BOA | bill of activities |
| BCME | bis-chloromethyl ether |
| Btu | British Thermal Units |
| BW | body weight |
| CAA | Clean Air Act |
| CC | concern concentration |
| CEB | Chemical Engineering Branch |
| CERCLA | Comprehensive Environmental Response, Compensation and Liability Act |
| CO | carbon monoxide |
| $CO_2$ | carbon dioxide |
| CTSA | Cleaner Technologies Substitutes Assessment |
| $CuSO_4$ | copper sulfate |
| CWA | Clean Water Act |
| DEC | Digital Equipment Corporation of Canada |
| DfE | Design for the Environment |
| ED | exposure duration |
| EDTA | ethylenediaminetetraacedic acid |
| EPA | Environmental Protection Agency |
| EPCRA | Emergency Planning and Community Right-to-Know Act |
| FTE | full-time employee equivalent |
| g | gram |
| gal | gallon |
| GI | gastro intestinal |
| gpm | gallons per minute |
| $H_2SO_4$ | sulfuric acid |
| HASL | hot air solder leveling |
| $H_c$ | Henry's Law Constant |
| HEAST | Health Effects Assessment Summary Tables |
| HQ | hazard quotient |
| HSDB | Hazardous Substances Data Bank |
| IARC | International Agency for Research on Cancer |
| IPC | Institute for Interconnecting and Packaging Electronics Circuits |
| IRIS | Integrated Risk Information System |
| ISCLT | Industrial Source Complex - Long Term |
| IST | Interconnect Stress Test |
| KUB | Knoxville Utility Board |
| kW | kilowatt |
| LADD | lifetime average daily dose |
| LEPC | Local Emergency Planning Commission |
| LOAEL | lowest-observed-adverse-effect level |

| | |
|---|---|
| MACT | maximum achievable control technology |
| MCC | Microelectronics and Computer Technology Corporation |
| MHC | making holes conductive |
| $MnO_2$ | manganese dioxide |
| MOE | margin of exposure |
| MSDS | material safety data sheet |
| MTL | Master Testing List |
| MW | molecular weight |
| NCP | National Contingency Plan |
| NIOSH | National Institute for Occupational Safety and Health |
| NOAEL | no-observed-adverse-effect level |
| NPDES | National Pollutant Discharge Elimination System |
| NPDWR | National Primary Drinking Water Regulations |
| NSDWR | National Secondary Drinking Water Regulations |
| NTP | National Toxicology Program |
| OEM | original equipment manufacturer |
| OSHA | Occupational Safety and Health Administration |
| PEL | permissible exposure limit |
| PDR | potential dose rate |
| POTW | publicly-owned treatment work |
| PPE | personal protective equipment |
| psi | per square inch |
| PTH | plated-through holes |
| PWB | printed wiring board |
| RCRA | Resource Conservation and Recovery Act |
| RfC | reference concentration |
| RfD | reference dose |
| RTECS | Registry of Toxic Effects of Chemical Substances |
| RQ | reportable quantity |
| SARA | Superfund Amendments and Reauthorization Act |
| SAT | Structure-Activity Team |
| SDWA | Safe Drinking Water Act |
| SERC | State Emergency Response Commission |
| SF | slope factor |
| SIC | standard industrial code |
| $SO_x$ | sulfur oxides |
| SPC | statistical process control |
| ssf | surface square feet |
| TMCR | Technology Market Research Council |
| TPY | tons per year |
| TRI | Toxic Release Inventory |
| TSCA | Toxic Substances Control Act |
| TWA | time-weighed average |
| UT | University of Tennessee |
| UR | utilization ratio |
| VOC | volatile organic compounds |
| WOE | weight-of-evidence |

# Executive Summary

The *Printed Wiring Board Cleaner Technologies Substitutes Assessment: Making Holes Conductive* is a technical document that presents comparative risk, competitiveness, and resource requirements information on seven technologies for performing the "making holes conductive" (MHC) function during printed wiring board (PWB) manufacturing. MHC technologies are used by PWB manufacturers to deposit a seed layer or coating of conductive material into the drilled through-holes of rigid, multi-layer PWBs prior to electroplating. Volume I describes the MHC technologies, methods used to assess the technologies, and cleaner technologies substitutes assessment (CTSA) results. Volume II contains appendices, including detailed chemical properties and methodology information, as well as comprehensive results of the exposure assessment and risk characterization.

Information presented in the CTSA was developed by the U.S. Environmental Protection Agency (EPA) Design for the Environment (DfE) Printed Wiring Board (PWB) Project and the University of Tennessee (UT) Center for Clean Products and Clean Technologies. The technologies evaluated are electroless copper, carbon, conductive polymer, graphite, non-formaldehyde electroless copper, organic-palladium, and tin-palladium. Chemical and process information is also presented for a conductive ink technology, but this technology is not evaluated fully.[1]

The DfE PWB Project is a voluntary, cooperative partnership among EPA, industry, public-interest groups, and other stakeholders to promote implementation of environmentally beneficial and economically feasible manufacturing technologies by PWB manufacturers. Project partners participated in the planning and execution of this CTSA by helping define the scope and direction of the CTSA, developing project workplans, reviewing technical information contained in this CTSA, and by donating time, materials, and their manufacturing facilities for project research. Much of the process-specific information presented here was provided by chemical suppliers to the PWB industry, PWB manufacturers who completed project information requests, and PWB manufacturers who volunteered their facilities for a performance demonstration of the baseline and alternative technologies.

The CTSA is intended to provide PWB manufacturers with information that can assist them in making decisions that incorporate environmental concerns along with performance and cost information when choosing an MHC technology. While the DfE PWB Project is especially designed to assist small-and medium-sized PWB manufacturers who may have limited time or resources to compare MHC technologies, the primary audience for the CTSA is environmental health and safety personnel, chemical and equipment manufacturers and suppliers in the PWB manufacturing industry, community groups concerned about community health risks, and other technically informed decision-makers.

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[1] Only limited analyses were performed on the conductive ink technology for two reasons: 1) the process is not applicable to multi-layer boards, which were the focus of the CTSA; and 2) sufficient data were not available to characterize the risk, cost, and energy and natural resources consumption of all of the relevant process steps (e.g., preparation of the screen for printing, the screen printing process itself, and screen reclamation).

# I. DESIGN FOR THE ENVIRONMENT PRINTED WIRING BOARD PROJECT

The DfE PWB Project is a joint effort of the EPA DfE Program and the UT Center for Clean Products and Clean Technologies in voluntary and cooperative partnerships with the PWB industry national trade association, the Institute for Interconnecting and Packaging Electronic Circuits (IPC); individual PWB manufacturers and suppliers; the industry research consortium, Microelectronics and Computer Technology Corporation (MCC); and public-interest organizations, including Silicon Valley Toxics Coalition and Communities for a Better Environment.

**EPA's Design for the Environment Program**

The EPA DfE Program was formed by the Office of Pollution Prevention and Toxics to use EPA's expertise and leadership to facilitate information exchange and research on risk reduction and pollution prevention opportunities. DfE works on a voluntary basis with mostly small- and medium-sized businesses to evaluate the risks, performance, costs, and resource requirements of alternative chemicals, processes, and technologies.

Additional goals of the program include:

- Changing general business practices to incorporate environmental concerns.
- Helping individual businesses undertake environmental design efforts through the application of specific tools and methods.

**DfE Partners include:**

- Industry
- Professional institutions
- Academia
- Public-interest groups
- Other government agencies

In part, the project is an outgrowth of industry studies to identify key cleaner technology needs in electronic systems manufacturing. These studies include *Environmental Consciousness: A Strategic Competitiveness Issue for the Electronics Industry* (MCC, 1993) and *Electronics Industry Environmental Roadmap* (MCC, 1994). The latter study identified wet chemistry processes, such as the traditional electroless copper process for performing the MHC function, as potentially significant sources of hazardous waste, which require substantial amounts of water and energy, and use chemicals that may pose environmental and health risks. The potential for improvement in these areas led EPA's DfE Program to forge the working partnerships that resulted in the DfE PWB Project.

Since its inception in 1994, the PWB Project has fostered open and active participation in addressing environmental challenges faced by the PWB industry. The Project has also identified, evaluated, and disseminated information on viable pollution prevention opportunities in the industry. Over the long-term, the Project seeks to encourage companies to consider implementing cleaner technologies that will improve the environmental performance and competitiveness of the PWB industry. Toward this goal, the CTSA presents the first complete set of information developed by the Project on the risk, competitiveness (i.e., cost, performance, etc.), and resource requirements of cleaner technologies.

# II. OVERVIEW OF MHC TECHNOLOGIES

Until the late 1980s, virtually all PWB manufacturers employed an electroless copper plating process to accomplish the MHC function. This process is used to plate a thin layer of copper onto the hole walls to create the conductive surface required for electrolytic copper

plating. Although the traditional electroless copper process is a mature technology that produces reliable interconnects, the typical process line is long (17 or more tanks, depending on rinse configurations) and may have eight or more process baths. It is also a source of formaldehyde emissions and a major source of wastewater containing chelated, complexed copper. In recent years, wastewater treatment requirements and new formaldehyde regulations have provided an impetus for an intensified search for less polluting alternatives.

### Process Description

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

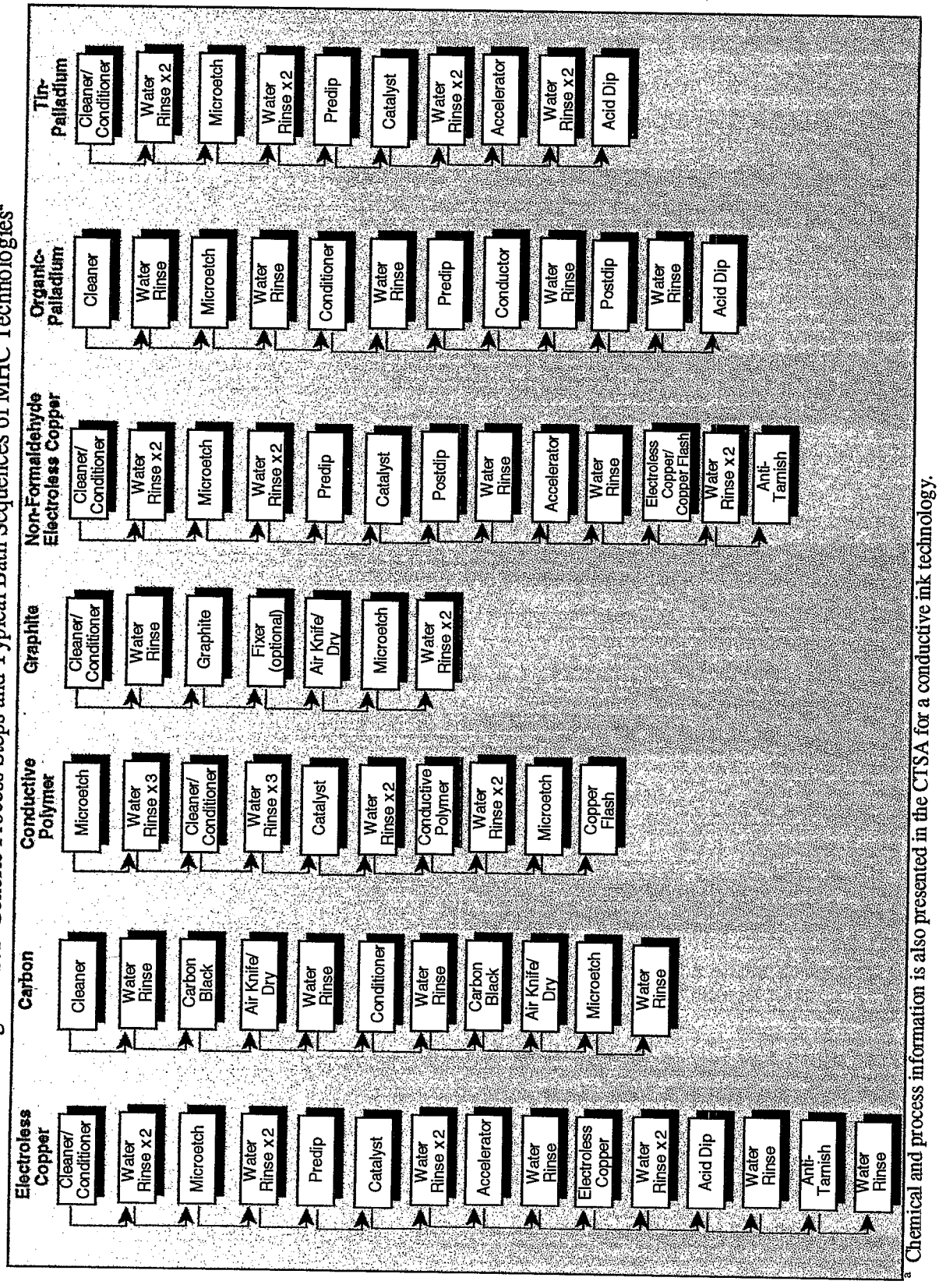
Most process baths are followed by a water rinse tank to remove drag-out (i.e., the clinging film of process solution covering the rack and boards when they are removed from a tank). Rinsing is necessary to clean the surface of the rack and boards and avoid contaminating subsequent process baths. Many PWB manufacturers employ a variety of rinse water reduction methods to reduce rinse water usage and consequent wastewater generation rates. The nature and quantity of wastewater generated from MHC process lines are discussed in Section 3.1, Source Release Assessment, while rinse water reduction techniques are discussed in Section 6.1, Pollution Prevention.

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

### Generic Process Steps and Bath Sequences of MHC Technologies

Figure ES.1 presents the generic process steps and typical bath sequences evaluated in the CTSA. The process baths depicted in the figure are an integration of the various products submitted for evaluation by chemical suppliers within a technology category. For example, six different electroless copper processes were submitted by chemical suppliers for evaluation in the CTSA, and these and other suppliers offer additional electroless copper processes that may have slightly different bath chemistries or bath sequences. In addition, the bath sequences (bath order and rinse tank configuration) were aggregated from data collected from various PWB facilities using the different MHC technologies. Thus, Figure ES.1 lists the types and sequences of baths in generic process lines, but the types and sequence of baths in actual lines may vary.

Figure ES.1 Generic Process Steps and Typical Bath Sequences of MHC Technologies[a]




[a] Chemical and process information is also presented in the CTSA for a conductive ink technology.

Table ES.1 presents the processes evaluated in the CTSA. These are distinguished both by process technology and equipment configuration (e.g., non-conveyorized or conveyorized). The non-conveyorized electroless copper process is the industry standard for performing the MHC function and is the baseline process against which alternative technologies and equipment configurations are compared.

**Table ES.1 MHC Processes Evaluated in the CTSA[a]**

| MHC Technology | Equipment Configuration | |
|---|---|---|
| | Non-Conveyorized | Conveyorized |
| Electroless Copper (BASELINE) | ✓ | ✓ |
| Carbon | | ✓ |
| Conductive Polymer | | ✓ |
| Graphite | | ✓ |
| Non-Formaldehyde Electroless Copper | ✓ | |
| Organic-Palladium | ✓ | ✓ |
| Tin-Palladium | ✓ | ✓ |

[a] The human health and aquatic toxicity hazards and chemical safety hazards of a *conductive ink technology* were also evaluated, but risk was not characterized.

## III. CLEANER TECHNOLOGIES SUBSTITUTES ASSESSMENT METHODOLOGY

The CTSA methodology is a means of systematically evaluating and comparing human health and environmental risk, competitiveness (i.e., performance, cost, etc.), and resource requirements of traditional and alternative chemicals, manufacturing methods, and technologies that can be used to perform the same function. The publication, *Cleaner Technologies Substitutes Assessment: A Methodology & Resource Guide* (Kincaid et al., 1996), presents the basic CTSA methodology in detail. Chapters 2 through 6 in Volume I of the PWB MHC CTSA and the appendices in Volume II describe the particular methods used in this assessment.

Key to the successful completion of any CTSA is the active participation of manufacturers and their suppliers. This assessment was open to any MHC chemical supplier who wanted to submit a technology, provided the technology met the following criteria:

- It is an existing or emerging technology.
- There are equipment and facilities available to demonstrate its performance.

In addition, suppliers agreed to provide information about their technologies, including chemical product formulation data, process schematics, process characteristics and constraints (e.g., cycle time, limitations for the acid copper plating process, substrate and drilling compatibilities, aspect ratio capacity, range of hole sizes), bath replacement criteria, and cost information.

### Issues Evaluated

The CTSA evaluated a number of issues related to the risk, competitiveness, and resource requirements (conservation) of MHC technologies. These include the following:

- Risk: occupational health risks, public health risks, ecological hazards, and process safety concerns.
- Competitiveness: technology performance, cost, regulatory status, and international market status.
- Conservation: energy and natural resource use.

Occupational and public health risk information is for chronic exposure to long-term, day-to-day releases from a PWB facility rather than short-term, acute exposures to high levels of hazardous chemicals as could occur with a fire, spill, or periodic release. Risk information is based on exposures estimated for a model facility, rather than exposures estimated for a specific facility. Ecological hazards, but not risks, are evaluated for aquatic organisms that could be exposed to MHC chemicals in wastewater discharges. Process safety concerns are summarized from material safety data sheets (MSDSs) for the technologies and process operating conditions.

Technology performance is based on a snapshot of the performance of the MHC technologies at volunteer test sites in the U.S. and abroad. Panels were electrically prescreened, followed by electrical stress testing and mechanical testing, in order to distinguish variability in the performance of the MHC interconnect. Comparative costs of the MHC technologies were estimated with a hybrid cost model that combines traditional costs with simulation modeling and activity-based costs. Costs are presented in terms of dollars per surface square feet (ssf) of PWB produced.

Federal environmental regulatory information is presented for the chemicals in the MHC technologies. This information is intended to provide an indication of the regulatory requirements potentially associated with a technology, but not to serve as regulatory guidance. Information on the international market status of technologies is presented as an indicator of the effects of a technology choice on global competitiveness.

Quantitative resource consumption data are presented for the comparative rates of energy and water use of the MHC technologies. The large amounts of water consumed and wastewater generated by the traditional electroless copper process have been of particular concern to PWB manufacturers, as well as to the communities in which they are located.

**Data Collection**

Determining the risks of the baseline and alternative MHC technologies required information on the MHC chemical products. Chemical information provided by chemical suppliers included the following publicly-available sources of information: MSDSs for the chemical products in their MHC technology lines; Product Data Sheets, which are technical specifications prepared by suppliers for PWB manufacturers that describe how to mix and maintain the chemicals baths; and, in some cases, copies of patents. Suppliers were also asked to provide the identities and concentrations of proprietary chemical ingredients to the project.

Electrochemicals, LeaRonal, and Solution Technology Systems provided information on proprietary chemical ingredients to the project. Atotech provided information on one proprietary chemical ingredient in one product line. W.R. Grace was preparing to provide information on proprietary chemical ingredients in the conductive ink technology when it was determined that

this information was no longer necessary because risk from the conductive ink technology could not be characterized. The other suppliers participating in the project (Enthone-OMI, MacDermid, and Shipley) declined to provide any proprietary information on their MHC technologies. The absence of information on proprietary chemical ingredients is a significant source of uncertainty in the risk characterization. Risk information for proprietary ingredients, as available, is included in this CTSA, but chemical identities, concentration, and chemical properties are not listed.

**Data Collection Forms**

Appendix A in Volume II of the CTSA presents data collection forms used by the project, including the following:

- The IPC Workplace Practices Questionnaire, which requested detailed information on facility size, process characteristics, chemical consumption, worker activities related to chemical exposure, water consumption, and wastewater discharges.
- The Facility Background Information Sheet (developed from the IPC Workplace Practices Questionnaire), which was sent to PWB facilities participating in the Performance Demonstration prior to their MHC technology test date and requested detailed information on facility and process characteristics, chemical consumption, worker activities related to chemical exposure, water consumption, and wastewater discharges.
- The Observer Data Sheet, which was used by an on-site observer to collect data during the Performance Demonstration. In addition to ensuring that the performance test was performed according to the agreed upon test protocol, the on-site observer collected measured data, such as bath temperature and process line dimensions, and checked survey data for accuracy.
- The Supplier Data Sheet, which included information on chemical cost, equipment cost, water consumption rates, product constraints, and the locations of test sites for the Performance Demonstration.

**Chemical Information**

Appendix B presents chemical properties and selected environmental fate properties for the non-proprietary chemicals in MHC chemical products. Proprieties of proprietary chemical ingredients are not included to protect proprietary chemical identities. Properties that were measured or estimated (using a variety of standard EPA methods) included melting point, solubility, vapor pressure, octanol-water partition coefficient, boiling point, and flash point. These properties can be used to determine the environmental fate of the MHC chemicals when they are released to the environment.

**Health Hazard Assessments**

Inherent in determining the risk associated with the MHC chemicals is a determination of the hazard or toxicity of the chemicals. Human health hazard information for non-proprietary chemicals is presented in Section 3.3. Detailed toxicity data for proprietary chemicals are not included to protect proprietary chemical identities. Many of the chemicals in the MHC chemical

products have been studied to determine their health effects, and data from those studies are available in published scientific literature. In order to collect available testing data for the MHC chemicals, literature searches were conducted of standard chemical references and on-line databases, including EPA's Integrated Risk Information System (IRIS), the National Library of Medicine's Hazardous Substances Data Bank (HSDB), TOXLINE, TOXLIT, GENETOX, and the Registry of Toxic Effects of Chemical Substances (RTECS).

For many of the chemicals, EPA has identified chemical exposure levels that are known to be hazardous if exceeded or met (e.g., no- or lowest-observed-adverse-effect level [NOAEL or LOAEL]), or levels that are protective of human health (reference concentration [RfC] or reference dose [RfD]). These values were taken from on-line databases and published literature. For many of the chemicals lacking toxicity data, EPA's Structure-Activity Team (SAT) estimated human health concerns based on analogous chemicals. Hazard information is combined with estimated exposure levels to develop an estimate of the risk associated with each chemical.

## Ecological Hazard Assessments

Similar information was gathered on the ecological effects that may be expected if MHC chemicals are released to water. Acute and chronic toxicity values were taken from on-line database searches (TOXNET and ACQUIRE) or published literature, or were estimated using structure-activity relationships if measured data were not available. Based on the toxicity values, MHC chemicals were assigned concern concentrations (CCs). A CC is the concentration of a chemical in the aquatic environment which, if exceeded, may result in significant risk to aquatic organisms. CCs were determined by dividing acute or chronic toxicity values by an assessment factor (ranging from one to 1,000) that incorporates the uncertainty associated with toxicity data. Chemicals were also ranked according to established EPA criteria for aquatic toxicity of high, moderate, or low concern.

Section 3.3 of the CTSA presents ecological hazard data, CCs, and aquatic toxicity concern levels for each of the non-proprietary MHC chemicals. Table ES.2 presents the number of MHC chemicals evaluated for each technology, the number of chemicals in each technology with aquatic toxicity of high, moderate, or low concern, and the chemicals with the lowest CC by technology.

### Limitations

There are a number of limitations to the project, both because of the limit of the project's resources, the predefined scope of the project, and uncertainties inherent to risk characterization techniques. Some of the limitations related to the risk, competitiveness, and conservation components of the CTSA are summarized below. More detailed information on limitations and uncertainties for a particular portion of the assessment is given in the applicable sections of this document. A limitation common to all components of the assessment is that the MHC chemical products assessed in this report were voluntarily submitted by participating suppliers and may not represent the entire MHC technology market.

**Table ES.2 Aquatic Hazard Data**

| MHC Technology | No. of Chemicals Evaluated[a] | No. of Chemicals by Aquatic Hazard Concern Level[a] | | | Chemical with Lowest CC |
|---|---|---|---|---|---|
| | | High | Moderate | Low | |
| Electroless Copper | 50[b] | 9 | 19 | 21 | copper sulfate (0.00002 mg/l) |
| Carbon | 8[b] | 2 | 2 | 3 | copper sulfate (0.00002 mg/l) |
| Conductive Ink | 11[b] | 2 | 1 | 7 | silver (0.000036 mg/l) |
| Conductive Polymer | 6 | 0 | 1 | 5 | peroxymonosulfuric acid (0.030 mg/l) |
| Graphite | 13 | 3 | 3 | 7 | copper sulfate (0.00002 mg/l) |
| Non-Formaldehyde Electroless Copper | 10 | 3 | 3 | 4 | copper sulfate (0.00002 mg/l) |
| Organic-Palladium | 7 | 2 | 3 | 2 | sodium hypophosphite (0.006 mg/l) |
| Tin-Palladium | 26[b] | 9 | 6 | 10 | copper sulfate (0.00002 mg/l) |

[a] This includes chemicals from both publicly-available and proprietary data. This indicates the number of unique chemicals; there is some overlap between public and proprietary lists for electroless copper. For technologies with more than one chemical supplier (i.e., electroless copper, graphite, and tin-palladium), all chemicals may not be present in any one product line.

[b] No aquatic hazard data available for one chemical.

## Risk

The risk characterization is a screening level assessment of multiple chemicals used in MHC technologies. The focus of the risk characterization is on chronic (long-term) exposure to chemicals that may cause cancer or other toxic effects, rather than on acute toxicity from brief exposures to chemicals. The exposure assessment and risk characterization use a "model facility" approach, with the goal of comparing the exposures and health risks of the MHC process alternatives to the baseline non-conveyorized electroless copper technology. Characteristics of the model facility were aggregated from questionnaire data, site visits, and other sources. This approach does not result in an absolute estimate or measurement of risk.

In addition, the exposure and risk estimates reflect only a portion of the potential exposures within a PWB manufacturing facility. Many of the chemicals found in MHC technologies may also be present in other process steps of PWB manufacturing, and other risk concerns for human health and the environment may occur from these other process steps. Incremental reduction of exposures to chemicals of concern from an MHC process, however, will reduce cumulative exposures from all sources in a PWB facility, provided that increased production does not increase plant-wide pollution.

Finally, as discussed previously, Enthone-OMI, MacDermid, and Shipley submitted publicly-available chemistry information for evaluation in the risk characterization, but declined

to submit proprietary information. Atotech submitted publicly-available information and limited proprietary information for one chemical in one product line. Electrochemicals, LeaRonal, and Solution Technology Systems submitted both publicly-available and proprietary chemistry information. The absence of complete information on proprietary chemical ingredients in products supplied by Atotech, Enthone-OMI, MacDermid, and Shipley is a significant source of uncertainty in the risk characterization.

### Competitiveness

The Performance Demonstration was designed to provide a snapshot of the performance of different MHC technologies. The test methods used to evaluate performance were intended to indicate characteristics of a technology's performance, not to define parameters of performance or to substitute for thorough on-site testing. Because the test sites were not chosen randomly, the sample may not be representative of all PWB manufacturing facilities in the U.S. (although there is no specific reason to believe they are not representative).

The cost analysis presents comparative costs of using an MHC technology in a model facility to produce 350,000 ssf of PWB. As with the risk characterization, this approach results in a comparative evaluation of cost, not an absolute evaluation or determination. The cost analysis focuses on private costs that would be incurred by facilities implementing a technology. It does not evaluate community benefits or costs, such as the effects on jobs from implementing a more efficient MHC technology. However, the Social Benefits/Costs Assessment (see Section 7.2) qualitatively evaluates some of these external (i.e., external to the decision-maker at a PWB facility) benefits and costs.

The regulatory information contained in the CTSA may be useful in evaluating the benefits of moving away from processes containing chemicals that trigger compliance issues. However, this document is not intended to provide compliance assistance. If the reader has questions regarding compliance concerns, they should contact their federal, state, or local authorities.

### Conservation

The analysis of energy and water consumption is also a comparative analysis, rather than an absolute evaluation or measurement. Similar to the cost analysis, consumption rates were estimated based on using an MHC technology in a model facility to produce 350,000 ssf of PWB.

## IV. CLEANER TECHNOLOGIES SUBSTITUTES ASSESSMENT RESULTS

### Occupational Exposures and Health Risks

Health risks to workers were estimated for inhalation exposure to vapors and aerosols from MHC baths and for dermal exposure to MHC bath chemicals. Inhalation exposure estimates are based on the assumptions that emissions to indoor air from conveyorized lines are negligible, that the air in the process room is completely mixed and chemical concentrations are constant over time, and that no vapor control devices (e.g., bath covers) are used in non-

conveyorized lines. Dermal exposure estimates are based on the assumption that workers do not wear gloves[2] and that all non-conveyorized lines are operated by manual hoist. Dermal exposure to line operators on non-conveyorized lines could occur from routine line operation and maintenance (e.g., bath replacement, filter replacement). Dermal exposure to line operators on conveyorized lines was assumed to occur from bath maintenance activities alone.

The exposure assessment for this risk characterization used, whenever possible, a combination of central tendency and high-end assumptions (i.e., 90 percent of actual values are expected to be less) to yield an overall high-end exposure estimate. Some values used in the exposure calculations, however, are better characterized as "what-if,"[3] especially pertaining to bath concentrations, use of gloves, and process area ventilation rates for a model facility. Because some part of the exposure assessment for both inhalation and dermal exposures qualifies as a "what-if" descriptor, the entire assessment should be considered "what-if."

Risk results indicate that alternatives to the non-conveyorized electroless copper process pose lower occupational risks due to reduced cancer risks and to the reduced number of inhalation and dermal risk concerns for the alternatives. However, there are occupational inhalation risk concerns for some chemicals in the non-formaldehyde electroless copper and tin-palladium non-conveyorized processes. In addition, there are occupational risk concerns for dermal contact with some chemicals in the conveyorized electroless copper process, the non-conveyorized non-formaldehyde electroless copper process, and in the organic-palladium and tin-palladium processes for either conveyorized or non-conveyorized equipment. Finally, occupational health risks could not be quantified for one or more of the chemicals used in each of the MHC technologies. This is due to the fact that proprietary chemicals in the baths were not identified by suppliers of some chemical products and to missing toxicity or chemical property data for some chemicals known to be present in the baths.

Table ES.3 presents chemicals of concern for potential occupational risk from inhalation. Table ES.4 presents chemicals of concern for potential occupational risk from dermal contact.

[2] Many PWB manufacturers report that their employees routinely wear gloves in the process area. However, risk from dermal contact was estimated assuming workers do not wear gloves to account for those workers who do not wear proper personal protective equipment.

[3] A "what-if" description represents an exposure estimate based on postulated questions, making assumptions based on limited data where the distribution is unknown.

**Table ES.3 MHC Chemicals of Concern for Potential Occupational Inhalation Risk**

| Chemical[a] | Non-Conveyorized Process[b] | | |
|---|---|---|---|
| | Electroless Copper | Non-Formaldehyde Electroless Copper | Tin-Palladium |
| Alkene Diol | ✔ | | |
| Copper Chloride | ✔ | | |
| Ethanolamine | ✔ | | ✔ |
| 2-Ethoxyethanol | ✔ | | |
| Ethylene Glycol | ✔ | | |
| **Formaldehyde** | ✔ | | |
| Formic Acid | ✔ | | |
| **Methanol** | ✔ | | |
| Sodium Hydroxide | ✔ | | |
| **Sulfuric Acid**[c] | ✔ | ✔ | ✔ |

[a] For technologies with more than one chemical supplier (e.g., electroless copper and tin-palladium), chemicals of concern that are present in all of the product lines evaluated are indicated in bold.
[b] Occupational inhalation exposure from conveyorized lines was assumed to be negligible.
[c] Sulfuric acid was listed on the MSDSs for all of the electroless copper lines evaluated and four of the five tin-palladium lines evaluated.

**Table ES.4 MHC Chemicals of Concern for Potential Occupational Dermal Risk**

| Chemical[a] | Electroless Copper | | | Non-Formaldehyde Electroless Copper | Tin-Palladium | | | Organic-Palladium | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Line Operator | | Lab Tech (NC or C) | Line Operator (NC) | Line Operator | | Lab Tech (NC or C) | Line Operator | | Lab Tech (NC or C) |
| | NC | C | | | NC | C | | NC | C | |
| Copper Chloride | ✔ | ✔ | ✔ | | ✔ | ✔ | ✔ | | | |
| Fluoroboric Acid | ✔ | ✔ | ✔ | | ✔ | ✔ | ✔ | | | |
| **Formaldehyde** | ✔ | ✔ | | | | | | | | |
| Nitrogen Heterocycle | ✔ | ✔ | | | | | | | | |
| **Palladium**[b] | ✔ | ✔ | ✔ | | ✔ | ✔ | ✔ | | | |
| **Palladium Chloride**[b] | | | | | ✔ | ✔ | ✔ | | | |
| Palladium Salt | | | | | | | | ✔ | ✔ | ✔ |
| Sodium Carboxylate | ✔ | ✔ | | | | | | | | |
| Sodium Chlorite | ✔ | ✔ | | ✔ | | | | | | |
| **Stannous Chloride**[c] | ✔ | | | ✔ | ✔ | ✔ | | | | |
| Tin Salt | | ✔ | | | | | | | | |

[a] For technologies with more than one chemical supplier (e.g., electroless copper and tin-palladium), chemicals of concern that are present in all of the product lines evaluated are indicated in bold.
[b] Palladium or palladium chloride was listed on the MSDSs for three of the five tin-palladium lines evaluated. The MSDSs for the two other lines did not list a source of palladium. Palladium and palladium chloride are not listed on the MSDSs for all of the electroless copper lines evaluated.
[c] Stannous chloride was listed on the MSDSs for four of the five tin-palladium lines evaluated. The MSDSs for the remaining line did not list a source of tin. Stannous chloride is not listed on the MSDSs for all of the electroless copper lines evaluated.
NC: Non-Conveyorized.
C: Conveyorized.

Occupational cancer risks were estimated for inhalation exposure to formaldehyde and alkyl oxide in the non-conveyorized electroless copper process, and for dermal exposure to cyclic ether and alkyl oxide in the conveyorized graphite, conveyorized electroless copper, and non-conveyorized electroless copper processes. Formaldehyde has been classified by EPA as Group B1, a Probable Human Carcinogen. Results indicate clear concern for formaldehyde inhalation exposure; the upper bound excess individual cancer risk estimate for line operators in the non-conveyorized electroless copper process from formaldehyde inhalation may be as high as one in 1,000, but may be 50 times less, or one in 50,000.[4] Inhalation risks to other workers were assumed to be proportional to the amount of time spent in the process area, which ranged from three percent to 61 percent of the risk for a line operator. Occupational risks associated with dermal and inhalation exposure to cyclic ether and alkyl oxide were below $1 \times 10^{-6}$ (one in one million) for the graphite and electroless copper processes and are therefore considered to be of low concern.

Other non-proprietary chemicals in the MHC processes are suspected carcinogens. Dimethylformamide and carbon black have been determined by the International Agency for Research on Cancer (IARC) to possibly be carcinogenic to humans (IARC Group 2B). Like formaldehyde, the evidence for carcinogenic effects is based on animal data. However, unlike formaldehyde, slope factors are not available for either chemical. There are potential cancer risks to workers from both chemicals, but they cannot be quantified. Dimethylformamide is used in the electroless copper process. Workplace exposures have been estimated but cancer potency and cancer risk are unknown. Carbon black is used in the carbon and conductive ink processes. Occupational exposure due to air emissions from the carbon baths in the carbon process is expected to be negligible because this process is typically conveyorized and enclosed. There may be some airborne carbon black, however, from the drying oven steps. Exposures from conductive ink were not characterized. One proprietary chemical used in the electroless copper process, trisodium acetate amine B, was determined to possibly be carcinogenic to humans but does not have an established slope factor.

**Public Exposures and Health Risks**

Public health risks were estimated for inhalation exposure only for the general population living near a facility. Environmental releases and risk from exposure to contaminated surface water were not quantified due to a lack of data; chemical constituents and concentrations in wastewater resulting only from the MHC process could not be adequately characterized. Public health risk estimates are based on the assumption that emissions from both conveyorized and non-conveyorized process configurations are steady-state and vented to the outside. Risk was not characterized for short-term exposures to high levels of hazardous chemicals when there is a spill, fire, or other release.

[4] To provide further information on the possible variation of formaldehyde exposure and risk, an additional exposure estimate was provided in the Risk Characterization (Section 3.4) using average and median values (rather than high-end) as would be done for a central tendency exposure estimate. This results in approximately a 35-fold reduction in occupational formaldehyde exposure and risk from the estimates presented here.

The risk indicators for ambient exposures to humans, although limited to airborne releases, indicate low concern from all MHC technologies for nearby residents. The upper bound excess individual cancer risk from formaldehyde inhalation for nearby residents from the non-conveyorized electroless copper process was estimated to be from approaching zero to $1 \times 10^{-7}$ (one in ten million), and from approaching zero to $3 \times 10^{-7}$ (one in three million) for the conveyorized electroless copper process. Formaldehyde has been classified by EPA as Group B1, a Probable Human Carcinogen. The risk characterization for ambient exposure to MHC chemicals also indicates low concern from the estimated air concentrations for chronic non-cancer effects. The upper bound excess individual cancer risk for nearby residents from alkyl oxide in the conveyorized graphite process was estimated to be from approaching zero to $9 \times 10^{-11}$ (one in 11 billion); in the non-conveyorized electroless copper process from approaching zero to $1 \times 10^{-11}$ (one in 100 billion); and in the conveyorized electroless copper process from approaching zero to $3 \times 10^{-11}$ (one in 33 billion). All hazard quotients are less than one for ambient exposure to the general population, and all MOEs for ambient exposure are greater than 1,000 for all processes, indicating low concern from the estimated air concentrations for chronic non-cancer effects.

### Ecological Hazards

The CTSA methodology typically evaluates ecological risks in terms of risks to aquatic organisms in streams that receive treated or untreated effluent from manufacturing processes. Stream concentrations of MHC chemicals were not available, however, and could not be estimated because of insufficient chemical characterization of constituents and their concentrations in facility wastewater. This is primarily because PWB manufacturers combine effluent from the MHC process line with effluent from other manufacturing steps prior to on-site wastewater treatment or discharge. No information was available on the contribution of the MHC process effluents to overall pollutant discharges. To qualitatively assess risk to aquatic organisms, MHC chemicals were ranked based on aquatic toxicity values according to established EPA criteria for aquatic toxicity of high, moderate, or low concern. Aquatic hazards data are summarized in Section III of the Executive Summary and Section 3.3 of the CTSA.

### Process Safety

In order to evaluate the chemical safety hazards of the various MHC technologies, MSDSs for chemical products used with each of the MHC technologies were reviewed. Table ES.5 summarizes the hazardous properties listed on MSDSs for MHC chemical products.

Other potential chemical hazards can occur because of hazardous decomposition of chemical products, or chemical product incompatibilities with other chemicals or materials. With few exceptions, most chemical products used in MHC technologies can decompose under specific conditions to form potentially hazardous chemicals. In addition, all of the MHC processes have chemical products with incompatibilities that can pose a threat to worker safety if the proper care is not taken to prevent such occurrences.

**Table ES.5 Hazardous Properties of MHC Chemical Products**

| MHC Technology | Types of Hazardous Properties Reported on MSDSs[a] |
|---|---|
| Electroless Copper | flammable, combustible, explosive, fire hazard, corrosive, oxidizer, reactive, unstable, acute health hazard, chronic health hazard, eye damage |
| Carbon | flammable, corrosive, oxidizer, reactive, acute health hazard, chronic health hazard, eye damage |
| Conductive Ink | explosive, eye damage |
| Conductive Polymer[b] | flammable, corrosive, eye damage |
| Graphite | fire hazard, corrosive, oxidizer, unstable, acute health hazard, chronic health hazard, eye damage |
| Non-Formaldehyde Electroless Copper | flammable, corrosive, oxidizer, reactive, acute health hazard, chronic health hazard, eye damage |
| Organic-Palladium[b] | unstable, eye damage |
| Tin-Palladium | flammable, combustible, explosive, fire hazard, corrosive, reactive, sensitizer, acute health hazard, chronic health hazard, eye damage |

[a] For technologies with more than one chemical supplier (i.e., electroless copper, graphite, and tin-palladium), all hazardous properties may not be listed for any one product line.
[b] Based on German equivalent of MSDS, which may not have as stringent reporting requirements as U.S. MSDS.

Work-related injuries from equipment, improper use of equipment, bypassing equipment safety features, failure to use personal protective equipment, and physical stresses that may appear gradually as a result of repetitive motion are all potential process safety hazards to workers. Reducing the potential for work-related injuries is critical in an effective and ongoing safety training program. Without appropriate training, the number of work-related accidents and injuries is likely to increase, regardless of the technology used.

### Performance

The performance of the MHC technologies was tested using production run tests. In order to complete this evaluation, PWB panels, designed to meet industry "middle-of-the-road" technology, were manufactured at one facility, run through individual MHC lines at 26 facilities, then electroplated at one facility. The panels were electrically prescreened, followed by electrical stress testing and mechanical testing, in order to distinguish variability in the performance of the MHC interconnect. The Performance Demonstration was conducted with extensive input and participation from PWB manufacturers, their suppliers, and PWB testing laboratories. The test vehicle was a 24" x 18" x 0.062" 8-layer panel. (See Section 4.1 for a detailed description of the test vehicle.) Each test site received three panels for processing through the MHC line.

Test sites were submitted by suppliers of the technologies, and included production facilities, testing facilities (beta sites), and supplier testing facilities. Because the test sites were not chosen randomly, the sample may not be representative of all PWB manufacturing facilities (although there is no specific reason to believe that they are not representative). In addition, the number of test sites for each technology ranged from one to ten. Due to the smaller number of test sites for some technologies, results for these technologies could more easily be due to chance than the results from technologies with more test sites. Statistical relevance could not be determined.

Product performance for this study was divided into two functions: plated through-hole (PTH) cycles to failure and the integrity of the bond between the internal lands (post) and PTH (referred to as "post separation"). The PTH cycles to failure observed in this study is a function of both electrolytic plating and MHC process. The results indicate that each MHC technology has the capability to achieve comparable (or superior) levels of performance to electroless copper. Post separation results indicated percentages of post separation that were unexpected by many members of the industry. It was apparent that all MHC technologies, including electroless copper, are susceptible to this type of failure.

### Cost

Comparative costs were estimated using a hybrid cost model which combined traditional costs with simulation modeling and activity-based costs. The cost model was designed to determine the total cost of processing a specific amount of PWBs through a fully operational MHC line, in this case, 350,000 ssf. The cost model did not estimate start-up costs for a facility switching to an alternative MHC technology or the costs of other process changes that may be required to implement an alternative technology. Total costs were divided by the throughput (350,000 ssf) to determine a unit cost in dollars per ssf.

The cost components considered include capital costs (primary equipment, installation, and facility costs), materials costs (limited to chemical costs), utility costs (water, electricity, and natural gas costs), wastewater costs (limited to wastewater discharge cost), production costs (production labor and chemical transport costs), and maintenance costs (tank clean up, bath setup, sampling and analysis, and filter replacement costs). Other cost components may contribute significantly to overall costs, but could not be quantified. These include wastewater treatment cost, sludge recycling and disposal cost, other solid waste disposal costs, and quality costs.

Table ES.6 presents results of the cost analysis, which indicate all of the alternatives are more economical than the non-conveyorized electroless copper process. In general, conveyorized processes cost less than non-conveyorized processes. Chemical cost was the single largest component cost for nine of the ten processes. Equipment cost was the largest cost for the non-conveyorized electroless copper process. Three separate sensitivity analyses of the results indicated that chemical costs, production labor costs, and equipment costs have the greatest effect on the overall cost results.

## Table ES.6 Cost Analysis Results[a]

| MHC Technology | Average Cost | | Capital Cost | | Chemical Cost | | Water Cost | | Electricity Cost | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $/ssf | % change | $/ssf | % change | $/ssf | % change | $/ssf | % change | $/ssf | % change |
| Electroless Copper, non-conveyorized (BASELINE) | $ 0.51 | | $ 0.24 | | $ 0.06 | | $ 0.02 | | $ 0.008 | |
| Electroless Copper, conveyorized | $ 0.15 | -71 | $ 0.03 | -88 | $ 0.06 | 0 | $ 0.002 | -90 | $ 0.002 | -75 |
| Carbon, conveyorized | $ 0.18 | -65 | $ 0.03 | -88 | $ 0.10 | +66 | $ 0.002 | -90 | $ 0.001 | -88 |
| Conductive Polymer, conveyorized | $ 0.09 | -82 | $ 0.02 | -92 | $ 0.03 | -50 | $ 0.001 | -95 | $ 0.001 | -88 |
| Graphite, conveyorized | $ 0.22 | -57 | $ 0.01 | -96 | $ 0.17 | +183 | $ 0.001 | -95 | $ 0.004 | -50 |
| Non-Formaldehyde Electroless Copper, non-conveyorized | $ 0.40 | -22 | $ 0.11 | -54 | $ 0.20 | +233 | $ 0.01 | -50 | $ 0.004 | -50 |
| Organic-Palladium, non-conveyorized | $ 0.15 | -71 | $ 0.02 | -92 | $ 0.08 | +33 | $ 0.002 | -90 | $ 0.001 | -88 |
| Organic-Palladium, conveyorized | $ 0.17 | -67 | $ 0.02 | -92 | $ 0.08 | +33 | $ 0.002 | -90 | $ 0.002 | -75 |
| Tin-Palladium, non-conveyorized | $ 0.14 | -73 | $ 0.02 | -92 | $ 0.06 | 0 | $ 0.003 | -85 | $ 0.002 | -75 |
| Tin-Palladium, conveyorized | $ 0.12 | -77 | $ 0.01 | -96 | $ 0.07 | +17 | $ 0.001 | -95 | $ 0.001 | -88 |

| MHC Technology | Natural Gas Cost | | Wastewater Cost | | Production Cost | | Maintenance Cost | |
|---|---|---|---|---|---|---|---|---|
| | $/ssf | % change | $/ssf | % change | $/ssf | % change | $/ssf | % change |
| Electroless Copper, non-conveyorized (BASELINE) | $ - | | $ 0.04 | | $ 0.11 | | $ 0.04 | |
| Electroless Copper, conveyorized | $ - | NA | $ 0.004 | -90 | $ 0.02 | -82 | $ 0.03 | -25 |
| Carbon, conveyorized | $ 0.001 | NA | $ 0.005 | -88 | $ 0.03 | -73 | $ 0.01 | -75 |
| Conductive Polymer, conveyorized | $ - | NA | $ 0.003 | -93 | $ 0.02 | -82 | $ 0.02 | -50 |
| Graphite, conveyorized | $ 0.0004 | NA | $ 0.002 | -95 | $ 0.02 | -82 | $ 0.01 | -75 |
| Non-Formaldehyde Electroless Copper, non-conveyorized | $ - | NA | $ 0.01 | -75 | $ 0.05 | -55 | $ 0.02 | -50 |
| Organic-Palladium, non-conveyorized | $ - | NA | $ 0.005 | -88 | $ 0.02 | -82 | $ 0.03 | -25 |
| Organic-Palladium, conveyorized | $ - | NA | $ 0.004 | -90 | $ 0.02 | -82 | $ 0.03 | -25 |
| Tin-Palladium, non-conveyorized | $ - | NA | $ 0.007 | -83 | $ 0.03 | -73 | $ 0.02 | -50 |
| Tin-Palladium, conveyorized | $ - | NA | $ 0.002 | -95 | $ 0.02 | -82 | $ 0.02 | -50 |

[a] Table lists costs and percent change in cost from baseline.

NA: Not Applicable. Percent change cannot be calculated because baseline has zero cost in this cost category.

### Regulatory Status

Discharges of MHC chemicals may be restricted by federal, state or local air, water or solid waste regulations, and releases may be reportable under the federal Toxic Release Inventory program. Federal environmental regulations were reviewed to determine the federal regulatory status of MHC chemicals.[5] Table ES.7 lists the number of chemicals used in an MHC technology that are subject to federal environmental regulations. Different chemical suppliers of a technology do not always use the same chemicals in their particular product lines. Thus, all of these chemicals may not be present in any one product line.

### International Information

Several suppliers indicated that market shares of the MHC alternatives are increasing internationally quicker than they are increasing in the U.S. The cost-effectiveness of an alternative has been the main driver causing PWB manufacturers abroad to switch from an electroless copper process to one of the newer alternatives. In addition to the increased capacity and decreased labor requirements of some of the MHC alternatives over the electroless copper process, environmental concerns also affected the process choice. For instance, the rate at which an alternative consumes water and the presence or absence of strictly regulated chemicals are two factors which have a substantial effect on the cost-effectiveness of MHC alternatives abroad.

### Resource Conservation Summary

Resources typically consumed by the operation of an MHC process include water used for rinsing panels, process chemicals used on the process line, energy used to heat process baths and power equipment, and wastewater treatment chemicals. The energy and water consumption rates of the MHC process alternatives were calculated to determine if implementing an alternative to the baseline process would reduce consumption of these resources during the manufacturing process. Process chemical and treatment chemical consumption rates could not be quantified due to the variability of factors that affect the consumption of these resources. Table ES.8 presents the energy and water consumption rates of MHC technologies.

The rate of water consumption is directly related to the rate of wastewater generation. Most PWB facilities discharge process rinse water to an on-site wastewater treatment facility for pretreatment prior to discharge to a publicly-owned treatment works (POTW). A pollution prevention analysis identified a number of pollution prevention techniques that can be used to reduce rinse water consumption. These include use of more efficient rinse configurations, use of flow control technologies, and use of electronic sensors to monitor contaminant concentrations in rinse water. Further discussion of these and other pollution prevention techniques can be found in the Pollution Prevention section of the CTSA (Section 6.1) and in PWB Project pollution prevention case studies, which are available from the Pollution Prevention Information Clearinghouse (see p. ii).

[5] In some cases, state or local requirements may be more restrictive than federal requirements. However, due to resource limitations, only federal regulations were reviewed.

## Table ES.7 Regulatory Status of MHC Technologies[a]

| MHC Technology | Chemicals Subject to Applicable Regulation | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CWA | | | | SDWA | | CAA | | | SARA 110 | EPCRA | | TSCA | | | RCRA Waste | |
| | 304b | 307a | 311 | Priority Pollutant | NPDWR | NSDWR | 111 | 112b | 112r | | 302a | 313 | 8d HSDR | MTL | 8a PAIR | P | U |
| Electroless Copper | 4 | 4 | 13 | 8 | 4 | 5 | 8 | 8 | 2 | 6 | 6 | 13 | 2 | 4 | 3 | 2 | 4 |
| Carbon | 1 | 1 | 3 | 2 | 1 | 1 | | | | 1 | | 1 | | | | | |
| Conductive Ink | 2 | 2 | | 2 | | 1 | 5 | 3 | | 1 | | 2 | 2 | | 3 | | 1 |
| Conductive Polymer | | | 3 | | | | 1 | | | | 1 | 2 | | | | | |
| Graphite | 2 | 1 | 3 | 1 | 1 | 1 | 1 | | 1 | 2 | 2 | 3 | | | | | |
| Non-Formaldehyde Electroless Copper | 1 | 1 | 5 | 1 | 1 | 1 | 1 | 1 | 1 | 3 | 3 | 4 | | 1 | 1 | | |
| Organic-Palladium | | | 2 | | | | | 1 | 1 | | 1 | 1 | | | | | |
| Tin-Palladium | 2 | 2 | 7 | 2 | 3 | 3 | 3 | 1 | 1 | 6 | 3 | 6 | | 3 | 3 | | 1 |

[a] Tables 4.38 through 4.45 in Section 4.3 give more detailed regulatory summaries by MHC technology, including potentially regulated chemical names. PWB manufacturers can refer to the MSDSs for the MHC chemical products they use to determine if a particular chemical is present.

Abbreviations and definitions:

CAA - Clean Air Act
CAA 111 - Standards of Performance for New Stationary Sources of Air Pollutants - Equipment Leaks Chemical List
CAA 112b - Hazardous Air Pollutant
CAA 112r - Risk Management Program
CWA - Clean Water Act
CWA 304b - Effluent Limitations Guidelines
CWA 307a - Toxic Pollutants
CWA 311 - Hazardous Substances
CWA Priority Pollutants
EPCRA - Emergency Planning and Community Right-to-Know Act
EPCRA 302a - Extremely Hazardous Substances
EPCRA 313 - Toxic Chemical Release Inventory
RCRA - Resource Conservation and Recovery Act
RCRA P Waste - Listed acutely hazardous waste
RCRA U Waste - Listed hazardous waste
SARA - Superfund Amendments and Reauthorization Act
SARA 110 - Superfund Site Priority Contaminant
SDWA - Safe Drinking Water Act
SDWA NPDWR - National Primary Drinking Water Rules
SDWA NSDWR - National Secondary Drinking Water Rules
TSCA - Toxic Substances Control Act
TSCA 8d HSDR - Health & safety data reporting rules
TSCA MTL - Master Testing List
TSCA 8a PAIR - Preliminary Assessment Information Rule

**Table ES.8 Energy and Water Consumption Rates of MHC Technologies**

| Process Type | Water Consumption (gal/ssf) | Energy Consumption (Btu/ssf) |
|---|---|---|
| Electroless Copper, non-conveyorized (BASELINE) | 11.7 | 573 |
| Electroless Copper, conveyorized | 1.15 | 138 |
| Carbon, conveyorized | 1.29 | 514 |
| Conductive Polymer, conveyorized | 0.73 | 94.7 |
| Graphite, conveyorized | 0.45 | 213 |
| Non-Formaldehyde Electroless Copper, non-conveyorized | 3.74 | 270 |
| Organic-Palladium, non-conveyorized | 1.35 | 66.9 |
| Organic-Palladium, conveyorized | 1.13 | 148 |
| Tin-Palladium, non-conveyorized | 1.80 | 131 |
| Tin-Palladium, conveyorized | 0.57 | 96.4 |

### Social Benefits/Costs Assessment

The social benefits and costs of the MHC technologies were qualitatively assessed to compare the benefits and costs of switching from the baseline technology to an alternative, while considering both the private and external costs and benefits. Private costs typically include any direct costs incurred by the decision-maker and are generally reflected in the manufacturer's balance sheet. In contrast, external costs are incurred by parties other than the primary participants to the transaction. Economists distinguish between private and external costs because each will affect the decision-maker differently. Although external costs are real costs to some members of society, they are not incurred by the decision-maker and firms do not normally take them into account when making decisions.

Table ES.9 compares some of the relative benefits and costs of each technology to the baseline, including production costs, worker health risks, public health risks, aquatic toxicity concerns, water consumption, and energy consumption. The effects on jobs of wide-scale adoption of an alternative is not included in the table because the potential for job losses was not evaluated in the CTSA. However, the results of the CTSA cost analysis suggest there are significantly reduced labor requirements for the alternatives. Clearly, if manufacturing jobs were lost, it would be a significant external cost to the community and should be considered by PWB manufacturers when choosing among MHC technologies.

While each alternative presents a mixture of private and external benefits and costs, it appears that each of the alternatives have social benefits as compared to the baseline. In addition, at least three of the alternatives appear to have social benefits over the baseline in every category. These are the conveyorized conductive polymer process and both conveyorized and non-conveyorized organic-palladium processes. Note, however, that the supplier of these technologies declined to provide complete information on proprietary chemical ingredients, meaning health risks could not be fully assessed.

## Table ES.9 Relative Benefits and Costs of MHC Alternatives Versus Baseline

| MHC Technology | Production Costs ($/ssf) | Number of Chemicals of Concern[a] | | | | Water Consumption (gal/ssf) | Energy Consumption (Btu/ssf) |
|---|---|---|---|---|---|---|---|
| | | Worker Health Risks[b,c,d] | | Public Health Risks[e] | High Aquatic Toxicity Concern[b,f] | | |
| | | Inhalation | Dermal | Inhalation | | | |
| Electroless Copper, non-conveyorized (BASELINE) | $0.51 | 10 | 8 | 0[g] | 9 | 11.7 | 573 |
| Electroless Copper, conveyorized | ↗↗ | ↗↗ | ↔ | ↔[h] | ↔ | ↗↗ | ↗↗ |
| Carbon, conveyorized | ↗↗ | ↗↗ | ↗↗ | ↗ | ↔ | ↗↗ | ↔ |
| Conductive Polymer, conveyorized | ↗↗ | ↗↗ | ↗↗ | ↗ | ↗ | ↗↗ | ↗↗ |
| Graphite, conveyorized | ↗↗ | ↗↗ | ↗↗[i] | ↗[j] | ↔ | ↗↗ | ↗↗ |
| Non-Formaldehyde Electroless Copper, non-conveyorized | ↗ | ↗ | ↗ | ↗ | ↔ | ↗↗ | ↗↗ |
| Organic-Palladium, non-conveyorized | ↗↗ | ↗↗ | ↗ | ↗ | ↗ | ↗↗ | ↗↗ |
| Organic-Palladium, conveyorized | ↗↗ | ↗↗ | ↗ | ↗ | ↗ | ↗↗ | ↗↗ |
| Tin-Palladium, non-conveyorized | ↗↗ | ↗ | ↗ | ↗ | ↔ | ↗↗ | ↗↗ |
| Tin-Palladium, conveyorized | ↗↗ | ↗↗ | ↗ | ↗ | ↔ | ↗↗ | ↗↗ |

[a] Includes proprietary chemicals that were identified.

[b] For technologies with more than one chemical supplier (i.e., electroless copper, graphite, and tin-palladium) all chemicals may not be present in any one product line.

[c] For the most exposed individual (i.e., an MHC line operator).

[d] Because the risk characterization did not estimate the number of incidences of adverse health outcomes, the amount of reduced risk benefit cannot be quantifed. However, based on the level of formaldehyde risk and the number of chemicals of concern for the baseline, it appears all of the alternatives have at least some reduced risk benefits from the baseline.

[e] Because the risk characterization did not estimate the number of incidences of adverse health outcomes, the amount of reduced risk benefit cannot be quantifed. However, based on the level of formaldehyde risk for the baseline, it appears all of the alternatives except the conveyorized electroless copper process have at least some reduced risk benefits from the baseline.

[f] Technologies using copper sulfate were assigned a neutral benefit or cost; other technologies were assigned "some benefit" because none of their chemicals are as toxic to aquatic organisms as copper sulfate. This assessment is based on hazard, not risk.

[g] No chemical risks above concern levels. However, it should be noted that formaldehyde cancer risks as high as $1 \times 10^{-7}$ were estimated.

[h] No chemical risks above concern levels. However, it should be noted that formaldehyde cancer risks as high as $3 \times 10^{-7}$ were estimated.

[i] No chemical risks above concern levels. However, it should be noted that proprietary chemical cancer risks as high as $1 \times 10^{-7}$ were estimated.

[j] No chemical risks above concern levels. However, it should be noted that proprietary chemical cancer risks as high as $9 \times 10^{-11}$ were estimated.

Key:

↔ - Neutral, less than 20 percent increase or decrease from baseline.

↗ - Some benefit, 20 to <50 percent decrease from baseline.

↗↗ - Greater benefit, 50 percent or greater decrease from baseline.

## V. CONCLUSIONS

The CTSA evaluated the risk, competitiveness, and resource requirements of seven technologies for performing the MHC function during PWB manufacturing. These technologies are electroless copper, carbon, conductive polymer, graphite, non-formaldehyde electroless copper, organic-palladium, and tin palladium. Chemical and process information are also presented for a conductive ink technology.

The results of the CTSA suggest that the alternatives to traditional non-conveyorized electroless copper processes (the baseline process) not only have environmental and economic benefits, but also perform the MHC function as well as the baseline. While there appears to be enough information to show that a switch away from traditional electroless copper processes has reduced risk benefits, there is not enough information to compare the alternatives to this process among themselves for all their environmental and health consequences. This is because not all proprietary chemicals have been identified, and because toxicity values are not available for some chemicals. In addition, it is important to note that there are additional factors beyond those assessed in this CTSA which individual businesses may consider when choosing among alternatives. The actual decision of whether or not to implement an alternative is made outside of the CTSA process.

To assist PWB manufacturers who are considering switching to an MHC alternative, the DfE PWB Project has prepared an implementation guide that describes lessons learned by other PWB manufacturers who have switched from non-conveyorized electroless copper to one of the alternative processes.[6] In addition, the University of Tennessee Department of Industrial Engineering can provide technical support to facilities that would like to use the cost model developed for the CTSA to estimate their own manufacturing costs should they switch to an MHC alternative.

[6] *Implementing Cleaner Technologies in the Printed Wiring Board Industry: Making Holes Conductive* (EPA 744-R-97-001, February 1997). This and other DfE PWB Project documents can be obtained by contacting EPA's Pollution Prevention Information Clearinghouse at (202) 260-1023.

# Chapter 1
# Introduction

This document presents the results of a cleaner technologies substitutes assessment (CTSA) of seven technologies for performing the "making holes conductive" (MHC) function during the manufacture of printed wiring boards (PWBs). MHC technologies are used by PWB manufacturers to deposit a seed layer or coating of conductive material into the drilled through-holes of rigid, multi-layer PWBs prior to electroplating. The technologies evaluated here are electroless copper, carbon, conductive polymer, graphite, non-formaldehyde electroless copper, organic-palladium, and tin-palladium. Chemical and process information is also presented for a conductive ink technology, but this technology is not evaluated fully.[1]

For the purposes of this evaluation, the non-conveyorized electroless copper process is considered the baseline process against which alternative technologies and equipment configurations (e.g., non-conveyorized or conveyorized) are compared. This CTSA is the culmination of over two years of research by the U.S. Environmental Protection Agency (EPA) Design for the Environment (DfE) PWB Project and the University of Tennessee (UT) Center for Clean Products and Clean Technologies on the comparative risk, performance, cost, and natural resource requirements of the alternatives as compared to the baseline.

The DfE PWB Project is a voluntary, cooperative partnership among EPA, industry, public-interest groups, and other stakeholders to promote implementation of environmentally beneficial and economically feasible manufacturing technologies by PWB manufacturers. Project partners participated in the planning and execution of this CTSA by helping define the scope and direction of the CTSA, developing project workplans, donating time, materials, and their manufacturing facilities for project research, and reviewing technical information contained in this CTSA. Much of the process-specific information presented here was provided by chemical suppliers to the PWB industry, PWB manufacturers who responded to project information requests, and PWB manufacturers who volunteered their facilities for a performance demonstration of the baseline and alternative technologies.

Section 1.1 presents project background information, including summary descriptions of the EPA DfE Program and the DfE PWB Project. Section 1.2 is an overview of the PWB industry, including the types of PWBs produced, the market for PWBs, and the overall PWB manufacturing process. Section 1.3 summarizes the CTSA methodology, including a discussion of how technologies were selected for evaluation in the CTSA, the boundaries of the evaluation, issues evaluated, data sources, and project limitations. Section 1.4 describes the organization of the remainder of the CTSA document.

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[1] Only limited analyses were performed on the conductive ink technology for two reasons: 1) the process is not applicable to multi-layer boards, which were the focus of the CTSA; and 2) sufficient data were not available to characterize the risk, cost, and energy and natural resources consumption of all of the relevant process steps (e.g., preparation of the screen for printing, the screen printing process itself, and screen reclamation).

## 1.1 PROJECT BACKGROUND

The PWB is the underlying link between semiconductors, computer chips, and other electronic components. Therefore, PWBs are an irreplaceable part of many "high-tech" products in the electronics, defense, communications, and automotive industries. PWB manufacturing, however, typically generates a significant amount of hazardous waste, requires a substantial amount of water and energy, and uses chemicals that may pose potential environmental and health risks.

To address these issues, the PWB industry has been actively seeking to identify and evaluate cleaner technologies and pollution prevention opportunities. However, many PWB manufacturers are small businesses that cannot afford to independently develop the data needed to evaluate new technologies and redesign their processes. The DfE PWB Project was initiated to develop that data, by forming partnerships between the EPA DfE Program, the PWB industry, and other interested parties to facilitate the evaluation and implementation of alternative technologies that reduce health and environmental risks and production costs. The EPA DfE Program and the DfE PWB Project are discussed in more detail below.

### 1.1.1 EPA DfE Program

EPA's Office of Pollution Prevention and Toxics created the DfE Program in 1991. The Program uses EPA's expertise and leadership to facilitate information exchange and research on risk reduction and pollution prevention opportunities. DfE works on a voluntary basis with small- and mostly medium-sized businesses to evaluate the risks, performance, costs, and resource requirements of alternative chemicals, processes, and technologies. Additional goals of the program include:

- Changing general business practices to incorporate environmental concerns.
- Helping individual businesses undertake environmental design efforts through the application of specific tools and methods.

The DfE Program catalyzes voluntary environmental improvement through stakeholder partnerships. DfE partners include industry, trade associations, research institutions, environmental and public-interest groups, academia, and other government agencies. By involving representatives from each of these stakeholder groups, DfE projects gain the necessary expertise to perform the project's technical work and improve the quality, credibility, and utility of the project's results.

### 1.1.2 DfE Printed Wiring Board Project

The DfE PWB Project is a voluntary, cooperative partnership among EPA, industry, public-interest groups, and other stakeholders to promote implementation of environmentally beneficial and economically feasible manufacturing technologies by PWB manufacturers. In part, the project is an outgrowth of industry efforts to identify key cleaner technology needs in electronic systems manufacturing. The results of these industry studies are presented in two reports prepared by Microelectronics and Computer Technology Corporation (MCC), an industry research consortium: *Environmental Consciousness: A Strategic Competitiveness Issue for the*

*Electronics Industry* (MCC, 1993) and *Electronics Industry Environmental Roadmap* (MCC, 1994).

The first study identified wet chemistry processes, such as those used in PWB fabrication, as water- and energy-intensive processes that generate significant amounts of hazardous waste. The study concluded that effective collaboration among government, industry, academia, and the public is imperative to proactively address the needs of environmental technologies, policies, and practices (MCC, 1993). As follow-up, the industry embarked on a collaborative effort to develop an environmental roadmap for the electronics industry. The roadmap project involved more than 100 organizations, including EPA, the Department of Energy, the Advanced Research Projects Agency, and several trade associations. The PWB industry national trade association, the Institute for Interconnecting and Packaging Electronic Circuits (IPC), was instrumental in developing the information on PWBs through its Environmental, Health, and Safety Committee.

The highest priority need identified for PWB manufacturers was for more efficient use, regeneration, and recycling of hazardous wet chemistries. One proposed approach to meet this need was to eliminate formaldehyde from materials and chemical formulations by researching alternative chemical formulations. Another priority need for the industry was to reduce water consumption and discharge, which can also be accomplished with alternative wet chemistries that have reduced numbers of rinse steps. Electroless copper technologies for MHC use formaldehyde as a reducing agent and consume large amounts of water.

The potential for improvement in these areas led EPA's DfE Program to forge working partnerships with IPC, individual PWB manufacturers and suppliers, research institutions such as MCC and UT's Center for Clean Products and Clean Technologies, and public-interest organizations, including the Silicon Valley Toxics Coalition and Communities for a Better Environment. These partnerships resulted in the DfE PWB Project.

Since its inception in 1994, the primary focus of the Project has been the evaluation of environmentally preferable MHC technologies. This CTSA is the culmination of this effort. The project has also:

- Identified, evaluated, and disseminated information on viable pollution prevention opportunities for the PWB industry through a review of pollution prevention and control practices in the industry (EPA, 1995a).
- Prepared several case studies of pollution prevention opportunities (EPA, 1995b; EPA, 1995c; EPA, 1996a; EPA, 1996b; EPA, 1996c).
- Prepared a summary of federal environmental regulations affecting the electronics industry (EPA, 1995d).
- Developed a summary document that profiles the PWB industry and defines and describes the typical manufacturing steps in the manufacture of rigid, multi-layer PWBs (EPA, 1995e).
- Prepared an implementation guide for PWB manufacturers interested in switching from electroless copper to an alternative MHC technology (EPA, 1997).

Future activities will include an evaluation of alternative surface finishes that can substitute for the hot-air solder leveling process.

# 1.2 OVERVIEW OF PWB INDUSTRY

## 1.2.1 Types of Printed Wiring Boards

PWBs may be categorized in several ways, including by layer counts or by substrate. Layer counts are the number of circuit layers present on a single PWB, giving an indication of the overall complexity of the PWB. The most common categories of layer counts are multi-layer, double-sided, and single-sided PWBs. Multi-layer PWBs contain more than two layers of circuitry, with at least one layer imbedded in the substrate beneath the surface of the board. Multi-layer boards may consist of 20 or more interconnected layers, but four, six, and eight layer boards are more common. Double-sided boards have circuitry on both sides of a board, resulting in two interconnected layers, while single-sided PWBs have only one layer of circuitry. Double-sided and single-sided PWBs are generally easier to produce than multi-layer boards (EPA, 1995e).

PWB substrates, or base material types, fall into three basic categories: rigid PWBs, flexible circuits, and rigid-flex combinations. Rigid multi-layer PWBs dominate the domestic production value of all PWBs (see Section 1.2.2, below) and are the focus of this CTSA.

Rigid PWBs typically are constructed of glass-reinforced epoxy-resin systems that produce a board less than 0.1" thick. The most common rigid PWB thickness is 0.062", but there is a trend toward thinner PWBs. Flexible circuits (also called flex circuits) are manufactured on polyamide and polyester substrates that remain flexible at finished thicknesses. Ribbon cables are common flexible circuits. Rigid-flex PWBs are essentially combinations or assemblies of rigid and flexible PWBs. They may consist of one or more rigid PWBs that have one or more flexible circuits laminated to them during the manufacturing process. Three-dimensional circuit assemblies can be created with rigid-flex combinations (EPA, 1995e).

## 1.2.2 Industry Profile

The total world market for PWBs is about $21 billion, with U.S. production accounting for about one quarter (more than $5 billion). The U.S.-dominated world market for PWBs eroded from 1980 to 1990, but has come back slightly in recent years. The PWB industry is characterized by highly competitive global sourcing with low profit margins (EPA, 1995e).

The U.S. has approximately 700 to 750 independent PWB manufacturing plants and about 70 captive facilities (e.g., original equipment manufacturers [OEMs] that make PWBs for use internally in their own electronic products) (EPA, 1995e). California, Minnesota, Texas, Illinois, Massachusetts, and Arizona have the highest number of PWB manufacturing plants, but there are PWB manufacturing facilities in virtually all 50 states and territories. More than 75 percent of U.S.-made PWBs are produced by independent shops (EPA, 1995e).

Around 90 percent of independent PWB manufacturers are small- to medium-sized businesses with annual sales under $10 million, but these shops only account for 20 to 25 percent of total U.S. sales (EPA, 1995e). Conversely, about seven percent of PWB manufacturers are larger independent shops with annual sales over $20 million, but these shops account for about 55 to 62 percent of total U.S. sales (EPA, 1995e).

Currently, rigid multi-layer boards dominate the domestic production value of PWBs, accounting for approximately 66 percent of the domestic market (EPA, 1995e). Double-sided boards account for about one quarter of the domestic market, with single-sided and flexible circuits making up the remainder. The market for multi-layer boards was about $3.4 billion in 1993, up from approximately $700 million in 1980 (EPA, 1995e).

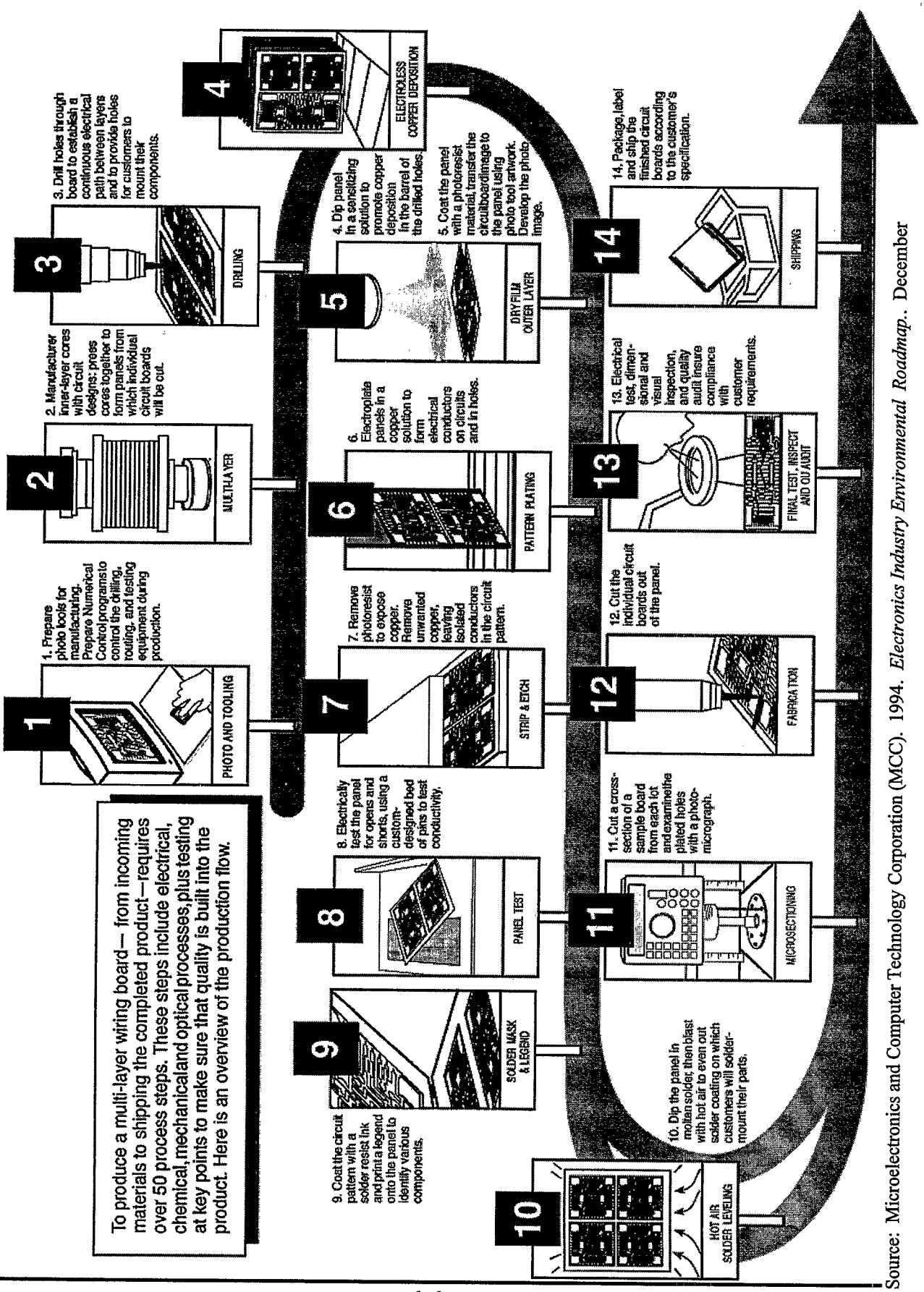
The PWB industry directly employs about 75,000 people, with about 68 percent of employment in production jobs. This is the highest ratio of production jobs for U.S. electronics manufacturing (EPA, 1995e). Additional jobs related to the industry are generated by PWB material and equipment suppliers and the OEMs that produce PWBs for internal use. Further information about the industry may be found in *Printed Wiring Board Industry and Use Cluster Profile* (EPA, 1995e).

### 1.2.3 Overview of Rigid Multi-Layer PWB Manufacturing

Multi-layer boards consist of alternating layers of conductor and insulating material bonded together. Holes are drilled through the boards to provide layer-to-layer connection on multi-layered circuits. Since most rigid PWB substrates consist of materials that will not conduct electricity (e.g., epoxy-resin and glass), a seed layer or coating of conductive material must be deposited into the hole barrels before electrolytic copper plating can occur. The MHC technologies evaluated in this report are processes to deposit this seed layer or coating of conductive material into drilled through-holes prior to electroplating. Traditionally, this has been done using an electroless copper technology to plate copper onto the hole barrels.

PWBs are most commonly manufactured by etching copper from a solid foil to form the desired interconnect pattern (subtractive processing). Another processing method, called additive processing, is used to selectively plate or metallize a board by building the circuits on catalyzed laminate with no metal foil on the surface. Additive processes to make multi-layer boards have only recently been under development in this country, and none are in widespread use (EPA, 1995e). Figure 1.1 illustrates the basic steps to fabricate rigid, multi-layer PWBs by subtractive processing.

**Figure 1.1 Rigid, Multi-Layter PWB Manufacturing Process Flow Diagram**




Source: Microelectronics and Computer Technology Corporation (MCC). 1994. *Electronics Industry Environmental Roadmap.*. December

## 1.3 CTSA METHODOLOGY

The CTSA *methodology* is a means of systematically evaluating and comparing human health and environmental risk, competitiveness (i.e., performance, cost, etc.), and resource requirements of traditional and alternative chemicals, manufacturing methods, and technologies in a particular use cluster. A use cluster is a set of chemical products, technologies, or processes that can substitute for one another to perform a particular function. A CTSA *document* is the repository for the technical information developed by a DfE project on a use cluster. Thus, MHC technologies comprise the use cluster that is the focus of this CTSA.

The overall CTSA methodology used in this assessment was developed by the EPA DfE Program, the UT Center for Clean Products and Clean Technologies, and other partners in voluntary, industry-specific pilot projects. The publication, *Cleaner Technologies Substitutes Assessment: A Methodology & Resource Guide* (Kincaid, et al., 1996) presents the CTSA methodology in detail. This section summarizes how the various technologies were selected for evaluation in the CTSA, identifies issues evaluated and data sources, and describes the project limitations. Chapters 2 through 6, and appendices, describe in detail the methods used to evaluate the technologies.

### 1.3.1 Identification of Alternatives and Selection of Project Baseline

Once the use cluster for the CTSA was chosen, industry representatives identified technologies that may be used to accomplish the MHC function. Initially, nine technology categories were identified, including seven wet chemistry processes, one screen printing process, and one mechanical process. These include:

- Wet chemistry: electroless copper, carbon, conductive polymer, electroless nickel, graphite, non-formaldehyde electroless copper, and palladium.
- Screen printing: conductive ink.
- Mechanical: lomerson.

Suppliers were contacted by EPA and asked to submit their product lines in these technology categories for evaluation in the CTSA. Criteria for including a technology in the CTSA were the following:

- It is an existing or emerging technology.
- There are equipment and facilities available to demonstrate its performance.

In addition, suppliers agreed to provide information about their technologies, including chemical product formulation data, process schematics, process characteristics and constraints (e.g., cycle time, limitations for the acid copper plating process, substrate and drilling compatibilities, aspect ratio capacity, range of hole sizes), bath replacement criteria, and cost information.

Product lines and publicly-available chemistry (e.g., product formulation) data were submitted for all of the technologies except electroless nickel and the lomerson process. Industry participants indicated the lomerson process is an experimental technology that has not been successfully implemented. Thus, seven categories of technologies were carried forward for

further evaluation in the CTSA. After review of publicly-available chemistry data submitted by the suppliers, the palladium technology category was further divided into two technology categories—organic-palladium and tin-palladium—bringing the total number of technology categories slated for evaluation to eight. For the purposes of a Performance Demonstration conducted as part of this CTSA, however, the organic-palladium and tin-palladium technologies were grouped together into a single palladium technology category.

Further review of the technologies indicated that the conductive ink technology is not applicable to multi-layer boards and sufficient data were not available to characterize the risk, cost, energy, and natural resources consumption of all of the relevant process steps (i.e., preparation of screen for printing, the screen printing process itself, and screen reclamation). Thus, only a process description, chemical hazard data (i.e., safety hazards, human health hazards, and aquatic toxicity), and regulatory information are presented for the conductive ink technology.

The electroless copper technology was selected as the project baseline for the following reasons:

- It is generally regarded to be the industry standard and holds the vast majority of the market for MHC technologies.
- Possible risk concerns associated with formaldehyde exposure, the large amount of water consumed and wastewater generated by electroless copper processes, and the presence of chelators that complicate wastewater treatment have prompted many PWB manufacturers to independently seek alternatives to electroless copper.

As with other MHC technologies, electroless copper processes can be operated using vertical, immersion-type, non-conveyorized equipment or horizontal, conveyorized equipment. Conveyorized MHC equipment is a relatively new innovation in the industry and is usually more efficient than non-conveyorized equipment. However, most facilities in the U.S. still use a non-conveyorized electroless copper process to perform the MHC function. Therefore, the baseline technology was further defined to only include non-conveyorized electroless copper processes. Conveyorized electroless copper processes, and both non-conveyorized and conveyorized equipment configurations of the other technology categories are all considered to be alternatives to non-conveyorized electroless copper.

### 1.3.2 Boundaries of the Evaluation

For the purposes of the environmental evaluation (e.g., health and environmental hazards, exposure, risk, and resource consumption), the boundaries of this evaluation can be defined in terms of the overall life cycle of the MHC products and in terms of the PWB manufacturing process. The life cycle of a product or process encompasses extraction and processing of raw materials, manufacturing, transportation and distribution, use/re-use/maintenance, recycling, and final disposal. As discussed in Section 1.2.3, rigid, multi-layer PWB manufacturing encompasses a number of process steps, of which the MHC process is one.

The life-cycle stages evaluated in this study are primarily the use of MHC chemicals at PWB facilities and the release or disposal of MHC chemicals from PWB facilities. However, in

addition to evaluating the energy consumed during MHC line operation, the analysis of energy impacts (Section 5.2) also discusses the pollutants generated from producing the energy to operate the MHC line as well as energy consumed in other life-cycle stages, such as the manufacture of chemical ingredients. In addition, while information is presented on the types and quantities of wastewater and solid waste generated by MHC process lines, there was insufficient information to characterize the risk from these environmental releases. This is discussed in more detail in Section 3.1, Source Release Assessment.

In terms of the PWB manufacturing process, this analysis focused entirely on the MHC process, defined as beginning with a panel that has been desmeared[2] and freed of all residual desmear chemistry and ending when a layer of conducting material has been deposited that is stable enough to proceed to either panel or pattern plating. The MHC process was defined slightly differently however, for the Performance Demonstration: beginning with the desmear step, proceeding through the MHC process, and ending with 0.1 mil of copper flash plating. The slightly different definition was needed to address compatibility issues associated with the desmear step and to protect the test boards during shipment to a single facility for electroplating (see Section 4.1, Performance Demonstration Results).

The narrow focus on MHC technologies yields some benefits to the evaluation, but it also has some drawbacks. Benefits include the ability to collect extremely detailed information on the relative risk, performance, cost, and resources requirements of the baseline technology and alternatives. This information provides a more complete assessment of the technologies than has previously been available and would not be possible if every step in the PWB manufacturing process was evaluated. Drawbacks include the inability to identify all of the plant-wide benefits, costs, or pollution prevention opportunities that could occur when implementing an alternative to the baseline electroless copper technology. However, given the variability in workplace practices and operating procedures at PWB facilities, these other benefits and opportunities are expected to vary substantially among facilities and would be difficult to assess in a comparative evaluation such as a CTSA. Individual PWB manufacturers are urged to assess their overall operations for pollution prevention opportunities when implementing an alternative technology.

### 1.3.3 Issues Evaluated

The CTSA evaluated a number of issues related to the risk, competitiveness, and resource requirements (conservation) of MHC technologies. These include the following:

- Risk: occupational health risks, public health risks, ecological hazards, and process safety concerns.
- Competitiveness: technology performance, cost, regulatory status, and international market status.
- Conservation: energy and natural resource use.

[2] Desmearing is the process step to remove a small amount of epoxy-resin from the hole barrels, including any that may have been smeared across the copper interface during drilling.

Occupational and public health risk information is for chronic exposure to long-term, day-to-day releases from a PWB facility rather than short-term, acute exposures to high levels of hazardous chemicals as could occur with a fire, spill, or other periodic release. Risk information is based on exposures estimated for a model facility, rather than exposures estimated for a specific facility. Ecological hazards, but not risks, are evaluated for aquatic organisms that could be exposed to MHC chemicals in wastewater discharges. Process safety concerns are summarized from material safety data sheets (MSDSs) for the technologies and process operating conditions.

Technology performance is based on a snapshot of the performance of the MHC technologies at volunteer test sites in the U.S. and abroad. Panels were electrically prescreened, followed by electrical stress testing and mechanical testing, in order to distinguish variability in the performance of the MHC interconnect. Comparative costs of the MHC technologies were estimated with a hybrid cost model that combines traditional costs with simulation modeling and activity-based costs. Costs are presented in terms of dollars per surface square feet (ssf) of PWB produced.

Federal environmental regulatory information is presented for the chemicals in the MHC technologies. This information is intended to provide an indication of the regulatory requirements associated with a technology, but not to serve as regulatory guidance. Information on the international market status of technologies is presented as an indicator of the effects of a technology choice on global competitiveness.

Quantitative resource consumption data are presented for the comparative rates of energy and water use of the MHC technologies. The large amounts of water consumed and wastewater generated by the traditional electroless copper process have been of particular concern to PWB manufacturers, as well as to the communities in which they are located.

### 1.3.4 Primary Data Sources

Much of the process-specific information presented in this CTSA was provided by chemical suppliers to the PWB industry, PWB manufacturers who responded to project information requests, and PWB manufacturers who volunteered their facilities for a performance demonstration of the baseline and alternative technologies. The types of information provided by chemical suppliers and PWB manufacturers are summarized below.

**Chemical Suppliers**

The project was open to any chemical supplier who wanted to participate, provided their technologies met the criteria described in Section 1.3.1. Table 1.1 lists the suppliers who participated in the CTSA and the categories of MHC technologies they submitted for evaluation. It should be noted that this is not a comprehensive list of MHC technology suppliers. EPA made every effort to publicize the project through trade associations, PWB manufacturers, industry conferences and other means, but some suppliers did not learn of the project until it was too late to submit technologies for evaluation.

**Table 1.1 MHC Technologies Submitted by Chemical Suppliers**

| Chemical Supplier | MHC Technology | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Electroless Copper | Carbon | Conductive Ink | Conductive Polymer | Graphite | Non-Formaldehyde Electroless Copper | Organic-Palladium | Tin-Palladium |
| Atotech U.S.A., Inc. | ✓ | | | ✓ | | | ✓ | |
| Electrochemicals, Inc. | ✓ | | | | ✓ | | | |
| Enthone-OMI, Inc. | ✓ | | | | | | | ✓ |
| W.R. Grace and Co. | | | ✓ | | | | | |
| LeaRonal, Inc. | | | | | | | | ✓ |
| MacDermid, Inc. | ✓ | ✓ | | | | ✓ | | |
| Shipley Company | ✓ | | | | ✓ | | | ✓ |
| Solution Technology Systems | | | | | | | | ✓ |

Each of the chemical suppliers provided the following: MSDSs for the chemical products in their MHC technology lines; Product Data Sheets, which are technical specifications prepared by suppliers for PWB manufacturers that describe how to mix and maintain the chemicals baths; and, in some cases, copies of patents.[3] Suppliers were also asked to complete a Supplier Data Sheet, designed for the project, which included information on chemical cost, equipment cost, water consumption rates, product constraints, and the locations of test sites for the Performance Demonstration. Appendix A contains a copy of the Supplier Data Sheet.

## PWB Manufacturers

PWB manufacturers were asked to participate in a study of workplace practices. The IPC Workplace Practices Questionnaire requested detailed information on facility size, process characteristics, chemical consumption, worker activities related to chemical exposure, water consumption, and wastewater discharges. The questionnaire was distributed to PWB manufacturers by IPC. PWB manufacturers returned the completed questionnaires to IPC, which removed all facility identification and assigned a code to the questionnaires prior to forwarding them to the UT Center for Clean Products. In this manner, PWB manufacturers were guaranteed confidentially of data. However, when Center staff had follow-up questions on a questionnaire response, many facilities allowed the Center to contact them directly, rather than go through IPC to discuss the data.

For the Performance Demonstration project the IPC Workplace Practices Questionnaire was modified and divided into two parts: a Facility Background Information Sheet and an Observer Data Sheet. The Facility Background Information Sheet was sent to PWB facilities participating in the Performance Demonstration prior to their MHC technology test date. It requested detailed information on facility and process characteristics, chemical consumption, worker activities related to chemical exposure, water consumption, and wastewater discharges. The Observer Data Sheet was used by an on-site observer to collect data during the Performance

[3] In addition, Electrochemicals, LeaRonal, and Solution Technology Systems provided information on proprietary chemical ingredients to the project. This is discussed further in Section 1.3.5.

Demonstration. In addition to ensuring that the performance test was performed according to the agreed upon test protocol, the on-site observer collected measured data, such as bath temperature and process line dimensions, and checked survey data for accuracy. Appendix A contains copies of the IPC Workplace Practices Questionnaire, the Facility Background Information Sheet, and the Observer Data Sheet forms.

Table 1.2 lists the number of PWB manufacturing facilities that completed the IPC Workplace Practices Questionnaire (original forms modified for the Performance Demonstration) by type of MHC process, excluding responses with poor or incomplete data. Of the 59 responses to the questionnaire, 25 were Performance Demonstration test sites.

**Table 1.2 Responses to the Workplace Practices Questionnaire**

| MHC Technology | No. of Responses | MHC Technology | No. of Responses |
|---|---|---|---|
| Electroless Copper | 36 | Non-Formaldehyde Electroless Copper | 1 |
| Carbon | 2 | Organic-Palladium | 2 |
| Conductive Polymer | 1 | Tin-Palladium | 13 |
| Graphite | 4 | | |

Information from the pollution prevention and control technologies survey conducted by the DfE PWB Project was also used in the CTSA. These data are described in detail in the EPA publication, *Printed Wiring Board Pollution Prevention and Control: Analysis of Survey Results* (EPA, 1995a).

### 1.3.5 Project Limitations

There are a number of limitations to the project, both because of the project's limited resources, the predefined scope of the project, and data limitations inherent to risk characterization techniques. Some of the limitations related to the risk, competitiveness, and conservation components of the CTSA are summarized below. More detailed information on limitations and uncertainties for a particular portion of the assessment is given in the applicable sections of this document. A limitation common to all components of the assessment is that the MHC chemical products assessed in this report were voluntarily submitted by participating suppliers and may not represent the entire MHC technology market. For example, the electroless nickel and lomerson technologies were not evaluated in the CTSA.

**Risk**

The risk characterization is a screening level assessment of multiple chemicals used in MHC technologies. The focus of the risk characterization is on chronic (long-term) exposure to chemicals that may cause cancer or other toxic effects, rather than on acute toxicity from brief exposures to chemicals. The exposure assessment and risk characterization use a "model facility" approach, with the goal of comparing the exposures and health risks of the MHC process alternatives to the baseline electroless copper technology. Characteristics of the model facility were aggregated from questionnaire data, site visits, and other sources. This approach does not result in an absolute estimate or measurement of risk.

In addition, the exposure and risk estimates reflect only a portion of the potential exposures within a PWB manufacturing facility. Many of the chemicals found in MHC technologies may also be present in other process steps of PWB manufacturing and other risk concerns for human health and the environment may occur from other process steps. Incremental reduction of exposures to chemicals of concern from an MHC process, however, will reduce cumulative exposures from all sources in a PWB facility, provided that increased production does not increase plant-wide pollution.

Finally, information presented in this CTSA is based on publicly-available chemistry data submitted by each of the participating suppliers, as well as proprietary data submitted by Electrochemicals, LeaRonal, and Solution Technology Systems. W.R. Grace was preparing to submit proprietary data for the conductive ink technology when it was determined that this information was no longer necessary because risk from the conductive ink technology could not be characterized. The other suppliers participating in the project (Atotech, Enthone-OMI, MacDermid, and Shipley) declined to provide proprietary information. The absence of information on proprietary chemical ingredients is a significant source of uncertainty in the risk characterization. Risk information for proprietary ingredients, as available, is included in this CTSA, but chemical identities and chemical properties are not listed.

**Competitiveness**

The Performance Demonstration was designed to provide a snapshot of the performance of different MHC technologies. The test methods used to evaluate performance were intended to indicate characteristics of a technology's performance, not to define parameters of performance or to substitute for thorough on-site testing. Because the test sites were not chosen randomly, the sample may not be representative of all PWB manufacturing facilities in the U.S. (although there is no specific reason to believe they are not representative).

The cost analysis presents comparative costs of using an MHC technology in a model facility to produce 350,000 ssf of PWBs. As with the risk characterization, this approach results in a comparative evaluation of cost, not an absolute evaluation or determination. The cost analysis focuses on private costs that would be incurred by facilities implementing a technology. It does not evaluate community benefits or costs, such as the effects on jobs from implementing a more efficient MHC technology. However, the Social Benefits/Costs Assessment (see Section 7.2) qualitatively evaluates some of these external (i.e., external to the decision-maker at a PWB facility) benefits and costs.

The regulatory information contained in the CTSA may be useful in evaluating the benefits of moving away from processes containing chemicals that trigger compliance issues. However, this document is not intended to provide compliance assistance. If the reader has questions regarding compliance concerns, they should contact their federal, state, or local authorities.

**Conservation**

The analysis of energy and water consumption is also a comparative analysis, rather than an absolute evaluation or measurement. Similar to the cost analysis, consumption rates were estimated based on using an MHC technology in a model facility to produce 350,000 ssf of PWB.

## 1.4 ORGANIZATION OF THIS REPORT

This CTSA is organized into two volumes: Volume I summarizes the methods and results of the CTSA; Volume II consists of appendices, including detailed chemical properties and methodology information, and comprehensive results of the risk characterization.

Volume I is organized as follows:

- Chapter 2 gives a detailed profile of the MHC use cluster, including process descriptions of the MHC technologies evaluated in the CTSA and the estimated concentrations of chemicals present in MHC chemical baths.
- Chapter 3 presents risk information, beginning with an assessment of the sources, nature, and quantity of selected environmental releases from MHC processes (Section 3.1); followed by an assessment of exposure to MHC chemicals (Section 3.2) and the potential human health and ecological hazards of MHC chemicals (Section 3.3). Section 3.4 presents quantitative risk characterization results, while Section 3.5 discusses process safety concerns.
- Chapter 4 presents competitiveness information, including Performance Demonstration results (Section 4.1), cost analysis results (Section 4.2), regulatory information (Section 4.3), and international market information (Section 4.4).
- Chapter 5 presents conservation information, including an analysis of water and other resource consumption rates (Section 5.1) and energy impacts (Section 5.2).
- Chapter 6 describes additional pollution prevention and control technology opportunities (Sections 6.1 and 6.2, respectively).
- Chapter 7 organizes data collected or developed throughout the CTSA in a manner that facilitates decision-making. Section 7.1 presents a summary of risk, competitiveness and conservation data. Section 7.2 assesses the social benefits and costs of implementing an alternative as compared to the baseline. Section 7.3 provides summary profiles for the baseline and each of the MHC alternatives.

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# Chapter 2
# Profile of the Making Holes Conductive Use Cluster

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

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

## 2.1 CHEMISTRY AND PROCESS DESCRIPTION OF MHC TECHNOLOGIES

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

### 2.1.1 Substitutes Tree of MHC Technologies

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

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

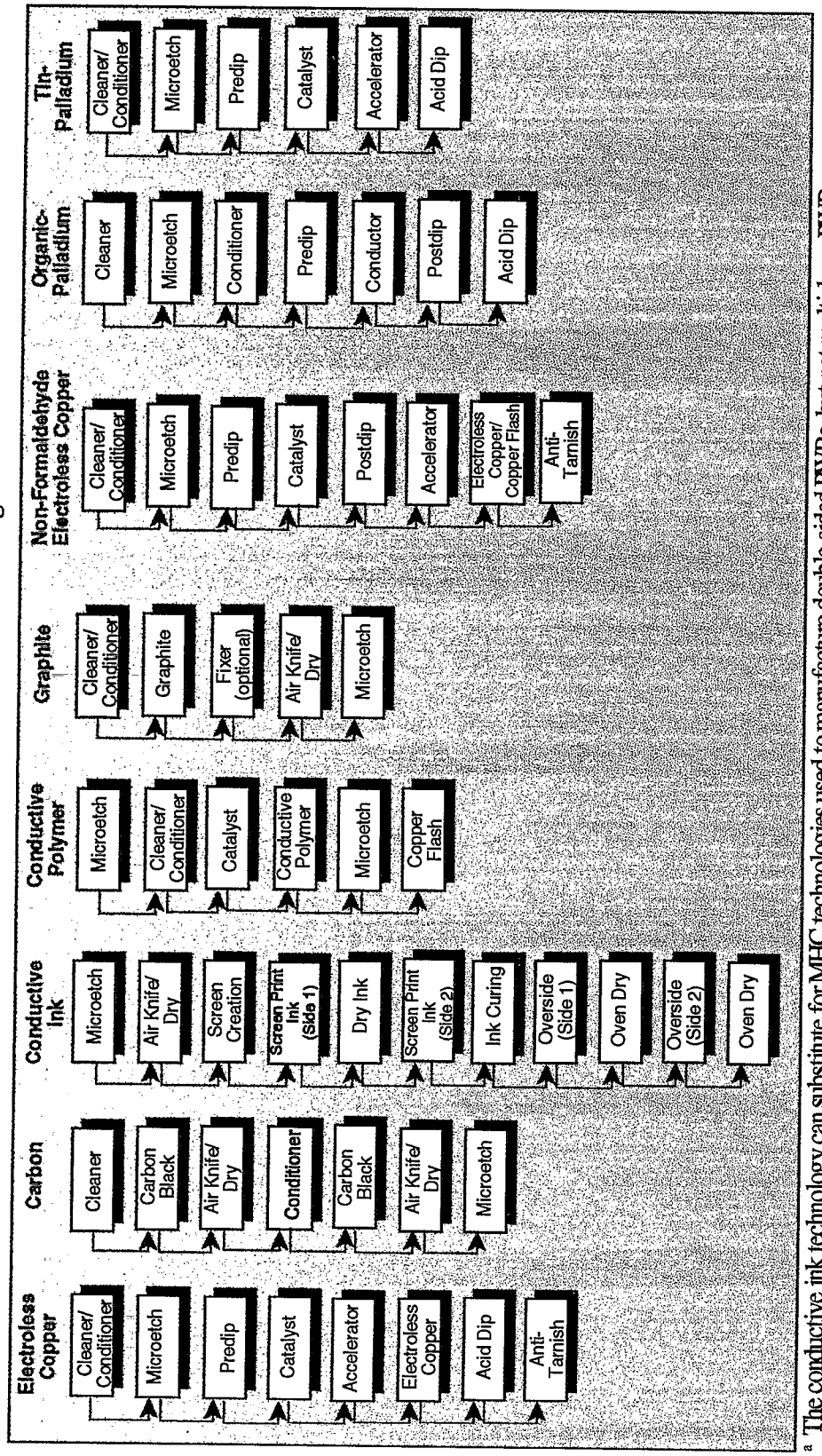



**Figure 2.1 Substitutes Tree of MHC Technologies[a]**

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

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

### 2.1.2 Overview of MHC Technologies

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

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

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

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

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

### 2.1.3 Chemistry and Process Descriptions of MHC Technologies

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

**Electroless Copper**

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

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

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

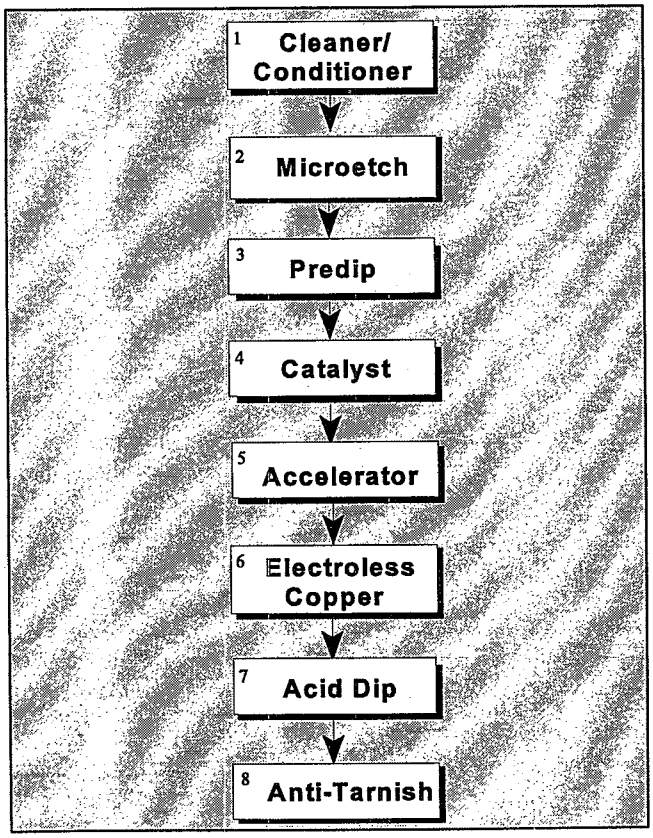
Step 2: A microetch solution, which typically consists of dilute hydrochloric or sulfuric acid, etches the existing copper surfaces to remove any contaminants or oxides to ensure good copper-to-copper adhesion at all of the copper interconnect points.

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

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

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

**Figure 2.2 Generic Process Steps for the Electroless Copper Technology**



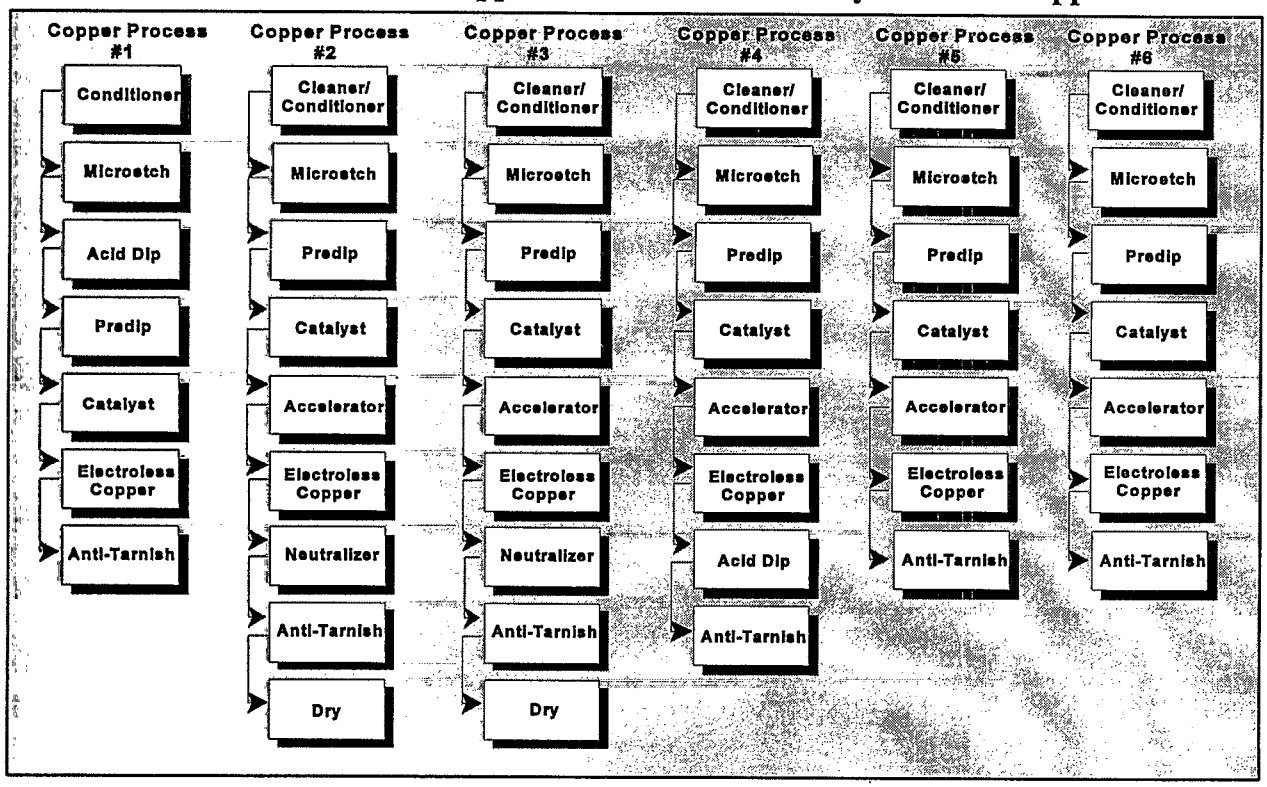

Step 6: An electroless copper solution plates a layer of copper onto the surface of the palladium catalyst. The electroless copper bath is an alkaline solution containing a source of copper ions, a chelator to keep the copper ions solubilized, a stabilizer to prevent the copper solution from plating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

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

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

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

**Figure 2.3 Electroless Copper Processes Submitted by Chemical Suppliers**




## Carbon

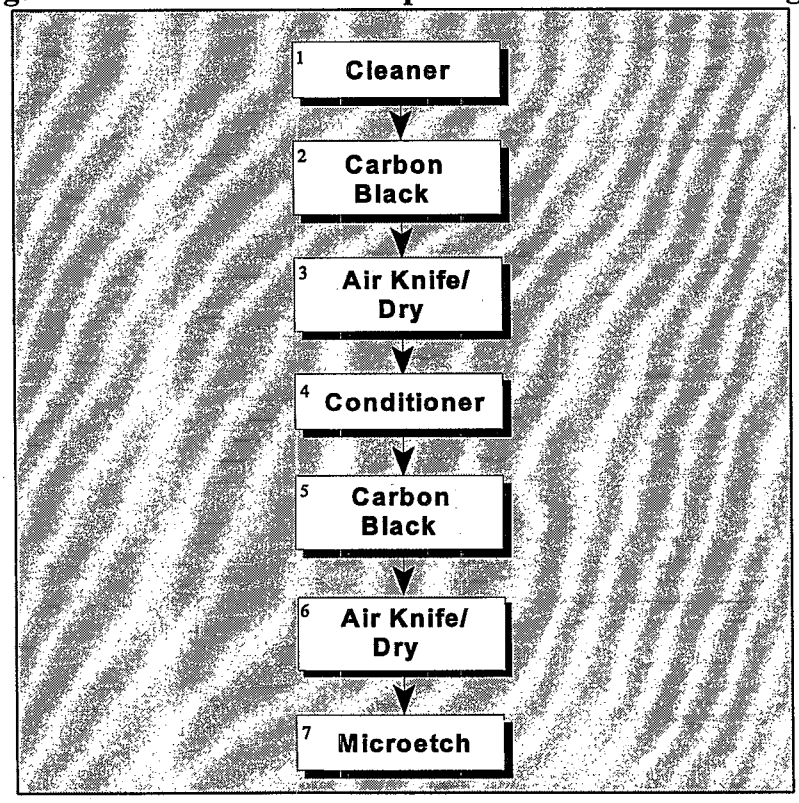
Carbon processes utilize a suspension of carbon black particles to deposit a conductive layer of carbon onto the substrate surface. The spherical carbon black particles form an amorphous, or noncrystalline, structure of randomly scattered crystallites, which create a conductive layer. The process is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

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

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

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

**Figure 2.4 Generic Process Steps for the Carbon Technology**




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

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

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

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

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

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

**Conductive Ink**

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

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

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

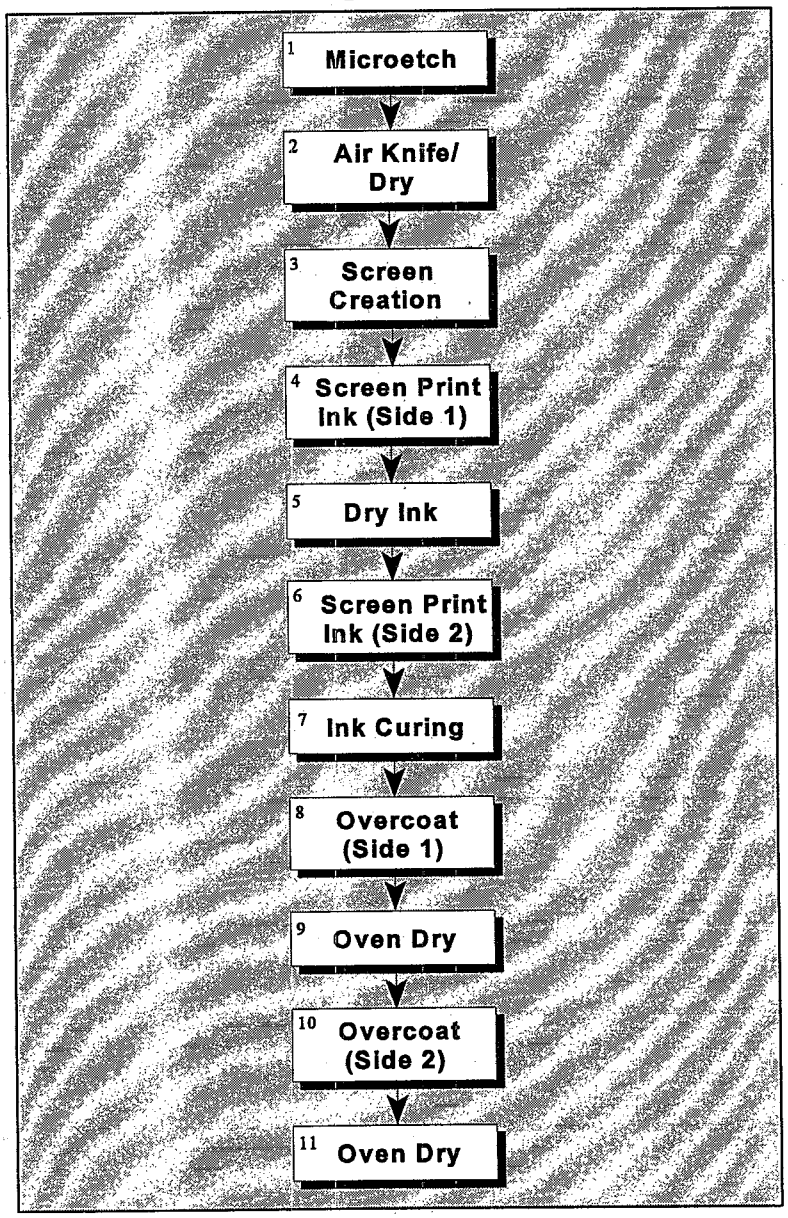
Step 2: An air knife removes any residual chemistry from the PWB panels before the panels are dried in a oven. The panels must be dried completely to remove any moisture from the substrate before screening.

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

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

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

**Figure 2.5 Generic Process Steps for the Conductive Ink Technology**




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

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

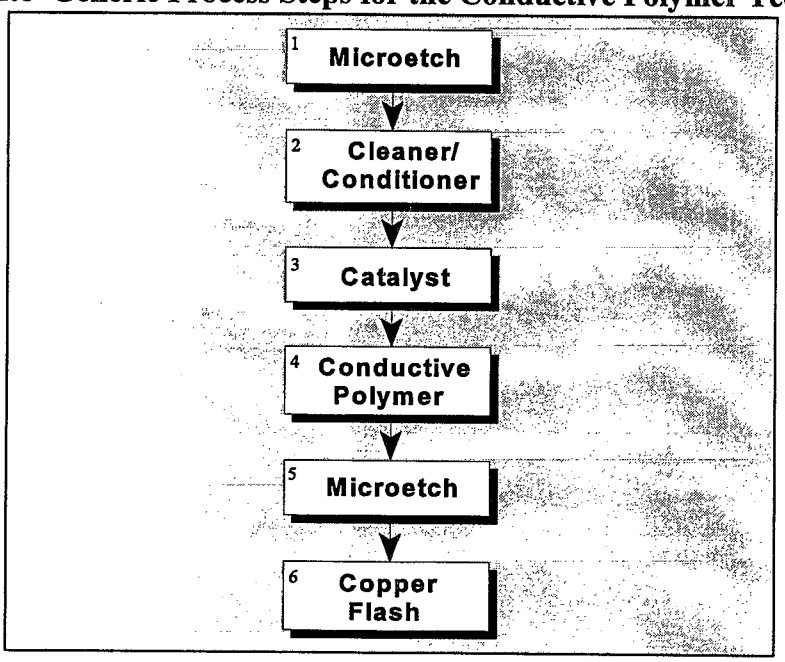
Steps 8-11: A final coating of soldermask is applied to cover the printed through-holes on both sides of the PWB, protecting them against oxidation and potential physical or chemical damage. The solder mask is typically applied using a screen printing and drying sequence similar to that described in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

## Conductive Polymer

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

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

**Figure 2.6 Generic Process Steps for the Conductive Polymer Technology**




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

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

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

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

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

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

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

**Graphite**

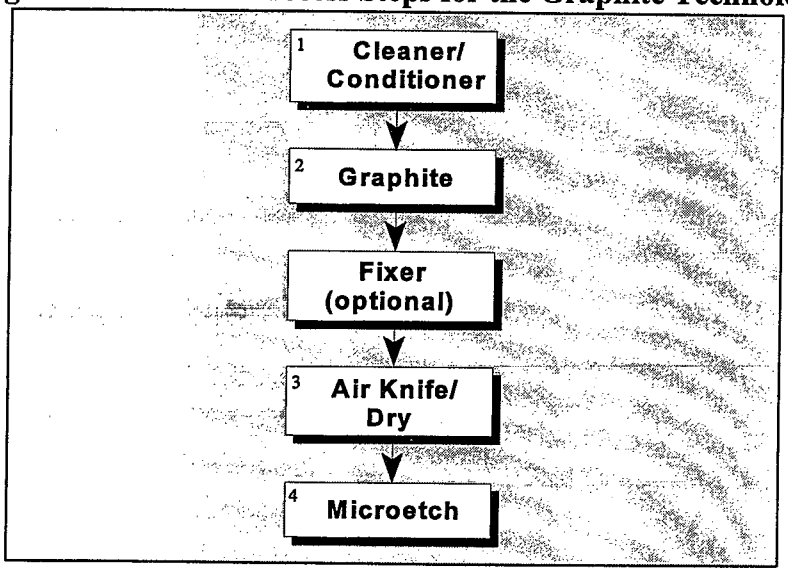
Graphite processes provide for the deposition of another form of carbon—graphite—onto the substrate surfaces of the through-holes, in a process similar to the carbon process described above. Graphite has a three-dimensional, crystalline structure as opposed to the amorphous, randomly arranged structure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

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

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

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

**Figure 2.7 Generic Process Steps for the Graphite Technology**




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

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

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

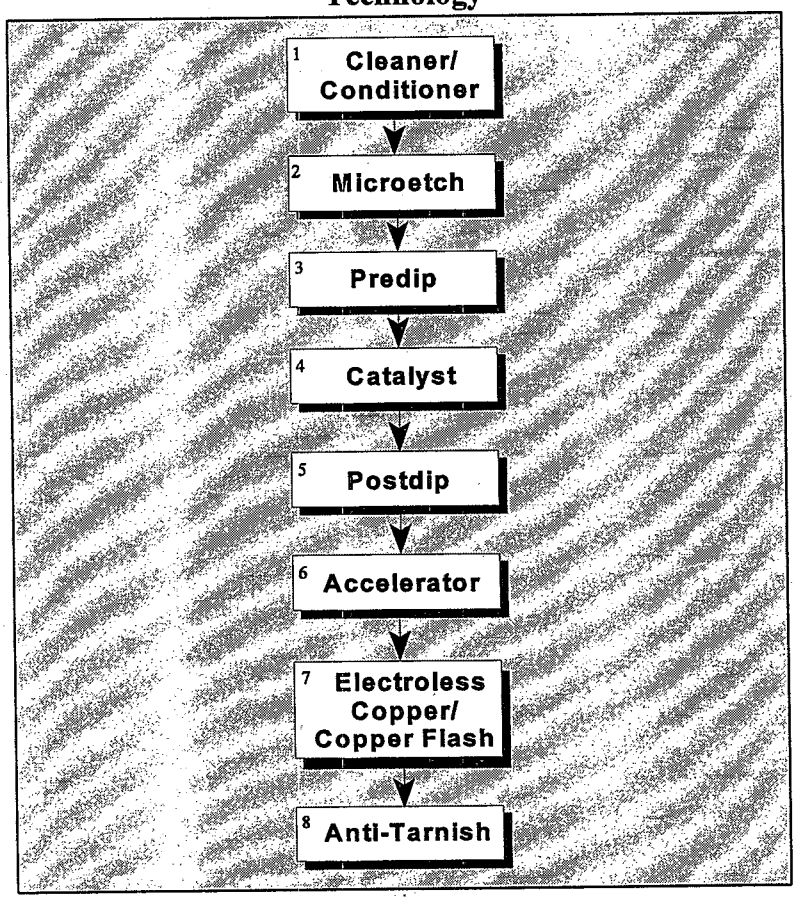
A fixer step can also be useful in conveyorized process modes where high aspect ratio holes (small diameter holes in thick panels) are being manufactured. The fixer causes the graphite to cover the entire hole barrel evenly and prevents the solution from accumulating at one end.

## Non-Formaldehyde Electroless Copper

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

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

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




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

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

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

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

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

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

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

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

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

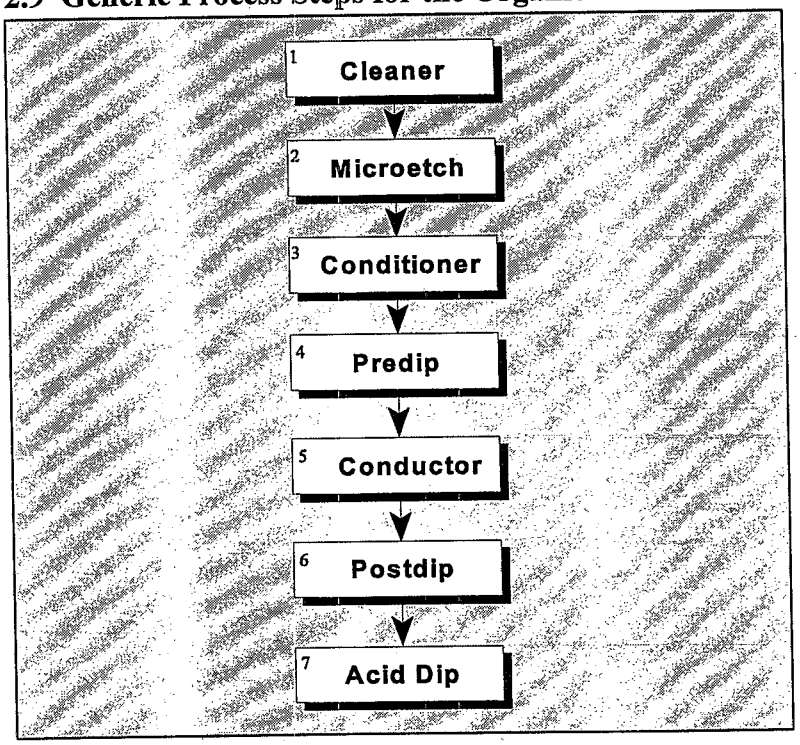
**Organic-Palladium**

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

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

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

**Figure 2.9 Generic Process Steps for the Organic-Palladium Technology**




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

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

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

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

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

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

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

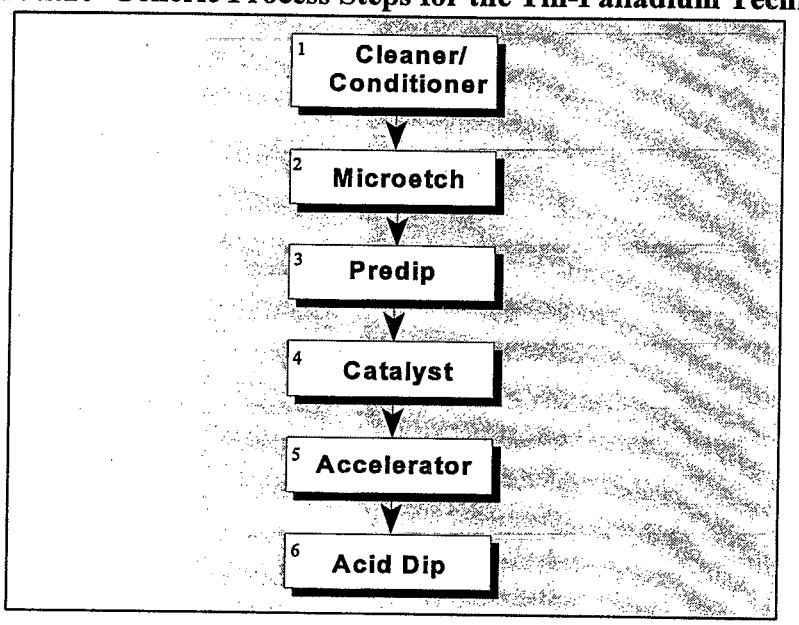
Organic-palladium can be operated successfully in either conveyorized or non-conveyorized modes. The process is compatible with all common substrates, including Teflon.

## Tin-Palladium

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

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

**Figure 2.10 Generic Process Steps for the Tin-Palladium Technology**



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

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

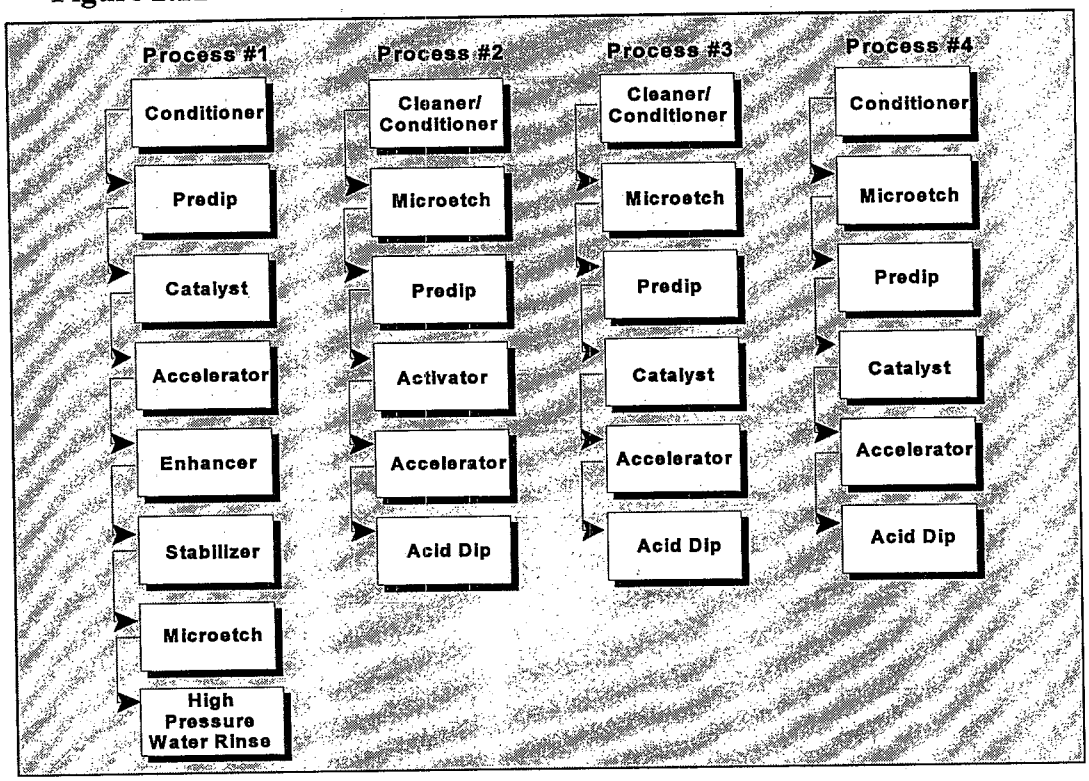
Step 4: Tin-palladium colloids adsorb from the colloidal suspension of the catalyst solution onto the slightly charged through-hole surfaces. The adsorbed palladium colloids form a relatively nonconductive coating on the substrate surfaces of the through-hole.

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

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

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

**Figure 2.11 Tin-Palladium Processes Submitted by Chemical Suppliers**



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

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

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

### 2.1.4 Chemical Characterization of MHC Technologies

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

**Use of Publicly-Available Chemical Formulation Data**

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

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

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

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

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

**Table 2.1 Non-Proprietary Chemicals and Associated MHC Technologies**

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

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

## Determining Chemical Formulations

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

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

The individual chemical concentrations in the baths were calculated by:

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

where:

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

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

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

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

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

## Data Limitations

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

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

**Table 2.2 Material Safety Data Sheet Trade Secret Information**

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

[a] Confidential ingredient 1: Cationic emulsifier - <10%. Confidential ingredient 2: 1-5%; oral 7460 mg/kg $LD_{50}$ rat, skin 16 g/kg $LD_{Lo}$ rabbit. Confidential ingredient 3: 1-5%, oral 350 mg/kg $LD_{50}$ mouse.

[b] Confidential ingredient: surfactant - < 2% by weight.

[c] Confidential ingredient 1: 5-15%; considered to be "relatively non-hazardous"; toxicity data: oral > 6400 mg/kg $LD_{50}$ rabbit. Confidential ingredient 2: 1-5%; toxicity data: oral 100 g/kg $LD_{50}$ rat, oral 1040 mg/kg $LD_{50}$ rabbit. Confidential ingredient 3: 10-20%; toxicity data: IPR 5600 mg/kg $LD_{50}$ MUS, INV 2350 mg/kg $LD_{50}$ MUS.

[d] Confidential ingredient 2: listed as a Class 3 carcinogen by IARC. A Class 3 carcinogen, as defined by IARC, is "not classifiable as to human carcinogenicity," which means that there is "inadequate or no evidence."

[e] Confidential ingredient: Non-ionic surfactant - <3%.

[f] An MSDS for one of the tin-palladium technologies states, "This product may contain small amounts of chemicals listed as being known to the State of California to cause cancer or birth defects or other reproductive harm, under the California Safe Drinking Water and Toxic Enforcement Act of 1986. It does not contain sufficient amounts of such chemicals to make it subject to federal rules on hazard communication for carcinogens administered by OSHA [29 CFR 1910.1200 (d), Reference (1)]." The reference to federal rules on hazardous communication for carcinogens means that it is present at <0.1%.

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

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

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

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

## Chemical Properties

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

## 2.2 ADDITIONAL MHC TECHNOLOGIES

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

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

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

### 2.2.1 Lomerson Process

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

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

### 2.2.2 Non-Formaldehyde Electroless Nickel

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

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

- Cleaner.
- Electroless nickel.

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

## 2.3 MARKET PROFILE OF MHC TECHNOLOGIES

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

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

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

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

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

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

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# Chapter 3
# RISK

This chapter of the Cleaner Technologies Substitutes Assessment (CTSA) addresses the health and environmental hazards, exposures, and risks that may result from using a making holes conductive (MHC) technology. The information presented here focuses entirely on MHC technologies. It does not, nor is it intended to, represent the full range of hazards or risks that could be associated with printed wiring board (PWB) manufacturing.

Section 3.1 identifies possible sources of environmental releases from MHC manufacturing and, in some cases, discusses the nature and quantity of those releases. Section 3.2 assesses occupational and general population (i.e., the public living near a PWB facility; fish in streams that receive wastewater from PWB facilities) exposures to MHC chemicals. This section quantitatively estimates inhalation and dermal exposure to workers and inhalation exposure to the public living near a PWB facility. Section 3.3 presents human health hazard and aquatic toxicity data for MHC chemicals. Section 3.4 characterizes the risks and concerns associated with the exposures estimated in Section 3.2. In all of these sections, the methodologies or models used to estimate releases, exposures, or risks are described along with the associated assumptions and uncertainties. In order to protect the identity of the proprietary chemicals, the chemical concentrations, exposures, and toxicological data for these chemicals are not given in the report. However, those proprietary chemicals that may present a potential risk to human health are identified by their generic chemical name in Section 3.4. Section 3.5 summarizes chemical safety hazards from material safety data sheets (MSDSs) for MHC chemical products and discusses process safety issues.

## 3.1 SOURCE RELEASE ASSESSMENT

This section of the CTSA uses data from the IPC Workplace Practices Questionnaire, together with other data sources, to identify sources and amounts of environmental releases. Both on-site releases (e.g., evaporative or fugitive emissions from the process, etc.) and off-site transfers (e.g., discharges to publicly-owned treatment works [POTWs]) are identified and, if sufficient data exist, characterized. The objectives of the Source Release Assessment are to:

- Identify potential sources of releases.
- Characterize the source conditions surrounding the releases, such as a heated bath or the presence of local ventilation.
- Where possible, characterize the nature and quantity of releases under the source conditions.

Many of these releases may be mitigated and even prevented through pollution prevention techniques and good operating procedures at some PWB facilities. However, they are included in this assessment to illustrate the range of releases that may occur from MHC processes.

A material balance approach was used to identify and characterize environmental releases associated with day-to-day operation of MHC processes. Modeling of air releases that could not be explicitly estimated from the data is done in the Exposure Assessment (See Section 3.2).

Section 3.1.1 describes the data sources and assumptions used in the Source Release Assessment. Section 3.1.2 discusses the material balance approach used and release information and data pertaining to all MHC process alternatives. Section 3.1.3 presents source and release information and data for specific MHC process alternatives. Section 3.1.4 discusses uncertainties in the Source Release Assessment.

### 3.1.1 Data Sources and Assumptions

This section presents a general discussion of data sources and assumptions for the Source Release Assessment. More detailed information is presented for specific inputs and releases in Sections 3.1.2 and 3.1.3.

Sources of data used in the Source Release Assessment include:

- IPC Workplace Practices Questionnaire and Performance Demonstration data (see Appendix A, Data Collection Sheets).
- Supplier-provided data, including publicly-available bath chemistry data and supplier Product Data Sheets describing how to mix and maintain baths (see Appendix B, Publicly-Available Bath Chemistry Data).
- Engineering estimates.
- The DfE PWB Project publication, *Printed Wiring Board Pollution Prevention and Control: Analysis of Survey Results* (EPA, 1995a).

Bath chemistry data were collected in the IPC Workplace Practices Questionnaire, but these data were not used due to inconsistencies in responses to the questions pertaining to bath chemistry. Instead, MHC chemical suppliers participating in the Performance Demonstration each submitted publicly-available data on their respective product lines; estimated bath concentration ranges were determined based on this information. The use of publicly-available bath chemistry data is discussed in detail in Section 2.1.4.

Several assumptions or adjustments were made to put the IPC Workplace Practices Questionnaire data in a consistent form for all MHC technologies. These include the following:

- To convert data reported on a per day basis to an annual basis, the number of days per year reported for questionnaire question 1.1 was used. For data on a weekly or monthly basis, 12 months per year and 50 weeks per year were assumed.
- If data were reported on a per shift basis, the number of shifts per day (from questionnaire question 1.4) was used to convert to a per day basis.
- Bath names in the questionnaire database were revised to be consistent with the generic MHC process descriptions in Section 2.1.3.

To facilitate comparison among process alternatives and to adjust for the wide variations in the data due to differing size of PWB facilities, questionnaire data are presented here both as

reported in the questionnaires (usually as an annual quantity consumed or produced), and normalized by annual surface square feet (ssf) of PWB produced. Normalizing the data, however, may not fully account for possible differences in processing methods that could result from higher production levels.

### 3.1.2 Overall Material Balance for MHC Technologies

A general material balance is presented here to identify and characterize inputs to and potential releases from the MHC process alternatives. Due to limitations and gaps in the available data, no attempt is made to perform a quantitative balance of inputs and outputs. This approach is still useful, however, as an organizing tool for discussing the various inputs to and outputs from MHC processes and presenting the available data. Figure 3.1 depicts inputs to a generalized MHC process line, along with possible outputs, including PWB product, solid waste, air emissions, and wastewater discharges. Many PWB manufacturers have an on-site wastewater treatment system for pretreating wastewaters prior to direct discharge to a stream or lake or indirect discharge to a POTW. Figure 3.2 describes a simplified PWB wastewater treatment system, including the inputs and outputs of interest in the Source Release Assessment.

**Inputs**

Possible inputs to an MHC process line include bath chemicals, copper-clad PWBs that have been processed through previous PWB manufacturing process steps, water, and cleaning chemicals. These inputs are described below.

$I_1$ *Bath chemicals used.* This includes chemical formulations used for initial bath make-up, bath additions, and bath replacement. Bath formulations and the chemical constituents of those formulations were characterized based on publicly-available bath chemistry data and some proprietary bath chemistry data (see Section 2.1.4 and Appendix B). PWB manufacturers were asked to report the quantity of MHC chemicals they use annually in the IPC Workplace Practices Questionnaire, but because the resulting data were of questionable quality, total chemical usage amounts could not be quantified.

$I_2$ *Copper-clad PWBs.* PWBs or inner layers with non-conductive drilled through-holes that come into the MHC line could add a small amount of copper to the MHC process. Trace amounts of other additives such as arsenic, chromium, and phosphate may also be introduced. This applies to all process alternatives where copper is etched off the boards in the microetch step at the beginning of the MHC process. The amount of copper added from this process is expected to be small, relative to the other chemical inputs. This would be, however, the only expected source of copper for the MHC processes where copper is not otherwise used. This input is not quantified.

$I_3$ *Water.* Water, usually deionized, is typically used in the MHC process for rinse water, bath make-up, and equipment cleaning. The water consumption of different MHC technologies varies according to the number of rinse tanks used in the MHC process. However, the number of rinse tanks can also vary from facility to facility within a technology category due to differences in facility operating procedures and water conservation measures.

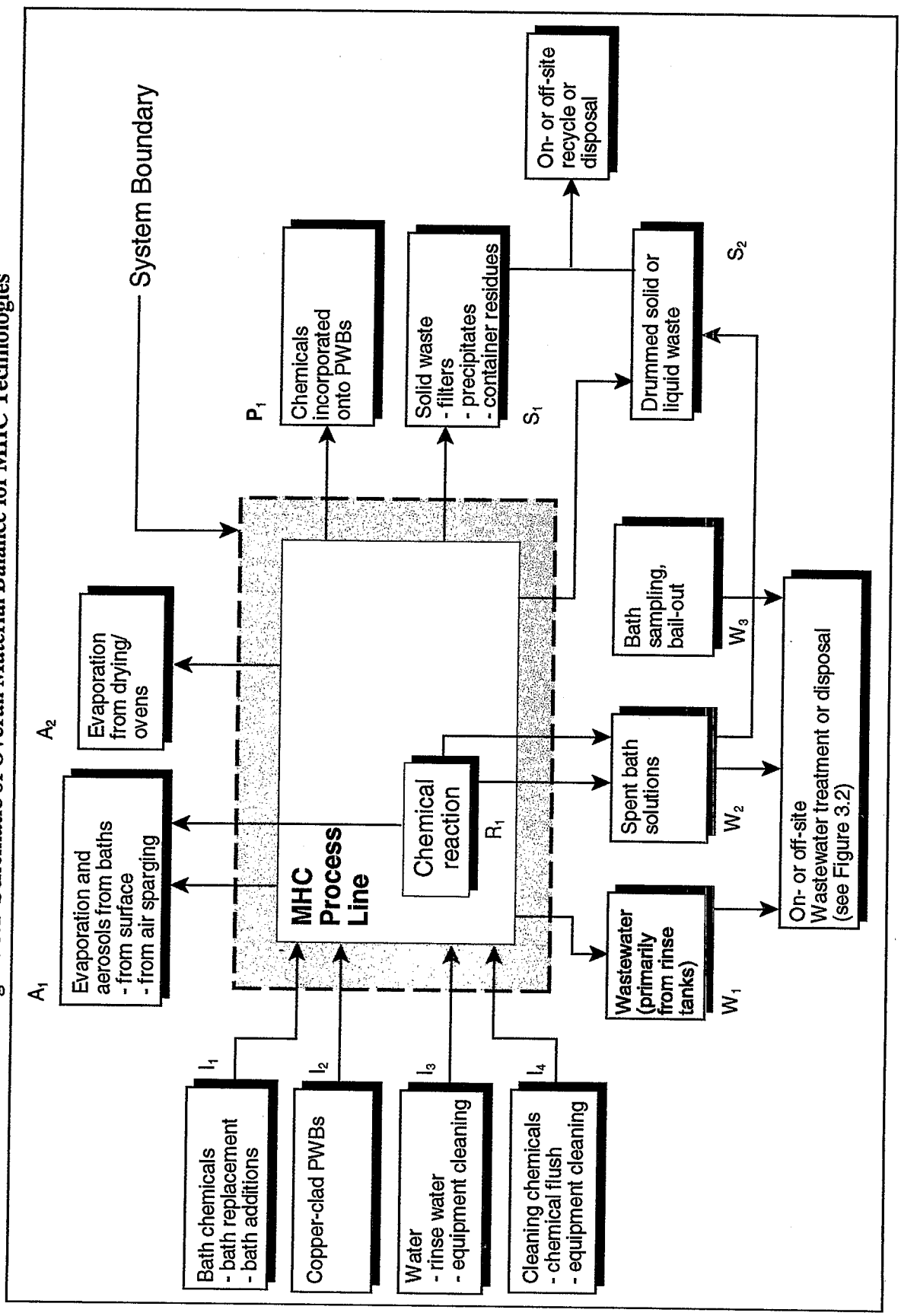
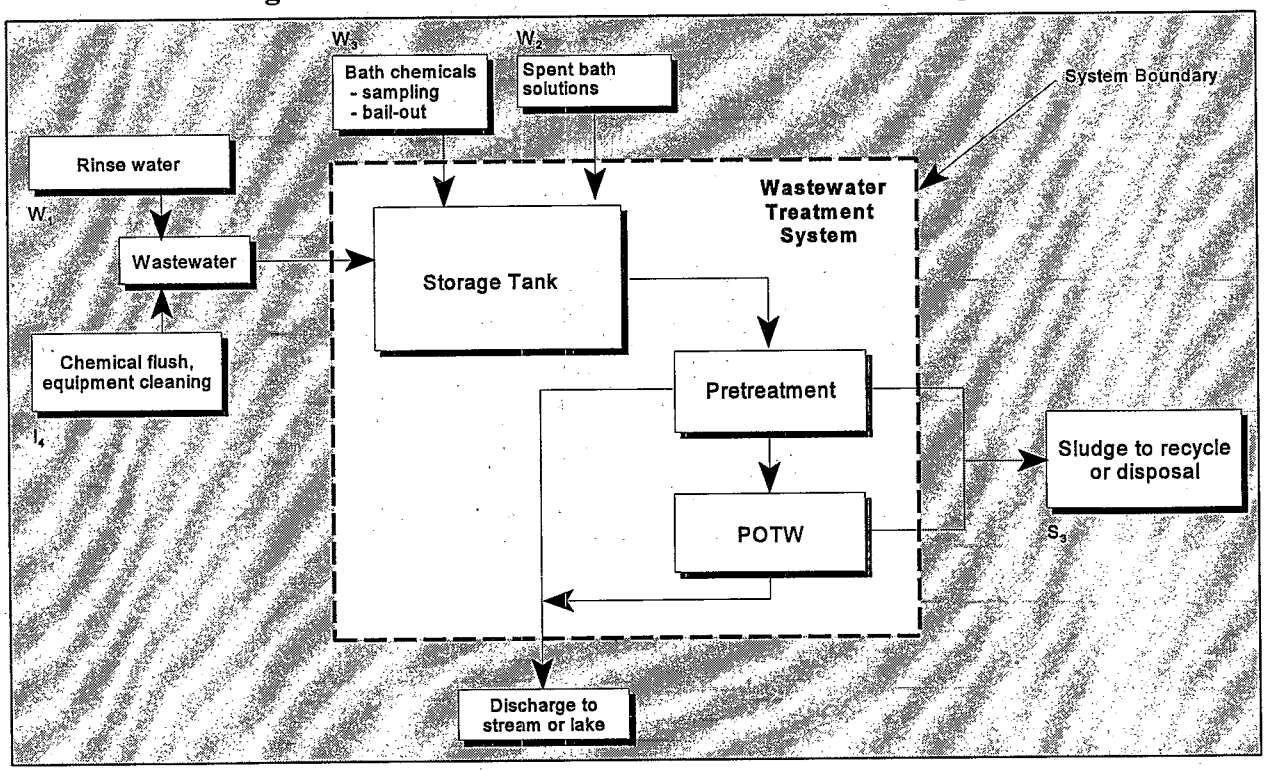



**Figure 3.1 Schematic of Overall Material Balance for MHC Technologies**

**Figure 3.2 Wastewater Treatment Process Flow Diagram**




Water usage data collected in the IPC Workplace Practices Questionnaire includes the annual amount of water used for bath make-up and rinse water. Annual water usage in gallons was normalized by dividing the annual water usage in gallons by annual production in ssf of PWB produced. Both annual and normalized water consumption data are summarized in Table 3.1.

Based on the normalized data, on average the questionnaire respondents with non-conveyorized MHC processes use more than ten times as much water as those with conveyorized processes. Due to the variability in questionnaire data, the relative rate of water consumption of the MHC technologies was estimated using both the questionnaire data and a simulation model of the MHC technologies. This is discussed further in Section 5.1, Resource Conservation.

$I_4$ *Cleaning chemicals.* This includes chemicals used for conveyor equipment cleaning, chemical flush, and other cleaning pertaining to the MHC process line. The amount of cleaning chemicals used is characterized qualitatively based on IPC Workplace Practices Questionnaire data and could include chemicals used to clean conveyor equipment (questionnaire question 3.5) and chemicals used in chemical flush (questionnaire question 4.4). Cleaning chemicals are discussed for specific MHC Technologies in Section 3.1.3.

The total inputs ($I_{tot}$) = $I_1 + I_2 + I_3 + I_4$.

**Table 3.1 Water Usage of MHC Technologies**

| Process Type | No. of Responses | Water Usage ($I_3$) (1,000 gal/year)[a] | Water Usage ($I_3$) (gal/ssf)[a] |
|---|---|---|---|
| **Electroless Copper** | | | |
| Non-conveyorized | 35 | 180 - 16,000 (4,000) | 1.2 - 120 (18) |
| Conveyorized | 1 | 3,300 | 1 |
| **Carbon** | | | |
| Conveyorized | 2 | 330 (330) | 0.28 - 0.29 (0.28) |
| **Conductive Polymer** | | | |
| Conveyorized | 0 | no data | no data |
| **Graphite** | | | |
| Conveyorized | 4 | 561 - 1,200 (914) | 1.2 - 3.4 (2.2) |
| **Non-Formaldehyde Electroless Copper** | | | |
| Non-conveyorized | 1 | 19.5 | 0.36 |
| **Organic-Palladium** | | | |
| Non-conveyorized | 1 | 7,700 | 300 |
| Conveyorized | 1 | 881 | 1.8 |
| **Tin-Palladium** | | | |
| Non-conveyorized | 11 | 300 - 2,900 (1,600) | 0.54 - 19 (7.1) |
| Conveyorized | 2 | 870 - 951 (912) | 0.49 - 0.68 (0.58) |
| **All Processes** | | | |
| Non-conveyorized | 48 | 20 - 16,000 (3,400) | 0.36 - 300 (21) |
| Conveyorized | 10 | 330 - 3,300 (1,000) | 0.28 - 3.4 (1.3) |

[a] Range and average values from IPC Workplace Practices Questionnaire data.

## Outputs

Possible outputs from an MHC process line include PWB products with conductive hole barrels, air emissions, wastewater discharges, and solid wastes.

**Product Outputs.** Product outputs include:

$P_1$ *Chemicals incorporated onto PWBs during the MHC process.* This includes copper or other conductive materials deposited into the hole barrels. This output is not quantified.

**Air Releases.** Chemical emission rates and air concentrations are estimated by air modeling performed in the Exposure Assessment (Section 3.2). The sources of air releases and factors affecting emission rates releases are summarized below.

$A_1$ *Evaporation and aerosol generation from baths.* Potential air releases include volatilization from open surfaces of the baths as well as volatilization and aerosols generated from air sparging. These releases are quantified in the Exposure Assessment (Section 3.2). Gasses formed in chemical reactions, side reactions, and electroplating in

baths could also contribute to air releases, but these are expected to be small compared to volatilization and aerosol losses and are not quantified.

Air releases may be affected by bath temperature, bath mixing methods, and vapor control methods employed. Questionnaire data for bath agitation and vapor control methods are summarized below:[1]

- Most facilities using conveyorized processes use fluid circulation to mix the baths. The only vapor control method reported is enclosure and venting, which is employed for all baths on the conveyorized lines. The process baths are completely enclosed and vented to the outside.
- For facilities using non-conveyorized processes, most use panel agitation and many use fluid circulation. Air sparging is used primarily in electroless copper and microetch baths. (More than one method can be used simultaneously.) Vapor control methods include push-pull for about ½ of the baths, a bath cover for about 1/4 of the baths, with enclosure and other methods reported for a few baths.[2]

Table 3.2 lists average bath surface area, volume, and bath temperature data from the IPC Workplace Practices Questionnaire. Some of this information (both surface area and temperature) is used to model air releases in the Exposure Assessment. Surface areas are calculated from reported bath length and width data. Larger bath surface areas enhance evaporation. Most baths are maintained at elevated temperatures which also enhances chemical evaporation.

$A_2$ *Evaporation from drying/oven.* Air losses due to evaporation from drying steps applies primarily to carbon and graphite processes with air knife/oven steps. Releases are discussed qualitatively in Section 3.1.3.

The total outputs to air ($A_{tot}$) = $A_1 + A_2$.

**Table 3.2 Average Bath Dimensions and Temperatures for All Processes[a]**

| Bath | No. of Responses | Length (in.) | Width (in.) | Surface Area (sq. in.) | Volume (gal.) | Temp (°F) |
|---|---|---|---|---|---|---|
| **Electroless Copper, non-conveyorized** | | | | | | |
| Accelerator | 31 | 41 | 23 | 874 | 123 | 81 |
| Acid Dip | 12 | 38 | 24 | 795 | 105 | 76 |
| Anti-Tarnish | 20 | 43 | 22 | 907 | 109 | 84 |
| Catalyst | 35 | 41 | 23 | 890 | 119 | 98 |
| Conditioner/Cleaner | 35 | 41 | 23 | 882 | 119 | 137 |

[1] From questionnaire question 4.1.

[2] Push-pull ventilation combines a lateral slot hood at one end of the tank with a jet of push air from the opposite end. It is used primarily for large surface area tanks where capture velocities are insufficient to properly exhaust fumes from the tank.

| Bath | No. of Responses | Length (in.) | Width (in.) | Surface Area (sq. in.) | Volume (gal.) | Temp (°F) |
|---|---|---|---|---|---|---|
| Electroless Copper | 35 | 45 | 34 | 1,618 | 229 | 102 |
| Microetch | 35 | 41 | 24 | 937 | 148 | 95 |
| Other | 9 | 41 | 16 | 682 | 116 | 72 |
| Predip | 35 | 40 | 23 | 875 | 117 | 79 |
| **Electroless Copper, conveyorized** | | | | | | |
| Acid Dip | 1 | 29 | 24 | 696 | 185 | 96 |
| Catalyst | 1 | 29 | 24 | 696 | 37 | 116 |
| Conditioner/Cleaner | 1 | 120 | 24 | 2,880 | 80 | 130 |
| Electroless Copper | 1 | 335 | 24 | 8,028 | 185 | 91 |
| Microetch | 1 | 38 | 24 | 912 | 54 | 98 |
| Other | 1 | 59 | 24 | 1,416 | 43 | 101 |
| Predip | 1 | 19 | 24 | 456 | 34 | |
| **Carbon, conveyorized** | | | | | | |
| Anti-Tarnish | 1 | 23 | 44 | 1,012 | 25 | 86 |
| Carbon | 4 | 49 | 44 | 2,156 | 128 | 87 |
| Cleaner | 2 | 44 | 44 | 1,936 | 48 | 129 |
| Conditioner | 2 | 44 | 44 | 1,936 | 47 | 81 |
| Microetch | 2 | 54 | 44 | 2,354 | 100 | 116 |
| **Conductive Polymer, conveyorized** | | | | | | |
| Catalyst | 1 | 48 | 30 | 1440 | 172 | 198 |
| Conditioner/Cleaner | 2 | 22 | 30 | 660 | 82 | 158 |
| Microetch | 1 | 19 | 30 | 570 | 82 | 72 |
| Polymer | 1 | 24 | 30 | 720 | 26 | 41 |
| **Graphite, conveyorized** | | | | | | |
| Anti-Tarnish | 3 | 20 | 26 | 532 | 29 | 75 |
| Conditioner/Cleaner | 4 | 30 | 28 | 833 | 43 | 125 |
| Graphite | 4 | 30 | 28 | 833 | 37 | 82 |
| Microetch | 4 | 34 | 28 | 938 | 55 | 88 |
| **Non-Formaldehyde Electroless Copper, non-conveyorized** | | | | | | |
| Accelerator | 1 | 12 | 32 | 384 | 40 | 124 |
| Catalyst | 1 | 12 | 32 | 384 | 40 | 100 |
| Conditioner/Cleaner | 1 | 12 | 32 | 384 | 40 | 124 |
| Electroless Copper | 1 | 32 | 16 | 512 | 62 | 163 |
| Microetch | 1 | 12 | 32 | 384 | 40 | 103 |
| Predip | 1 | 12 | 32 | 384 | 40 | |
| **Organic-Palladium, non-conveyorized** | | | | | | |
| Acid Dip | 1 | 20 | 63 | 1,260 | 274 | 70 |
| Cleaner | 1 | 18 | 63 | 1,134 | 247 | 122 |
| Conditioner | 1 | 20 | 63 | 1,260 | 274 | 105 |
| Conductor | 1 | 15 | 63 | 945 | 206 | 113 |

| Bath | No. of Responses | Length (in.) | Width (in.) | Surface Area (sq. in.) | Volume (gal.) | Temp (°F) |
|---|---|---|---|---|---|---|
| Microetch | 1 | 15 | 63 | 945 | 206 | 78 |
| Other | 1 | 12 | 63 | 756 | 157 | |
| Post Dip | 1 | 15 | 63 | 945 | 206 | 74 |
| **Organic-Palladium, conveyorized** | | | | | | |
| Acid Dip | 1 | 12 | 49 | 588 | 24 | 79 |
| Cleaner | 1 | 24 | 49 | 1,176 | 37 | 120 |
| Conditioner | 1 | 60 | 49 | 2,940 | 74 | 100 |
| Conductor | 1 | 98 | 49 | 4,802 | 108 | 115 |
| Microetch | 1 | 25 | 49 | 1,225 | 37 | 75 |
| Other | 1 | 24 | 49 | 1,176 | 48 | 81 |
| Post Dip | 1 | 26 | 49 | 1,274 | 45 | 77 |
| **Tin-Palladium, non-conveyorized** | | | | | | |
| Accelerator | 10 | 35 | 17[a] | 580 | 67 | 134 |
| Acid Dip | 4 | 29 | 19 | 532 | 59 | 76 |
| Anti-Tarnish | 3 | 34 | 10 | 344 | 51 | 73 |
| Catalyst | 11 | 31 | 16 | 515 | 56 | 111 |
| Conditioner/Cleaner | 11 | 34 | 18 | 576 | 65 | 164 |
| Microetch | 9 | 30 | 17 | 520 | 64 | 76 |
| Other | 4 | 31 | 18 | 593 | 61 | 74 |
| Predip | 11 | 31 | 16 | 497 | 53 | 75 |
| **Tin-Palladium, conveyorized** | | | | | | |
| Accelerator | 2 | 40 | 33 | 1,341 | 80 | 103 |
| Acid Dip | 2 | 24 | 33 | 780 | 53 | 94 |
| Anti-Tarnish | 1 | 30 | 30 | 900 | 80 | 71 |
| Catalyst | 2 | 86 | 33 | 2,742 | 173 | 117 |
| Conditioner/Cleaner | 2 | 45 | 33 | 1,410 | 98 | 114 |
| Microetch | 2 | 25 | 33 | 810 | 58 | 92 |
| Other | 1 | 30 | 30 | 900 | 80 | 75 |
| Predip | 2 | 24 | 33 | 780 | 58 | 81 |

[a] Based on IPC Workplace Practices Questionnaire data.

**Water Releases.** Potential outputs to water include chemical-contaminated wastewater from rinse tanks, spent bath solutions, and liquid discharges from bath sampling and bail-out. Chemical-contaminated rinse water is the largest source of wastewater from most MHC process lines and primarily results from drag-out or drag-in. Drag-out or drag-in is the transfer of chemicals from one bath to the next by dragging bath solution on a PWB out of one bath and into the subsequent bath. Drag-in or drag-out losses are estimated to be approximately 95 percent of uncontrolled bath losses (i.e., losses other than from bath replacement, bail-out, and sampling) (Bayes, 1996). The quantity of chemicals lost can be reduced through operational practices such as increased drip time (see Section 6.1, Pollution Prevention). Potential water releases are discussed further below.

$W_1$ *Wastewater.* MHC line wastewater primarily consists of chemical-contaminated water from rinse tanks used to rinse residual chemistry off PWBs between process steps. Water usage and wastewater composition were addressed by several questions in the IPC Workplace Practices Questionnaire, with resulting data of variable to poor quality. Because the volume of rinse water used in MHC processes is much greater than water used in all other applications, the quantity of wastewater generated is assumed to be equal to water usage ($I_3$). The previous discussion of water usage data also applies to wastewater amounts.

$W_2$ *Spent bath solution.* Bath concentrations vary over time (as the bath ages) and as PWBs are processed through the baths. Spent bath solutions are chemical bath solutions that have become too contaminated or depleted to properly perform a desired function. Spent bath solutions are removed from a process bath when a chemical bath is replaced.

As noted above, bath formulations and chemical constituents of those formulations were characterized based on publicly-available bath chemistry data and some proprietary bath chemistry data (see Section 2.1.4 and Appendix B). For the purposes of this assessment, chemical concentrations within the spent baths were assumed to be the same as bath make-up concentrations. The amount of spent bath disposed was addressed in the IPC Workplace Practices Questionnaire question 4.3, Chemical Bath Replacement, but many respondents did not have this information. Therefore, total chemical disposal amounts have not been quantified. Table 3.3 presents a summary of spent bath treatment methods reported in the questionnaire by MHC technology.

$W_3$ *Bath sampling and bail-out.* This includes bath solutions disposed of after sampling and analysis and bath bail-out (sometimes done prior to bath additions). In some cases sampling may be performed at the same time as bail-out if the process bath is on a controller.

Routine bail-out activities could result in a large amount of bath disposal. Because this activity was not included in the IPC Workplace Practices Questionnaire there is only limited information on frequency or amount of bail-out expected. Chemical loss due to bath sampling was assumed to be negligible.

The total outputs to water (Wtot) = $W_1 + W_2 + W_3$.

**Wastewater Treatment.** Figure 3.2 showed the overall water and wastewater treatment flows, including chemical bath solutions and wastewater inputs to treatment, any pre-treatment or treatment performed on-site or off-site, sludge generated from either on-site or off-site treatment, and final effluent discharge to surface water. PWB manufacturers typically combine wastewater effluent from other PWB manufacturing processes prior to on-site wastewater pretreatment. The pretreated wastewater is then discharged to a POTW.

## Table 3.3 Spent Bath Treatment and Disposal Methods

| Process Alternative | Total No. of Baths | Precipitation Pretreatment[a] | pH Neutralization[a] | Disposed to Sewer[a] | Drummed[a] | Recycled On-Site[a] | Other On-Site Treatment[a] | Sent to Recycle[a] | Discharged to POTW[a] | Other Off-Site Treatment[a] |
|---|---|---|---|---|---|---|---|---|---|---|
| Electroless Copper, non-conveyorized | 240 | 123 | 87 | 3 | 16 | 11 | 11 | 22 | 29 | 27 |
| Electroless Copper, conveyorized | 7 | 7 | 0 | 0 | 0 | 7 | 0 | 0 | 0 | 0 |
| Carbon, conveyorized | 10 | 7 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Conductive Polymer, conveyorized | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Graphite, conveyorized | 13 | 4 | 8 | 0 | 2 | 0 | 1 | 0 | 4 | 0 |
| Non-Formaldehyde Electroless Copper, non-conveyorized | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Organic-Palladium, non-conveyorized | 7 | 0 | 7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Organic-Palladium, conveyorized | 7 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Tin-Palladium, non-conveyorized | 64 | 52 | 56 | 0 | 6 | 0 | 1 | 0 | 6 | 11 |
| Tin-Palladium, conveyorized | 14 | 4 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

[a] Number of affirmative responses for any bath from the IPC Workplace Practices Questionnaire, for all facilities using a technology category.

Table 3.4 summarizes treatment and discharge methods and copper concentrations in PWB plant discharges reported in *Pollution Prevention and Control: Analysis of Survey Results* (EPA, 1995a). The primary purpose of most PWB manufacturer's wastewater treatment systems is the removal of dissolved metals. This is accomplished with conventional metals precipitation systems (a series of unit operations using hydroxide precipitation followed by separation of the precipitated metals), ion exchange-based metals removal systems, and combined precipitation/ion exchange systems. The most common type is conventional metals precipitation, which includes precipitation units followed by either clarifiers or membrane filters for solids separation. The use of clarifiers is the predominant method for separation of precipitated solids from the wastewater. Wastewater treatment systems are discussed further in Section 6.2, Recycle, Recovery, and Control Technologies Assessment.

**Table 3.4 Treatment and Discharge Methods and Copper Concentration Summarized from Pollution Prevention and Control Survey**

| Respondent Identification No. By MHC Technology | Copper Discharge Limitations | | Wastewater Copper Concentration (mg/l) | Discharge | Type of Wastewater Treatment |
|---|---|---|---|---|---|
| | Max (mg/l) | Avg (mg/l) | | | |
| **Electroless Copper** | | | | | |
| 31838 | 3 | 1.5 | NR | indirect | |
| 36930 | 4.34 | 2.6 | NR | indirect | |
| 44486 | 4.5 | 2.7 | NR | indirect | precipitation |
| 955703 | 3 | 2.07 | 0.4 | indirect | electrowinning/ion exchange |
| 36930 | 2.59 | 1.59 | 1 | indirect | ion exchange |
| 237900 | 2.7 | 1 | 1.2 | indirect | precipitation/clarifier |
| 502100 | 1 | 1.5 | 2 | indirect | |
| 358000 | 2 | 1.5 | 2 | indirect | ion exchange |
| 959951 | 3.22 | 0.45 | 5 | indirect | |
| t3 | 2.7 | 2.7 | 5 | indirect | precipitation/membrane |
| 44657 | 3 | 2.07 | 7 | indirect | precipitation/clarifier |
| 55595 | NR | NR | 10 | direct | precipitation/filter press |
| 3023 | 1.5 | none | 12.5 | indirect | ion exchange, precipitation/ membrane, resist strip |
| 42692 | 4.5 | 2.7 | 17.5 | direct | ion exchange |
| 6710 | 4.5 | 0.37 | 20 | indirect | precipitation/clarifier |
| 41739 | 4 | 0.4 | 25 | direct | precipitation/membrane |
| 955099 | 1.5 | none | 30 | indirect | precipitation/clarifier |
| t2 | 2.2 | 2.07 | 30 | indirect | precipitation/clarifier, sludge dryer, air scrubber |
| 947745 | 3.38 | 2.07 | 30 | indirect | precipitation/clarifier |
| 42751 | 3 | 2.07 | 33 | indirect | precipitation/clarifier, polishing filter, filter press |

| Respondent Identification No. By MHC Technology | Copper Discharge Limitations | | Wastewater Copper Concentration (mg/l) | Discharge | Type of Wastewater Treatment |
|---|---|---|---|---|---|
| | Max (mg/l) | Avg (mg/l) | | | |
| t1 | 1 | 0.03 | 35 | direct | precipitation/clarifier, sludge dryer, chemical tester |
| 946587 | 3.4 | none | 40 | indirect | precipitation/clarifier |
| 25503 | 3 | 2.07 | 40 | indirect | ion exchange |
| 965874 | 3.38 | 2.07 | 40 | indirect | ion exchange/electrowinning |
| 273701 | 3.38 | 2.07 | 50 | indirect | ion exchange, electrowinning |
| 953880 | 0.25 | none | 57 | indirect | |
| 133000 | 1.5 | none | 60 | indirect | precipitation/clarifier, sludge dryer |
| 32482 | 3.38 | 2.07 | 65 | indirect | precipitation/clarifier |
| 107300 | 2 | 1 | 80 | direct | precipitation/clarifier, sludge dryer, equalization |
| 33089 | 3.38 | 2.07 | 300 | indirect | precip/clarifier, filter press |
| 3470 | 1.5 | 2.07 | | indirect | ion exchange |
| **Graphite** | | | | | |
| 43841 | 4.3 | 2.6 | 200 | indirect | precipitation/filtration, filter press, equalization, etc. |
| **Palladium** | | | | | |
| 279 | 3 | 2.02 | NR | direct | |
| 37817[a] | 4.5 | 3.5 | 3 | indirect | ion exchange, electrowinning |
| 29710 | 0.49 | 0.41 | 4 | direct | ion exchange |
| 43694 | 3 | 2.07 | 30 | indirect | ion exchange |
| | | | | | |
| Average | 2.75 | 1.50 | 35.70 | | |
| Median | 3 | 2.07 | 30 | | |
| Max | 4.50 | 3.50 | 300.00 | | |
| Min | 0.25 | 0.03 | 0.2 | | |
| Standard Deviation | 1.20 | 0.97 | 57.54 | | |

[a] Respondent 37817 reported Cu max = 5.0 mg/l; assumed 4.5 mg/l in compliance with Federal regulations.
NR: Not Reported.
Source: EPA, 1995a.

Following any in-house wastewater treatment, facilities release wastewater either directly to surface water or indirectly to a POTW. Sludge from on-site wastewater treatment is discussed in the section below (Solid Waste). The data for discharge type (direct or indirect) are discussed for specific processes in Section 3.1.3.

Permit data for releases were not collected; this was deleted from the questionnaire upon request by industry participants. However, PWB manufacturers who responded to the IPC

Workplace Practices Questionnaire were asked to provide the maximum and average metals concentrations (e.g., copper, palladium, tin) in wastewater from their MHC line (questionnaire question 2.3, Wastewater Characterization). Several respondents indicated the question could not be answered, did not respond to this question, or listed their POTW permit discharge limits. This is because there are many sources of metals, especially copper, in PWB manufacturing. PWB manufacturers typically combine effluents from different process steps prior to wastewater treatment. Thus, the chemical constituents and concentration in wastewater could not be characterized.

**Solid Waste.** Solid wastes are generated by day-to-day MHC line operation and by wastewater treatment of MHC line effluents. Some of these solid wastes are recycled, while others are sent to incineration or land disposal. Solid waste outputs include:

$S_1$ *Solid waste.* Solid wastes could include spent bath filters, chemical precipitates (e.g., $CuSO_4$ crystals from etch bath), packaging or chemical container residues, and other solid waste from the process line, such as off-specification PWBs. Chemical baths are typically replaced before precipitation occurs. However, if precipitation does occur, some precipitates, such as copper sulfate crystals, may be recycled. Container residue is estimated by EPA to be up to four percent of the chemicals use volume (Froiman, 1996). An industry reviewer indicated this estimate would only occur with very poor housekeeping practices and is not representative of the PWB industry (Di Margo, 1996). The questionnaire data did not include chemical characterization of solid wastes.

$S_2$ *Drummed solid or liquid waste.* This includes other liquid or solid wastes that are drummed for on-site or off-site recycling or disposal. Some spent baths and wastes can be recycled or recharged, such as etchant. No data were available to characterize these wastes.

$S_3$ *Sludge from on-site wastewater treatment.* Questionnaire respondents were asked to report the amount of sludge they generated during on-site wastewater treatment that could be attributed to MHC line effluents (questionnaire question 2.4, Wastewater Discharge and Sludge Data). Both annual quantities and data normalized to pounds of sludge per ssf of PWB produced are presented in Table 3.5. However, many PWB manufacturers have indicated that the amount of sludge from the MHC process cannot be reliably estimated since effluents from various PWB manufacturing process steps are combined prior to wastewater treatment. In addition, the amount of sludge generated during wastewater treatment varies according to the MHC technology used, the treatment method used, facility operating procedures, the efficiency with which bath chemicals and rinse water are used, and other factors. Thus, the comparative amount of sludge generated due to the choice of an MHC technology could not be determined, nor were data available to characterize the concentrations of metals contributed by the MHC line.

The total solid waste output ($S_{tot}$) = $S_1 + S_2 + S_3$.

**Table 3.5 Sludge Generation from Wastewater Treatment of MHC Line Effluents**

| Process Type | No. of Responses | Sludge ($S_4$) (lbs/year)[a] | Sludge ($S_4$) (lbs/1,000 ssf)[a] |
|---|---|---|---|
| **Electroless Copper** | | | |
| Non-conveyorized | 35 | 600 - 100,000 (25,000) | 2 - 530 (96) |
| Conveyorized | 1 | 1,000 | 0.31 |
| **Carbon** | | | |
| Conveyorized | 2 | no data | no data |
| **Conductive Polymer** | | | |
| Conveyorized | 0 | no data | no data |
| **Graphite** | | | |
| Conveyorized | 4 | 5.5 - 920 (380) | 0.01 - 5.6 (2.2) |
| **Non-Formaldehyde Electroless Copper** | | | |
| Non-conveyorized | 1 | 200 | 3.7 |
| **Organic-Palladium** | | | |
| Non-conveyorized | 1 | 5,000 | 190 |
| Conveyorized | 1 | 21,600 | 45 |
| **Tin-Palladium** | | | |
| Non-conveyorized | 11 | 200 - 24,000 (6,700) | 1.3 - 94 (27) |
| Conveyorized | 2 | 17,000 | 9.5 |
| **All Processes** | | | |
| Non-conveyorized | 48 | 200 - 100,000 19,500) | 1.3 - 530 (79) |
| Conveyorized | 10 | 5.5 - 21,600 (6,800) | 0.01 - 45 (10) |

[a] Range and average values for each from questionnaire data.

**Transformations.** Transformations within the MHC system boundary could include:

$R_1$ *Chemical reaction gains or losses.* This includes any chemical species consumed, transformed, or produced in chemical reactions and side reactions occurring in the process baths. Reactions and side reactions within the baths could result in either chemical losses or production of new chemicals as degradation products. One important set of reactions involve formaldehyde in the electroless copper process. Formaldehyde, which is utilized as a reducing agent, is converted to formic acid. In a secondary or side reaction formaldehyde also breaks down into methanol and the formate ion. This reaction is the only source of formate ion in the electroless copper bath. Other side reaction products include BCME (bis-chloromethyl ether) which is produced in a reaction between hydrochloric acid and formaldehyde (Di Margo, 1996).

The overall material balance: $I_{tot} = A_{tot} + W_{tot} + S_{tot} + P_1 \pm R_1$.

### 3.1.3 Source and Release Information For Specific MHC Technology Categories

This section describes the specific inputs and outputs in the material balance for each MHC technology. To facilitate comparison among process alternatives, and to adjust for the wide variations in the data due to differing sizes of PWB facilities, data are presented both as reported in the IPC Workplace Practices Questionnaire, and normalized by production amounts (annual ssf of PWB produced). Average values from the IPC Workplace Practices Questionnaire database are reported here for summary purposes.

**Electroless Copper Process**

Figure 3.3 illustrates the generic electroless copper process steps and typical bath sequence evaluated in the CTSA. The process baths depicted in Figure 3.3 represent an integration of the various products offered within the electroless copper technology category. The number and location of rinse steps shown in the figure are based on the IPC Workplace Practices Questionnaire data. Figure 3.3 lists the types and sequence of baths in a generic electroless copper line, but the types and sequence of baths in an actual line could vary.

**Water Usage ($I_3$) and Wastewater ($W_1$).** Water usage data from the IPC Workplace Practices Questionnaire were presented in Table 3.1; the amount of wastewater generated is assumed equal to the amount of water used. Of respondents using an electroless copper process, 11 discharge wastewater directly to a stream or river following the appropriate treatment while 20 facilities use indirect discharge (e.g., to a POTW). (Five facilities did not respond to the question.) While several facilities using electroless copper completed the questionnaire, only a single facility used the conveyorized process. This large facility produces over three million ssf of PWB per year. In summary:

- Reported water usage for the facility using a conveyorized electroless copper process is 3.3 million gallons per year, or about one gallon per ssf of PWB produced.
- Reported water usage for the facilities using non-conveyorized processes average 4.0 million gallons per year, or 18 gallons per ssf of PWB produced.

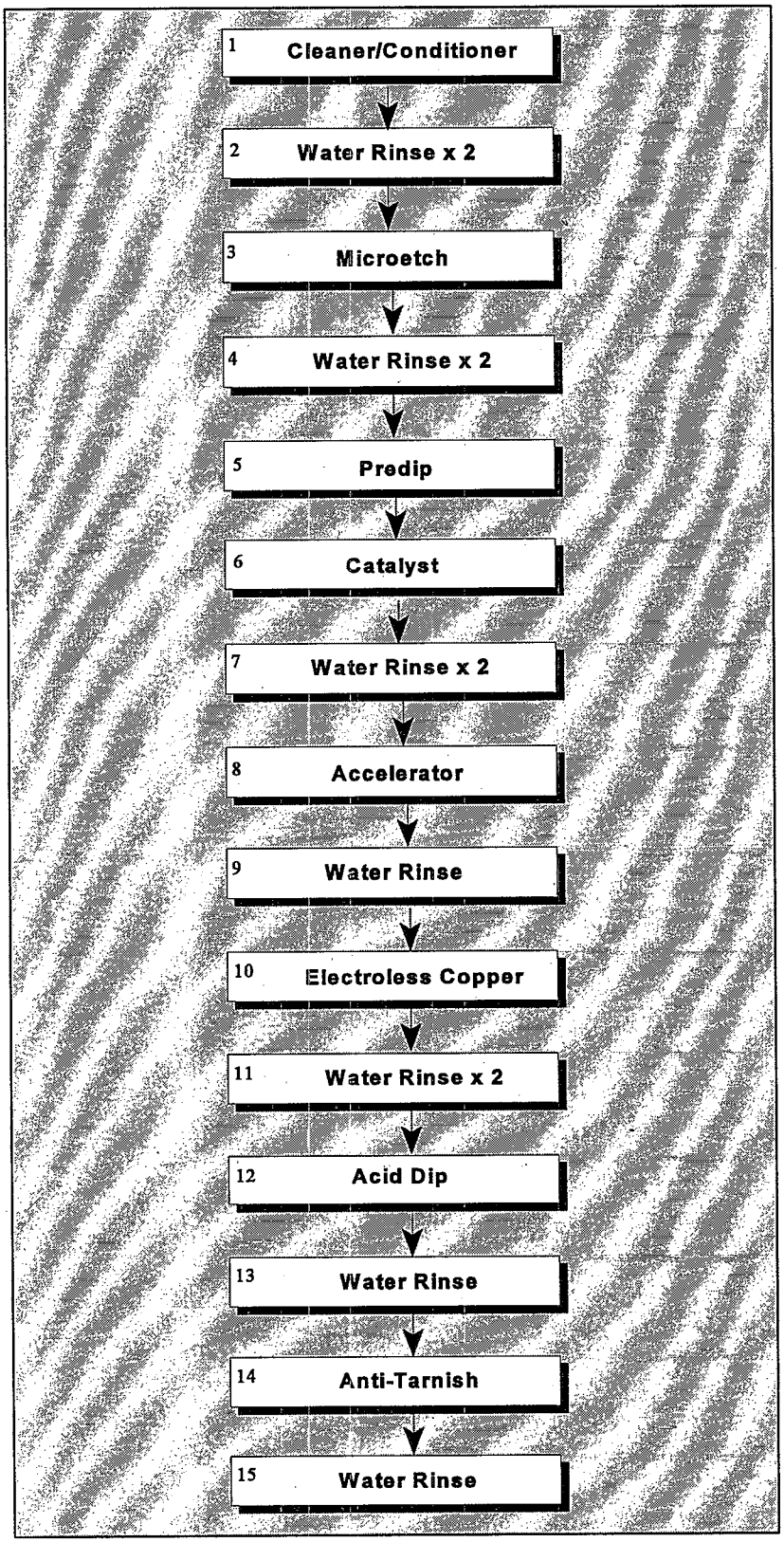
Chemical constituents and concentrations in wastewater could not be adequately characterized.

**Cleaning Chemicals ($I_4$).** Chemicals used for cleaning of electroless copper equipment, as reported in the IPC Workplace Practices Questionnaire, include water, sodium persulfate, sulfuric acid, hydrogen peroxide, nitric acid, and "211 solvent."

**Bath Chemicals Used ($I_1$).** Appendix B presents estimated bath chemical concentrations for the electroless copper process. The amount of bath chemicals used could not be quantified from questionnaire data.

**Spent Bath Solutions ($W_2$).** The quantity of spent bath solution could not be determined from the data. Spent bath treatment methods were presented in Table 3.3. Precipitation pretreatment and on-site recycling are reported treatment methods for the conveyorized electroless copper process; precipitation pretreatment and pH neutralization were most commonly reported as methods for the non-conveyorized electroless copper process.

**Figure 3.3 Generic Electroless Copper Process Steps and Typical Bath Sequence**



**Evaporation From Baths ($A_1$).** Air releases are modeled in the Exposure Assessment (Section 3.2). To summarize questionnaire data:

- For the single conveyorized electroless copper process, fluid circulation is used in all but the microetch bath. Enclosure is used for vapor control for all baths.
- For non-conveyorized electroless copper facilities, panel agitation is used in most baths, fluid circulation in about 1/3 of the baths, air sparging is primarily used in electroless copper and a few microetch baths, and a few baths use other mixing methods. Vapor control methods include push-pull for about ½ of the baths, a bath cover for about 1/4 of the baths, with enclosure and other methods reported for a few of the baths.
- Table 3.2 lists bath surface area, volume, and bath temperature data from the IPC Workplace Practices Questionnaire.

**Evaporation From Drying/Oven ($A_2$).** This source of air emissions does not apply to electroless copper processes since oven drying is not required and air drying immediately follows water rinsing.

**Chemicals Incorporated Onto PWBs ($P_1$).** Copper is added to the boards in the electroless copper process. Small quantities of palladium from the catalyst are also deposited on the PWBs.

**Drummed Solid or Liquid Waste ($S_2$).** This was reported as a spent bath treatment method for either solution or sludge for 16 out of 240 baths by the non-conveyorized electroless copper facilities (see Table 3.3). The total quantity of drummed waste was not reported.

**Sludge Amounts From On-Site Treatment ($S_3$).** Sludge generation data are presented in Table 3.5. In general:

- Reported sludge amounts for the facility using a conveyorized process are 1,000 lbs/year, or 0.31 lbs per 1,000 ssf of PWB produced.
- Reported sludge amounts for the facilities using non-conveyorized processes average 25,000 lbs/year, or 96 lbs per 1,000 ssf of PWB produced.

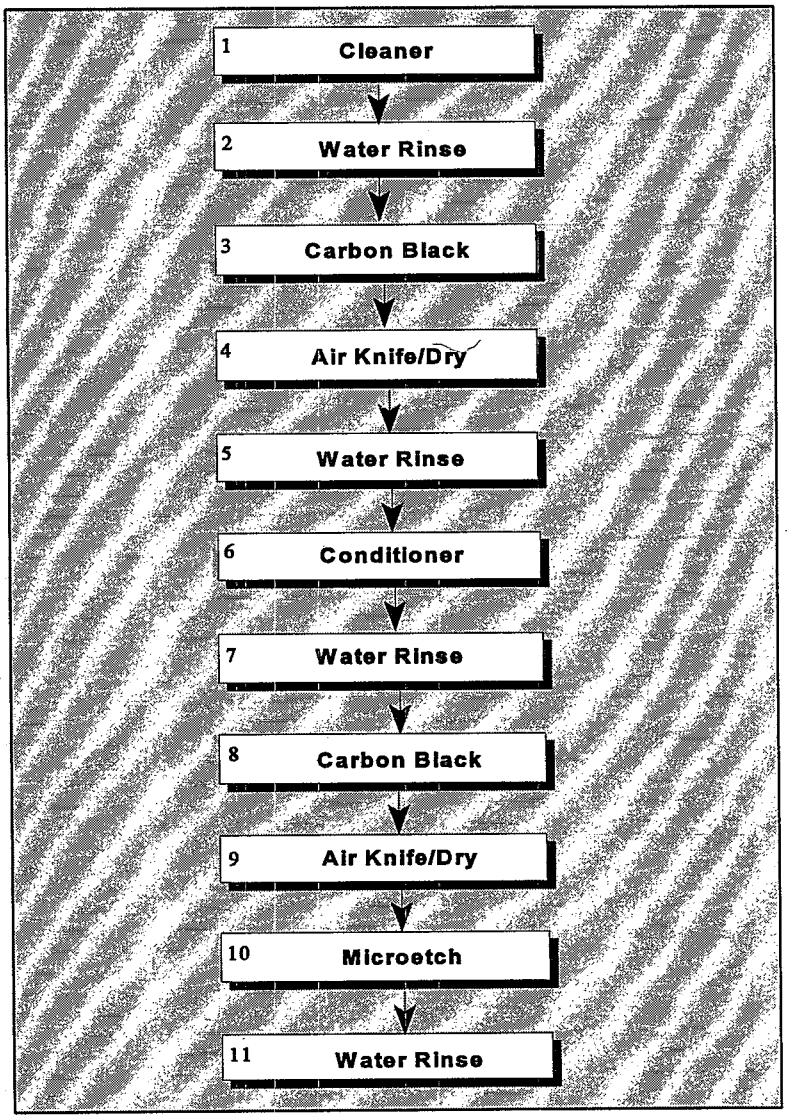
Metal concentrations in sludge could not be adequately characterized.

**Chemical Reaction Gains or Losses ($R_1$).** The most well-documented chemical reactions in electroless copper baths involve formaldehyde. Formaldehyde is used as a copper reducing agent, and in this reaction formaldehyde is converted to formic acid and hydrogen gas. In a secondary (unwanted) reaction called the Cannizzaro reaction, formaldehyde breaks down to methanol and the formate ion which in a caustic solution forms sodium formate. A study by Merix Corporation found that for every one mole of formaldehyde reacting in the intended copper deposition process, approximately one mole was reacting with hydroxide in the Cannizzaro reaction. Other studies have found that the side reaction tendency goes up with the alkalinity of the process bath (Williamson, 1996). A search of literature references failed to produce sufficient quantifiable data to characterize these reactions.

## Carbon Process

Figure 3.4 illustrates the carbon process steps and bath sequence evaluated in the CTSA. The number and location of rinse steps shown in the figure are based on IPC Workplace Practices Questionnaire data. Thus, Figure 3.4 lists the types and sequence of baths in a generic carbon line, but the types and sequence of baths in an actual line could vary. Both carbon facilities in the IPC Workplace Practices Questionnaire database use conveyorized equipment.

**Figure 3.4 Generic Carbon Process Steps and Typical Bath Sequence**




**Water Usage ($I_3$) and Wastewater ($W_1$).** Water usage data were summarized in Table 3.1; wastewater generation is assumed equal to water usage. Reported water usage for the two facilities is 330,000 gallons per year, or 0.28 gallon per ssf of PWB produced. Both carbon facilities use indirect discharge of wastewater. Chemical constituents and concentrations in wastewater could not be adequately characterized.

**Cleaning Chemicals ($I_4$).** Only water is used for equipment cleaning, as reported in the IPC Workplace Practices Questionnaire.

**Bath Chemicals Used ($I_1$).** Appendix B presents estimated bath chemical concentrations for the carbon process. The amount of bath chemicals used could not be quantified from the data.

**Spent Bath Solutions ($W_2$).** The quantity of spent bath solution could not be determined from available data. Spent bath treatment methods were presented in Table 3.3. Precipitation pretreatment and pH neutralization are reported methods for carbon processes.

**Evaporation From Baths ($A_1$).** Air releases are modeled in the Exposure Assessment (Section 3.2). For both facilities using conveyorized carbon, fluid circulation is used for bath agitation and enclosure is used for vapor control for all baths. Table 3.2 lists bath surface area, volume, and bath temperature data.

**Evaporation From Drying/Oven ($A_2$).** Air knife/oven drying occurs after the carbon black and fixer steps. Any solution adhering to the boards would be either blown off the boards and returned to the sump, or volatilized in the oven. Air emissions from air knife/oven drying were not modeled.

**Chemicals Incorporated Onto PWBs ($P_1$).** Carbon black is added to the boards in this process.

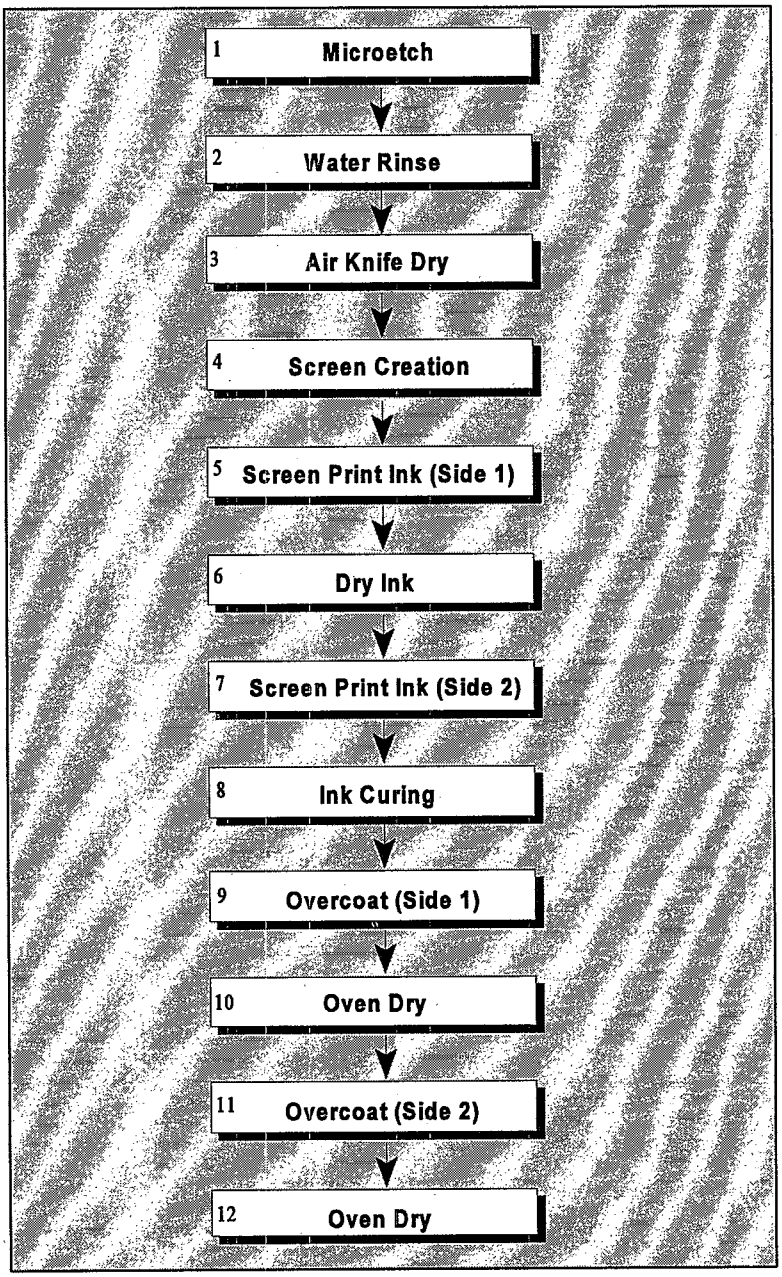
**Drummed Solid or Liquid Waste ($S_2$).** This was not reported as a spent bath treatment method for carbon processes (see Table 3.3).

**Sludge Amounts From On-Site Treatment ($S_3$).** Sludge data were not reported for the carbon processes.

Conductive Ink Process

A generic conductive ink sequence is shown in Figure 3.5. Source release data for conductive ink are not available since there are no facilities currently using the process for the production of multi-layer PWBs.

**Figure 3.5 Generic Conductive Ink Process Steps**

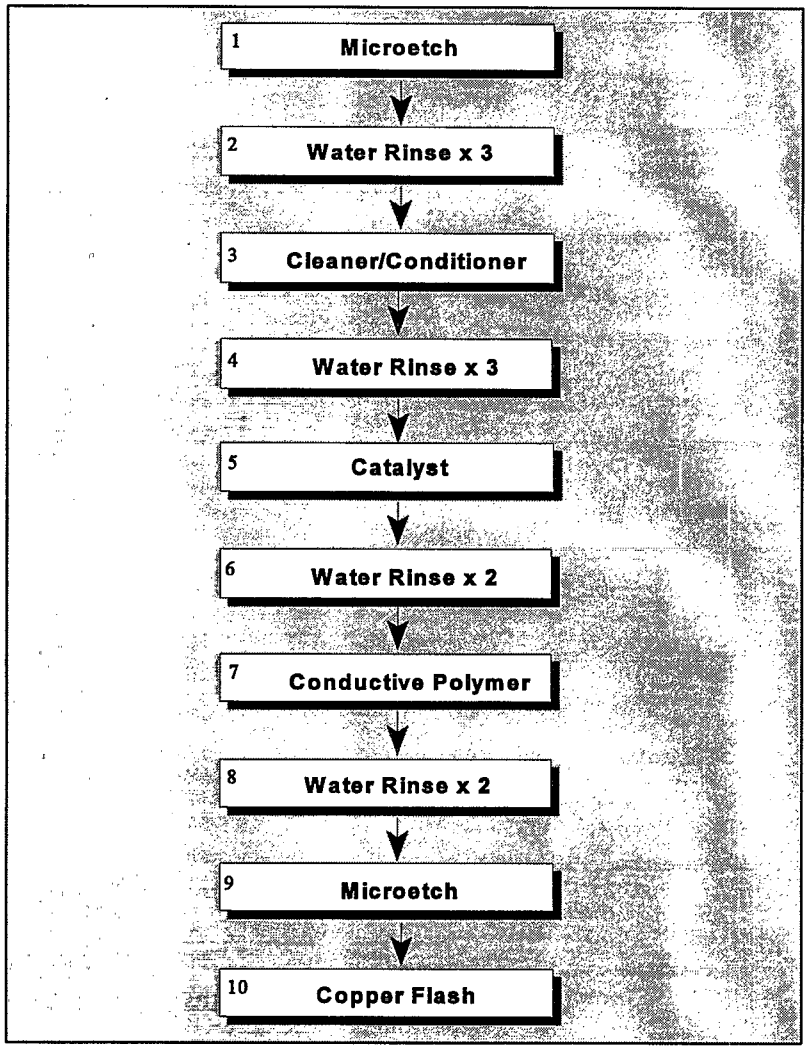



## Conductive Polymer Process

Figure 3.6 illustrates the generic conductive polymer process steps and typical bath sequence evaluated in the CTSA. The number and location of rinse steps shown in the figure are based on IPC Workplace Practices Questionnaire data. Thus, Figure 3.6 lists the types and sequence of baths in a generic conductive polymer line, but the types and sequence of baths in an actual line could vary. The single conductive polymer facility in the IPC Workplace Practices Questionnaire data uses conveyorized equipment.

**Water Usage ($I_3$) and Wastewater ($W_1$).** The single facility using a conductive polymer process uses indirect discharge of wastewater.

**Figure 3.6 Generic Conductive Polymer Process Steps and Typical Bath Sequence**




**Cleaning Chemicals ($I_4$).** Only water is used for equipment cleaning, as reported in the IPC Workplace Practices Questionnaire data.

**Bath Chemicals Used ($I_1$).** Appendix B presents estimated bath chemical concentrations for the conductive polymer process. The amount of bath chemicals used could not be quantified from the data.

**Spent Bath Solutions ($W_2$).** The quantity of spent bath solution could not be determined from the data. Spent bath treatment methods are presented in Table 3.3. pH neutralization is reported as a treatment method for the conductive polymer process.

**Evaporation From Baths ($A_1$).** Air releases are modeled in the Exposure Assessment (Section 3.2). The facility using a conveyorized conductive polymer process reported using fluid circulation for all baths and enclosure for vapor control for all baths. Table 3.2 shows bath surface area, volume, and bath temperature data.

**Evaporation From Drying/Oven ($A_2$).** This source of air emissions does not apply to the conductive polymer process since oven drying is not required and air drying immediately follows water rinsing.

**Chemicals Incorporated Onto PWBs ($P_1$).** A polymer is added to the boards in this process.

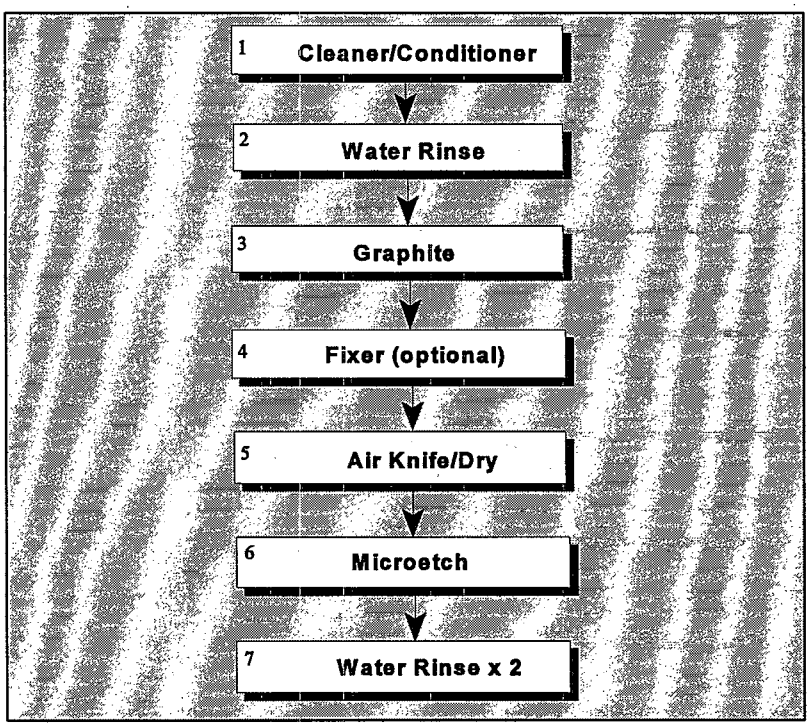
**Drummed Solid or Liquid Waste ($S_2$).** This was not reported as a spent bath treatment method for the conductive polymer process (see Table 3.3).

**Sludge Amounts From On-Site Treatment ($S_3$).** Sludge amounts were not reported for this process.

## Graphite Process

Figure 3.7 illustrates the generic graphite process steps and typical bath sequence evaluated in the CTSA. The process baths depicted in Figure 3.7 represent an integration of the various products offered within the graphite technology category. The number and location of rinse steps shown in the figure are based on the IPC Workplace Practices Questionnaire data. Thus, Figure 3.7 lists the types and sequence of baths in a generic graphite line, but the types and sequence of baths in an actual line could vary. The four facilities in the IPC Workplace Practices Questionnaire database use conveyorized equipment.

**Figure 3.7 Generic Graphite Process Steps and Typical Bath Sequence**



**Water Usage ($I_3$) and Wastewater ($W_1$).** Water usage data are presented in Table 3.1. For graphite, two facilities use direct and two facilities use indirect discharge. Reported water usage for the facilities using a conveyorized process averages 914,000 gallons per year, or 2.2 gallons per ssf of PWB produced.

**Cleaning Chemicals ($I_4$).** Chemicals used for equipment cleaning, as reported in the IPC Workplace Practices Questionnaire, include water and ammonia.

**Bath Chemicals Used ($I_1$).** Appendix B presents estimated bath chemical concentrations for the graphite process. The amount of chemicals used could not be determined from the data.

**Spent Bath Solutions ($W_2$).** Spent bath treatment methods are presented in Table 3.3. Precipitation pretreatment, pH neutralization, and discharge to a POTW are reported methods for the graphite process.

**Evaporation From Baths ($A_1$).** Air releases are modeled in the Exposure Assessment (Section 3.2). To summarize Workplace Practices data:

- For facilities using a conveyorized graphite process, fluid circulation is used in most baths. Enclosure for vapor control is employed for all of the baths.
- Table 3.2 lists bath surface area, volume, and bath temperature data from the IPC Workplace Practices Questionnaire.

**Evaporation From Drying/Oven ($A_2$).** Air knife/oven drying occurs after the graphite and fixer steps. Any solution adhering to the boards would be either blown off the boards and returned to the sump, or volatilized in the oven. Air emissions from air knife/oven drying were not modeled.

**Chemicals Incorporated Onto PWBs ($P_1$).** Graphite is added to the boards in this process.

**Drummed Solid or Liquid Waste ($S_2$).** This was reported as a spent bath treatment method for two out of 13 baths by the facilities using a conveyorized graphite process (see Table 3.3).

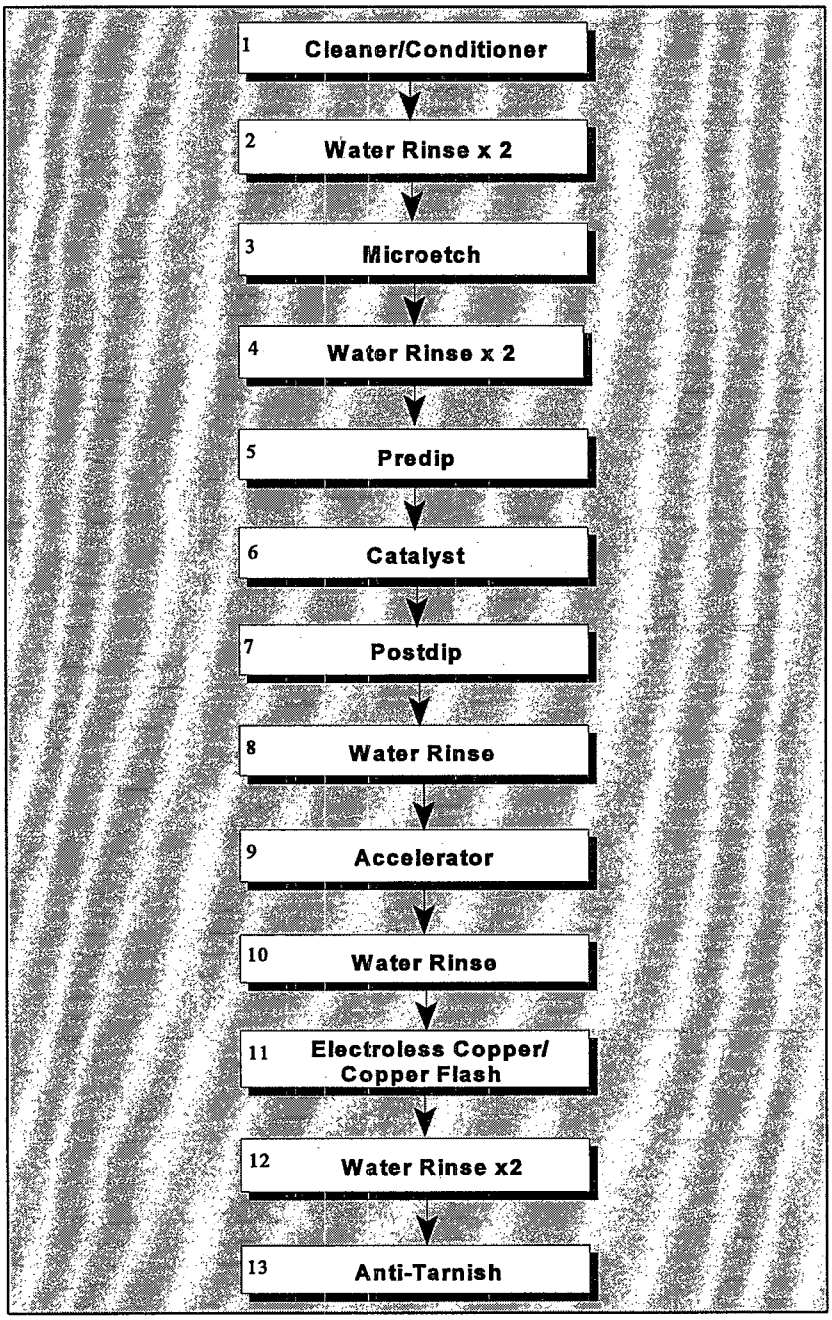
**Sludge Amounts From On-Site Treatment ($S_3$).** Sludge generation data are presented in Table 3.5. Reported sludge amounts for the facilities using a conveyorized process average 380 lbs/year, or 2.2 lbs per 1,000 ssf of PWB produced.

**Non-Formaldehyde Electroless Copper Process**

Figure 3.8 illustrates the generic non-formaldehyde electroless copper process steps and typical bath sequence evaluated in the CTSA. The number and location of rinse steps shown in the figure are based on IPC Workplace Practices Questionnaire data. Thus, Figure 3.8 lists the types and sequence of baths in a generic non-formaldehyde electroless copper line, but the types and sequence of baths in an actual line could vary. The single non-formaldehyde electroless

copper facility in the IPC Workplace Practices Questionnaire database uses a non-conveyorized equipment configuration. This is a small facility that produces just over 50,000 ssf of PWB per year.

**Figure 3.8 Generic Non-Formaldehyde Electroless Copper Process Steps and Typical Bath Sequence**




**Water Usage ($I_3$) and Wastewater ($W_1$).** Water usage data for the single non-formaldehyde electroless copper facility in the IPC Workplace Practices Questionnaire database were presented in Table 3.1; wastewater generation is assumed equal to water usage. The non-formaldehyde electroless copper facility indicated it discharges wastewater directly to a receiving

stream, rather than a POTW. Chemical constituents and concentrations in wastewater could not be adequately characterized.

**Cleaning Chemicals ($I_4$).** Only water is used for equipment cleaning, as reported in the IPC Workplace Practices Questionnaire.

**Bath Chemicals Used ($I_1$).** Appendix B presents estimated bath chemical concentrations for the non-formaldehyde electroless copper process. The amount of bath chemicals used could not be quantified from data.

**Spent Bath Solutions ($W_2$).** The quantity of spent bath solutions could not be determined from available data. Spent bath treatment methods are presented in Table 3.3. No treatment methods were reported for the non-formaldehyde electroless copper process.

**Evaporation From Baths ($A_1$).** Air releases are modeled in the Exposure Assessment (Section 3.2). The non-formaldehyde electroless copper facility uses panel agitation in all baths and fluid circulation in most baths. The only vapor control method reported is the use of a removable bath cover for the microetch bath. Table 3.2 lists bath surface area, volume, and bath temperature data from the IPC Workplace Practices Questionnaire.

**Evaporation From Drying/Oven ($A_2$).** This source of air emissions does not apply to non-formaldehyde electroless copper processes since oven drying is not required and air drying immediately follows water rinsing.

**Chemicals Incorporated Onto PWBs ($P_1$).** Copper is added to the boards in the non-formaldehyde electroless copper process.

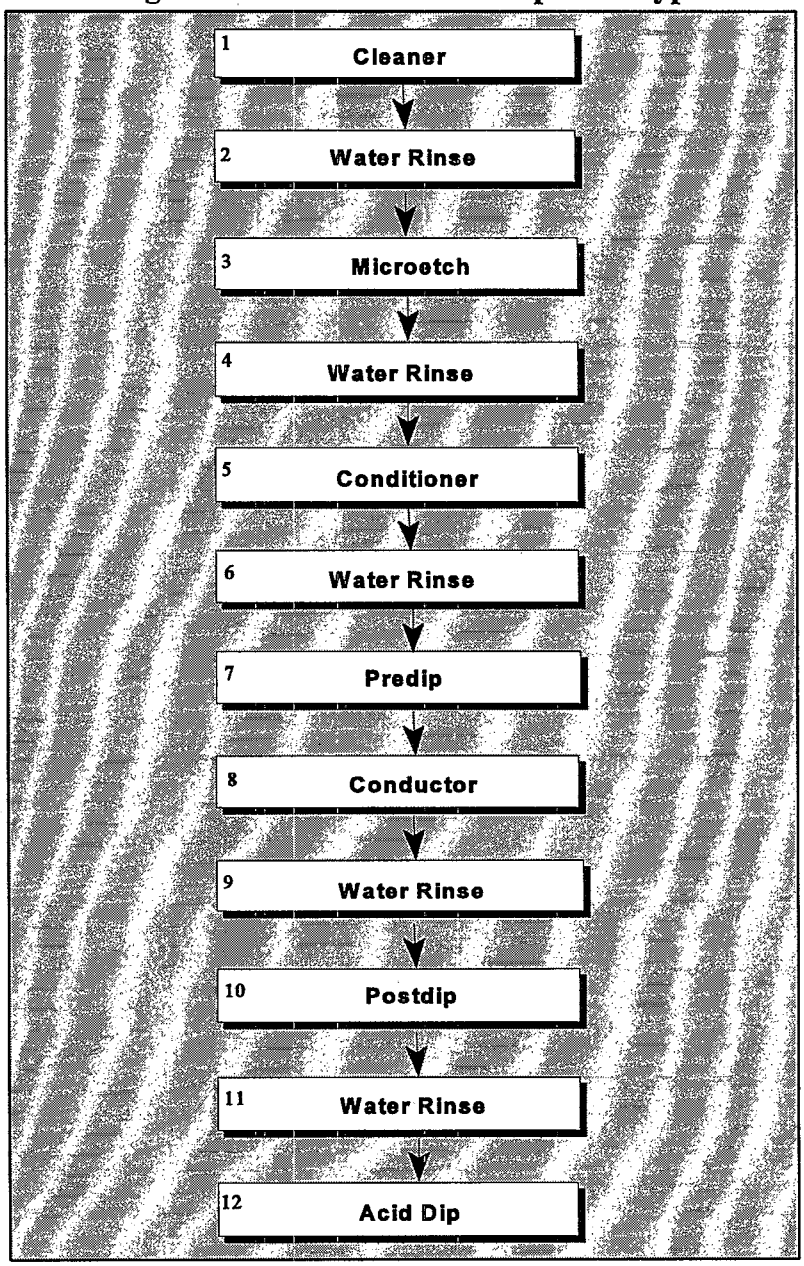
**Drummed Solid or Liquid Waste ($S_2$).** This was not reported as a spent bath treatment method for the non-formaldehyde copper facility (see Table 3.3).

**Sludge Amounts From On-Site Treatment ($S_3$).** These data are presented in Table 3.5. Reported sludge amounts for the non-formaldehyde electroless copper facility are 200 lbs/year, or 3.7 lbs per 1,000 ssf of PWB produced. Metal concentrations in sludge were not characterized.

**Organic-Palladium Process**

Figure 3.9 illustrates the generic organic-palladium process steps and bath sequence evaluated in the CTSA. The number and location of rinse steps shown in the figure are based on IPC Workplace Practices Questionnaire data. Thus, Figure 3.9 lists the types and sequence of baths in a generic organic-palladium line, but the types and sequence of baths in an actual line could vary. One organic-palladium facility in the IPC Workplace Practices Questionnaire database uses conveyorized equipment; the other uses non-conveyorized equipment.

**Figure 3.9 Generic Organic-Palladium Process Steps and Typical Bath Sequence**




**Water Usage ($I_3$) and Wastewater ($W_1$).** Water usage data from the questionnaire were presented in Table 3.1; wastewater generation is assumed equal to water usage. Of the two respondents using organic-palladium, one discharges directly to a stream or river following the appropriate treatment and one discharges to a POTW. In summary:

- Reported water usage for the facility using a conveyorized process is 881,000 gallons per year, or 1.8 gallons per ssf of PWB produced.
- Reported water usage for the facility using a non-conveyorized process is 7.7 million gallons per year, or 300 gallons per ssf of PWB produced.

**Cleaning Chemicals ($I_4$).** Chemicals used for equipment cleaning, as reported in the IPC Workplace Practices Questionnaire, include water, nitric acid, hydrogen peroxide, sulfuric acid, and iron chloride.

**Bath Chemicals Used ($I_1$).** Appendix B presents estimated bath chemical concentrations for the organic-palladium process. The amount of bath chemicals used could not be quantified from the data.

**Spent Bath Solutions ($W_2$).** The quantity of spent bath solution could not be determined from the data. Spent bath treatment methods are presented in Table 3.3. Precipitation pretreatment was reported for conveyorized organic-palladium and pH neutralization for non-conveyorized organic-palladium processes.

**Evaporation From Baths ($A_1$).** Air releases are modeled in the Exposure Assessment (Section 3.2). To summarize the data:

- For the organic-palladium facility using a conveyorized process, fluid circulation is reported for most of the baths and enclosure is used for vapor control for all baths.
- For the organic-palladium facility using a non-conveyorized process, panel agitation and fluid circulation are reported for most baths. Push-pull is used as a vapor control method for most baths.
- Table 3.2 lists bath surface area, volume, and bath temperature data.

**Evaporation From Drying/Oven ($A_2$).** This source of air emissions does not apply to the organic-palladium process since oven drying is not required and air drying immediately follows water rinsing.

**Chemicals Incorporated Onto PWBs ($P_1$).** Palladium is added to the board in this process.

**Drummed Solid or Liquid Waste ($S_2$).** This was not reported as a spent bath treatment method for organic-palladium processes (see Table 3.3).

**Sludge Amounts From On-Site Treatment ($S_3$).** These data are presented in Table 3.5. In summary:

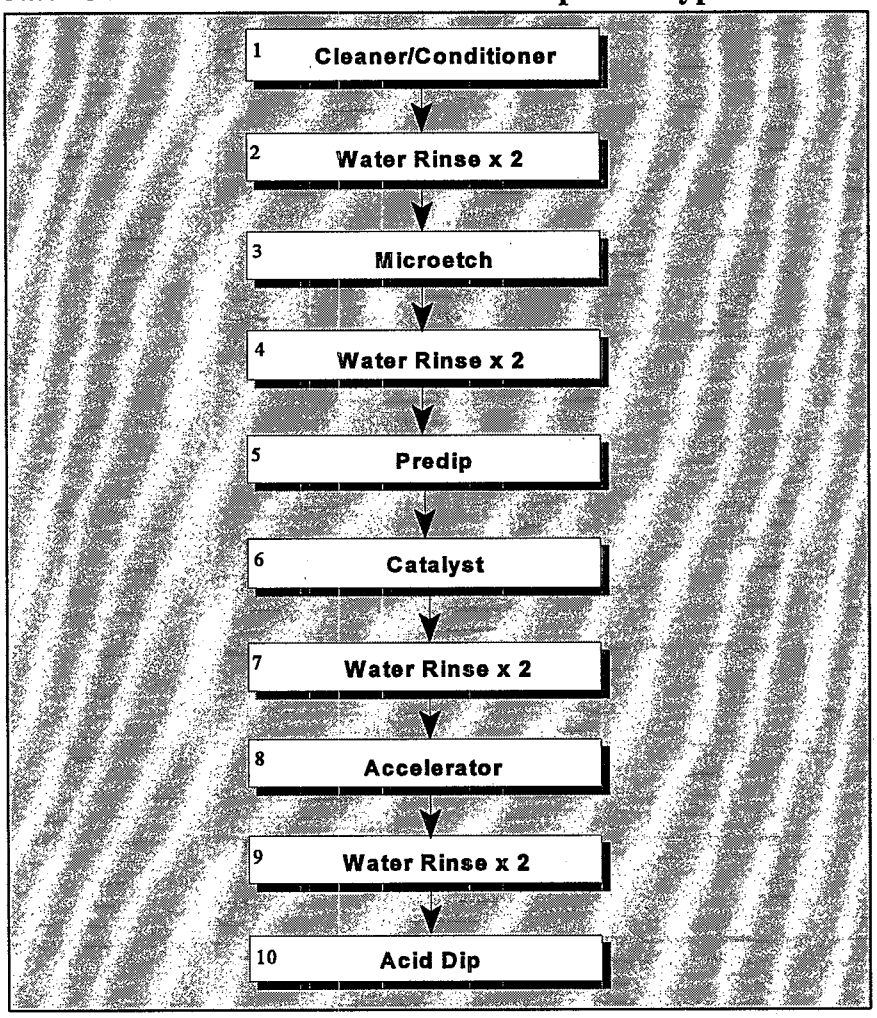
- Reported sludge amounts for the facility using a conveyorized process were 21,600 lbs/year, or 45 lbs per 1,000 ssf of PWB produced.
- Reported sludge amounts for the facility using a non-conveyorized process were 5,000 lbs/year, or 190 lbs per 1,000 ssf of PWB produced.

Metal concentrations in sludge could not be adequately characterized.

## Tin-Palladium Process

Figure 3.10 illustrates the generic tin-palladium process steps and bath sequence evaluated in the CTSA. The process baths depicted in Figure 3.10 represent an integration of the various products offered within the tin-palladium technology category. The number and location of rinse steps shown in the figure are based on IPC Workplace Practices Questionnaire data. Thus, Figure 3.10 lists the types and sequence of baths in a generic tin-palladium line, but the types and sequence of baths in an actual line could vary. Thirteen tin-palladium facilities are in the IPC Workplace Practices Questionnaire database. Of these, two use conveyorized equipment and 11 use non-conveyorized.

**Figure 3.10 Generic Tin-Palladium Process Steps and Typical Bath Sequence**




**Water Usage ($I_3$) and Wastewater ($W_1$).** Water usage data from the IPC Workplace Practices Questionnaire were presented in Table 3.1; wastewater generation is assumed equal to water usage. Of respondents using tin-palladium, two discharge wastewater directly to a stream or river following the appropriate treatment while ten facilities use indirect discharge (e.g., to a POTW). (One facility did not respond to the question.) In summary:

- Reported water usage for the facilities using conveyorized processes average 912,000 gallons per year, or 0.58 gallons per ssf of PWB produced.
- Reported water usage for the facilities using non-conveyorized processes average 1.6 million gallons per year, or 7.1 gallons per ssf of PWB produced.

**Cleaning Chemicals ($I_4$).** Chemicals used for equipment cleaning, as reported in the IPC Workplace Practices Questionnaire, include water, sodium hydroxide, hydrochloric acid, and nitric acid.

**Bath Chemicals Used ($I_1$).** Appendix B presents estimated bath chemical concentrations for the tin-palladium process. The amount of bath chemicals used could not be quantified from the data.

**Spent Bath Solutions ($W_2$).** The quantity of spent bath solution could not be determined from the data. Spent bath treatment methods are presented in Table 3.3. Precipitation pretreatment and pH neutralization are the only reported methods for the conveyorized process and are the most commonly reported methods for the non-conveyorized tin-palladium process.

**Evaporation From Baths ($A_1$).** Air releases are modeled in the Exposure Assessment (Section 3.2). To summarize questionnaire data:

- For the conveyorized tin-palladium process, fluid circulation is reported as a mixing method for all of the baths and enclosure is used for vapor control for all baths.
- For the non-conveyorized tin-palladium processes, panel agitation is used in about 2/3 of the baths, fluid circulation in about ½ of the baths, and air sparging for 1/3 of the microetch baths. Vapor control methods include push-pull and enclosure for a few baths, and covering for about 1/3 of the baths.
- Table 3.2 lists bath surface area, volume, and bath temperature data.

**Evaporation From Drying/Oven ($A_2$).** This source of air emissions does not apply to tin-palladium processes since oven drying is not required and air drying immediately follows water rinsing.

**Chemicals Incorporated Onto PWBs ($P_1$).** Palladium and small quantities of tin are added to the board in the tin-palladium process.

**Drummed Solid or Liquid Waste ($S_2$).** This was reported as a spent bath treatment method for six out of 64 baths by the facilities with non-conveyorized tin-palladium processes (see Table 3.3). The total quantity of drummed waste was not reported.

**Sludge Amounts From On-Site Treatment ($S_3$).** Sludge data are presented in Table 3.5. In general:

- Reported sludge amounts for the conveyorized facilities average 17,000 lbs/year, or 9.5 lbs per 1,000 ssf of PWB produced.

- Reported sludge amounts for the non-conveyorized facilities average 6,700 lbs/year, or 27 lbs per 1,000 ssf of PWB produced.

Metal concentrations in sludge could not be adequately characterized.

### 3.1.4 Uncertainties in the Source Release Assessment

Uncertainties and variations in the data include both gaps in knowledge (uncertainty) and variability among facilities and process alternatives. These are discussed below.

For the IPC Workplace Practices Questionnaire and Performance Demonstration data:

- There may be uncertainties due to misinterpretation of a question, not answering a question that applies to that facility, or reporting inaccurate information. Also, because of a limited number of responses for the alternative processes, information more typical for that process may not be reported.
- Variation includes variation within or among process alternatives, or difference due to PWB ssf produced. Again, for MHC process alternatives with a limited number of responses, statistical summaries of the data may be precluded, and data may not be representative of most PWB facilities.

For the supplier-provided data:

- Knowledge gaps include a lack of information on proprietary chemicals, incomplete bath composition data, and the reporting of wide ranges of chemical concentrations on a MSDS rather then specific amounts in the formulations.
- Variation includes variation in bath chemistries and process specifications among suppliers for a given process alternative. The publicly-available bath chemistry data, chemical concentrations, and supplier recommendations may not apply to a specific facility due to variation in process set-up and operation procedures.

Other uncertainties pertain to the applicability and accuracy of estimates and assumptions used in this assessment.

## 3.2 EXPOSURE ASSESSMENT

Evaluating exposure for the PWB CTSA involves a series of sequential steps. The first step is characterizing the exposure setting, which includes describing the physical setting and characterizing the population(s) of interest and their activities that may result in exposure. These are described in Section 3.2.1 for both workplace and surrounding population (ambient) exposure.

The next step is selecting a set of workplace and population exposure pathways for quantitative evaluation from the set of possible exposure pathways. This is discussed in Section 3.2.2.

Next, chemical concentrations are collected or estimated in all media where exposure could occur. For the MHC processes, this consists of collecting existing concentration data from workplace monitoring, estimating the chemical concentrations in the MHC baths, and performing fate and transport modeling to estimate workplace and ambient air concentrations (Section 3.2.3).

The exposure-point concentrations and other exposure parameters are combined in exposure models to estimate potential dose rates (PDRs) for all quantified pathways. These exposure models and parameter values are described in Section 3.2.4. The final step, characterizing uncertainties, is in Section 3.2.5.

Because this CTSA is a comparative evaluation, and standardization is necessary to compare results for the alternative processes, this assessment focuses on a "model" (generic) PWB facility and uses aggregated data. In addition, this assessment focuses on exposure from chronic, long-term, day-to-day releases from a PWB facility rather than short-term exposures to high levels of hazardous chemicals as there could be with a fire, spill, or periodic releases. Due to the limited resources available to the project and the lack of information to characterize such releases, high level, acute exposures could not be assessed.

### 3.2.1 Exposure Setting

Characterizing the exposure setting includes the following steps:

- Characterizing the physical environment (in this case, a model PWB facility, its MHC process area, and the surrounding environment).
- Identifying potentially exposed workers and their activities.
- Identifying any potentially exposed populations, human or ecological, that may be exposed through releases to the ambient environment from PWB facilities.
- Defining the exposure scenarios to evaluate. (As used here, the term *scenario* refers to a specified physical setting, exposed population, and activities that may result in exposure.)

**Physical Environment**

IPC Workplace Practices Questionnaire and Performance Demonstration data collected for 59 PWB facilities and their MHC process areas were used to characterize a model PWB facility. Information obtained from these sources includes the following:

- Regarding MHC process alternatives, the IPC Workplace Practices Questionnaire database includes information from 36 electroless copper facilities, two carbon facilities, one conductive polymer facility, four graphite facilities, one non-formaldehyde copper facility, two organic-palladium facilities, and 13 tin-palladium facilities.
- Of these facilities, 48 are independent and the other 11 are original equipment manufacturers (OEMs) who manufacture PWBs solely for use in that company's products.
- The size of the PWB manufacturing area ranges from 3,721 to 400,000 $ft^2$, with a geometric mean area of 33,800 $ft^2$.
- The size of the MHC process room ranges from 120 to 60,000 $ft^2$, with a geometric mean of 3,760 $ft^2$.
- The number of days per year the MHC line operates ranges from 80 to 360, with an average of 250 days/year and a 90th percentile of 306 days/year.
- The total PWB processed per year ranges from 24,000 ssf per year to 6.24 million ssf per year, with a geometric mean of 351,670 ssf per year.
- Temperature of the process room ranges from 60 to 94 °F, with an average of 75 °F.
- All 59 facilities responding to the question reported the use of some type of ventilation in the process area. A smaller number of facilities provided more specific information on the type of ventilation and air flow rates. Reported air flow rates range from 7 to 405,000 $ft^3$/min. with a geometric mean of 6,100 $ft^3$/min. Of the facilities reporting air flow rates, the types of ventilation reported are as follows:
  - Seven facilities reported using both local and general ventilation systems.
  - Six facilities reported using only general ventilation.
  - Twenty-three facilities reported using only local ventilation. (However, they may not have consistently reported general ventilation.)
  - One facility did not specify either local or general ventilation.

The initial intent was to focus on a generic small- to medium-sized facility that manufactures ≤ 6,000 ssf of PWB per day. However, larger facilities are now included in the database to account for all of the performance demonstration sites and all categories of process alternatives. The conductive ink facility is not included in this assessment.

The data summarized here are used to broadly characterize the exposure setting (i.e., a model PWB facility and MHC process area). Data used in the exposure models are discussed further in Section 3.2.4. Based on the workplace practices data and using arithmetic averages or geometric means, a model facility has the following characteristics:

- Is independent (rather than OEM).
- Uses 33,800 $ft^2$ of facility space in the PWB operation.
- Contains the MHC process in a room 3,760 $ft^2$ in size.
- Operates an MHC line 250 days/year.
- Manufactures 350,000 ssf of PWB per year.
- Is 75 °F in the process room.
- Has a typical ventilation air flow rate in the process area of 6,100 $ft^3$/min.

## Potentially Exposed Populations

Potentially exposed populations include both workers in the PWB facilities and ecological and human populations in the vicinity of the facilities. Each of these populations is discussed briefly below.

**General Employee Information from the IPC Workplace Practices Questionnaire.** A summary of IPC Workplace Practices Questionnaire data pertaining to employees at PWB facilities includes the following:

- The number of full-time employee equivalents (FTEs) ranges from 8 to 1,700, with a geometric mean of 103.
- The number of employee work days per year ranges from 200 to 360, with an average of 268 days/year. The number of days per year the MHC line operates is used to characterize worker exposure from MHC line operation, rather than the overall employee work days per year, because the latter could include workers not in the MHC process area or time when the MHC line is not in operation.
- The MHC process line operates from 1 to 12 hours/shift, with an average of 6.8 hours/shift.
- Fifty-eight out of 59 facilities reported a first shift, 52 a second shift, 29 a third shift, and one reported a fourth shift (one facility operates the second but not a first shift). For MHC operation, 54 facilities reported a first shift, 43 a second shift, 16 a third shift, and one reported a fourth shift. This exposure assessment uses first shift data as representative.
- Types of workers in the MHC process area include:
  - Line operators.
  - Laboratory technicians.
  - Maintenance workers.
  - Supervisory personnel.
  - Wastewater treatment operators.
  - Contract workers.
  - Other employees (i.e., manufacturing engineer, process control specialist).

**General Population Outside the Facility.** PWB facilities included in the IPC Workplace Practices Questionnaire and Performance Demonstration database are located in various cities in the U.S. and Europe. Many are in southern California. This assessment estimates potential exposure to a hypothetical community living near a model PWB facility.

Exposure to ecological populations could also occur outside a PWB facility. In past CTSAs, concentrations have been estimated for surface water to assess potential exposure to aquatic organisms. However, as discussed in the Source Release Assessment (Section 3.1), data limitations preclude estimating releases to surface water. Ecological toxicity and hazard for potential releases to surface water (based on bath constituents used in each alternative) are addressed in Section 3.3.

## Workplace Exposure Scenarios

A scenario describes the exposure setting, potentially exposed populations or individuals, and activities that could lead to exposure. For workplace exposures, the setting involves the MHC process in a PWB facility. The Workplace Practices data are used here to determine the types of workers who may be exposed and to characterize those worker's activities. Worker activities include working in the process area, MHC line operation, chemical bath sampling, chemical bath additions, chemical bath replacement, rack cleaning, conveyor equipment cleaning, and filter replacement.

**Working in the Process Area.** Exposure via inhalation of airborne chemicals is possible to workers in the MHC process area. Because of this, the questionnaire included questions about the types of workers who might be present in the area. Out of 59 facilities responding to this question:

- Fifty-nine have line operators in the MHC process area during the first shift.
- Fifty-two have laboratory technicians in the MHC process area.
- Thirty-eight have maintenance workers in the MHC process area.
- Fifty have supervisory personnel in the MHC process area.
- Thirty-six have wastewater treatment operators in the MHC process area.
- Two have contract workers in the MHC process area.
- Six have other employees in the MHC process area.

**MHC Line Operation.** Potential for exposure during MHC line operation is expected to vary significantly among process methods. In manual, non-conveyorized methods, a line operator stands at the bath and manually lowers and raises the panel racks into and out of each bath. A vertical/automated method is completely automated, where panel racks are lowered and raised into vertical tanks by a robotic arm; line operators load and unload panels from the racks. A manually-controlled vertical hoist is a semi-automated system where racks are lowered into and raised out of a series of vertical chemical baths by a line operator-controlled hoist. The hoist is controlled by a hand-held control panel attached to the hoist by a cable. The conveyorized method is an automated method where panels are transported into and out of process baths by means of a conveyor; line operators load and unload panels from the conveyor system. Based on the workplace practices data:

- For electroless copper lines, 35 out of 36 are non-conveyorized, of which 19 are vertical/automated, ten are manually controlled vertical hoist, and six are manual (with no automation). One facility is conveyorized.
- All carbon and graphite lines in the database are conveyorized.
- The single conductive polymer system is conveyorized.
- The single non-formaldehyde electroless copper system is non-conveyorized, with manually controlled vertical hoist.
- For organic-palladium lines, one is conveyorized and one is non-conveyorized with a vertical/automated system.
- For tin-palladium lines, 13 are non-conveyorized, of which one is vertical/automated, four are manually controlled vertical hoist, and six are manual (no automation). Two facilities are conveyorized.

Different assumptions are made about worker exposure for non-conveyorized and conveyorized systems. For the non-conveyorized systems, it is assumed that workers manually lower and raise panel racks. This is a conservative but consistent assumption made for all non-conveyorized process alternatives.

**Chemical Bath Sampling.** Based on the questionnaire database, chemical baths in the carbon, graphite, and organic-palladium alternatives are normally sampled by use of a drain or spigot on the bath. For electroless copper, the most common method is to dip a container (ladle, beaker, or sample bottle) into a bath. For tin-palladium, the most common method reported is to sample by pipette.

**Chemical Bath Additions.** Methods of chemical additions from the database are as follows:

- Most facilities pour chemical additions directly into the bath or tank (63 percent).
- Other reported options include: stirring into a tank (24 percent), pouring into an automated chemical addition system (20 percent), or other (two percent). Stirring typically involves fluid agitation while pouring the formulation into the bath.
- For carbon and graphite facilities, 100 percent reported pouring directly into the tanks.

This activity is characterized for a model facility by pouring chemicals directly into the tank for all process alternatives except conductive polymer, where all additions are made automatically.

**Chemical Bath Replacement.** This process includes removing the spent bath, cleaning the empty tank, and making up fresh bath solutions. In this process, a worker could be exposed to chemicals in the spent bath, on the inside walls of the emptied bath, or to chemicals in the new bath solution.

**Rack Cleaning.** Rack cleaning only applies to those process alternatives where a buildup of material on the panel racks occurs (e.g., copper plating onto the racks). This includes the electroless copper, non-formaldehyde electroless copper, and tin-palladium processes. Rack cleaning for these processes could occur either as part of the routine MHC line operation (called "continuous" rack cleaning) or as a separate step in the process. Of the facilities responding to this question, only nine out of 36 electroless copper facilities and four out of 13 tin-palladium facilities reported rack cleaning as a separate step in the process. An additional 17 electroless copper facilities reported continuous rack cleaning. All of the remaining facilities reported the question was not applicable, did not respond, or gave an unusable response.

Because there were a low number of applicable or usable responses to the question, and a majority of the electroless copper facilities responding to the question use continuous rack cleaning, this activity is not considered quantitatively as a separate worker activity performed at a model facility.

**Conveyor Equipment Cleaning.** Conveyor equipment cleaning involves regular equipment maintenance for conveyorized MHC lines; 11 of the facilities in the database are conveyorized. Examples include cleaning the fluid circulation heads and rollers for the graphite process, and vacuuming particulates from the drying areas of graphite and carbon lines.

**Filter Replacement.** Filter replacement could result in exposure to the material on the filter or in the bath. Whether the pathway is significant to worker risk will depend, in part, on the chemical constituents in the bath.

**Use of Personal Protective Equipment (PPE).** An overview of the data pertaining to the use of PPE indicates the following general trends for the various activities:

- Most facilities reported the use of eye protection and gloves, but some did not.
- Use of lab coats or aprons was reported approximately 1/4 to 1/2 of the time.
- Few facilities reported using boots.
- The use of respiratory protection was very rarely reported.

It is assumed that the only PPE used is eye protection and that the line operator's hands and arms may contact bath solutions. This is a conservative but consistent assumption for all process alternatives and worker activities, particularly for dermal exposure. While most PWB facilities reported that line operators do wear gloves, the assumption that the line operator's hands and arms may contact bath solutions is intended to account for the fraction of workers who do not. For workers who do wear gloves, dermal contact exposure is expected to be negligible.

**Summary of Scenarios.** *MHC Line Operators.* In general, line operators perform several activities, including MHC line operation (which includes working in the MHC process area); chemical bath replacement; rack cleaning; conveyor equipment cleaning; filter replacement; chemical bath sampling; making chemical bath additions; and bail-out of baths. Some kind of local ventilation is typically used for the process line.

There are two different scenarios for line operators depending on process configuration. For non-conveyorized processes, dermal exposure could occur through routine line operation as well as bath maintenance activities. Inhalation exposure could occur throughout the time period a line operator is in the MHC process area. Conveyorized processes are enclosed and the line operator does not contact the bath solutions in routine line operation; he or she only loads panels at the beginning of the process and unloads them at the end of the process. For conveyorized processes, dermal exposure is primarily expected through bath maintenance activities such as bath replacement, bath sampling, and conveyor equipment cleaning. Because the conveyorized lines are enclosed and typically vented to the outside, inhalation exposure to line operators and other workers is assumed to be negligible for the conveyorized processes.

*Laboratory Technicians.* In general, laboratory technicians perform one activity pertaining to the MHC line, chemical bath sampling, in addition to working in the MHC process area. Bath sampling exposure is quantified separately for laboratory technicians.

*Other Workers in the MHC Process Area.* Other workers in the MHC process area may include maintenance workers, supervisory personnel, wastewater treatment operators, contract workers, and other employees. They perform activities not directly related to the MHC line, but typically spend some time in the MHC process area. Because the line operators spend the most amount of time per shift, exposure via inhalation is quantified for them (for non-conveyorized processes), and characterized for the other employees in terms of the time spent in the process area relative to line operators.

### 3.2.2 Selection of Exposure Pathways

The definition of exposure scenarios leads to selection of the exposure pathways to be evaluated. An exposure scenario may comprise one or several pathways. A complete exposure pathway consists of the following elements:

- A source of chemical and mechanism for release.
- An exposure point.
- A transport medium (if the exposure point differs from the source).
- An exposure route.

Tables 3.6 and 3.7 present an overview of the pathways selection for workplace and surrounding population exposures, respectively. For the workplace, another potential pathway not quantified is oral exposure to vapors or aerosols. For example, oral exposure could occur if inhaled chemicals are coughed up and then swallowed.

Population exposures may occur through releases to environmental media (i.e., releases to air, water, and land). The only pathway for which exposure is estimated is inhalation of chemicals released from a facility to a nearby residential area. Approaches for the three environmental media are described below.

#### Air

Air releases from the MHC process are modeled for the workplace. Those modeled emission rates are used in combination with an air dispersion model to estimate air concentrations to a nearby population.

#### Surface Water

Little reliable data are available for water releases for the MHC alternatives. (This issue is discussed further in Section 3.2.3.) Exposures and risks from surface water are evaluated qualitatively by identifying chemicals potentially released to surface water from the publicly-available bath chemistry data (discussed in Section 2.1.4), bath chemistry data for disclosed proprietary ingredients, and using ecological toxicity data to highlight those chemicals of highest ecological concern if released to surface water (Section 3.3).

#### Land

Possible sources of releases to land from MHC processes include bath filters and other solid wastes from the process line, chemical precipitates from baths, and sludge from wastewater treatment. These are discussed in Section 3.1, Source Release Assessment. Reliable characterization data for potential releases to land are not available; therefore, the exposure assessment does not estimate the nature and quantity of leachate from landfills or effects on groundwater.

**Table 3.6 Workplace Activities and Associated Potential Exposure Pathways**

| Activities | Potential Pathways | Evaluation Approach and Rationale |
|---|---|---|
| **Line Operators**[a] | | |
| MHC Line Operation | Dermal contact with chemicals in MHC baths. | Exposure quantified for non-conveyorized lines; the highest potential dermal exposure is expected from this activity. Exposure for conveyorized lines assumed to be negligible for this activity. |
| | Inhalation of vapors or aerosols from MHC baths. | Exposure quantified for non-conveyorized lines. Exposure for conveyorized lines assumed to be negligible. |
| Working in Process Area | Inhalation of vapors or aerosols from MHC baths. | Exposure quantified for non-conveyorized lines. |
| Chemical Bath Replacement; Conveyor Equipment Cleaning; Filter Replacement; Chemical Bath Sampling | Dermal contact with replacement chemicals. | Exposure quantified for conveyorized lines for all activities together (bath sampling quantified separately for laboratory technicians). Exposure not quantified separately for these activities on non-conveyorized lines. |
| | Inhalation of vapors or aerosols from MHC baths. | Not quantified separately. Included in "working in process area" for non-conveyorized lines; not quantified due to modeling limitations for conveyorized lines. |
| Rack Cleaning | Dermal contact with chemicals on racks. | Not quantified; limited data indicate this is not performed by many facilities. |
| | Inhalation of vapors or aerosols from MHC baths. | Not quantified separately. Included in "working in process area" for non-conveyorized lines; not quantified due to modeling limitations for conveyorized lines. |
| Chemical Bath Additions | Dermal contact with chemicals added. | Not quantified separately from chemicals already in the baths. |
| | Inhalation of vapors or aerosols from MHC baths or while making bath additions. | Not quantified separately. Included in "working in process area" for non-conveyorized lines; not quantified due to modeling limitations for conveyorized lines. |
| **Laboratory Technicians** | | |
| Chemical Bath Sampling | Dermal contact with chemicals in MHC baths. | Exposure quantified for conveyorized and non-conveyorized lines. |
| | Inhalation of vapors or aerosols from MHC baths. | Not quantified separately (included in "working in process area"). |
| Working in Process Area | Inhalation of vapors or aerosols from MHC baths. | Exposure quantified for line operators for non-conveyorized lines; exposure for other workers is proportional to their exposure durations. |

| Activities | Potential Pathways | Evaluation Approach and Rationale |
|---|---|---|
| **Maintenance Workers, Supervisory Personnel, Wastewater Treatment Operators, Contract Workers, and Other Workers** | | |
| Working in Process Area | Inhalation of vapors or aerosols from MHC baths. | Exposure quantified for line operators for non-conveyorized lines; exposure for other workers is proportional to their exposure durations. |
| | Dermal contact with chemicals in MHC baths. | Not quantified.[a] |

[a] This assumes MHC line operators are the most exposed individuals and perform all direct maintenance on the MHC line, including filter replacement and equipment cleaning.

**Table 3.7 Potential Population Exposure Pathways**

| Population | Potential Pathways | Evaluation Approach and Rationale |
|---|---|---|
| Residents Living Near a PWB Facility | Inhalation of chemicals released to air. | Exposure quantified for all potential carcinogens and any other chemical released at a rate of at least 23 kg/year. |
| | Contact with chemicals released to surface water directly or through the food chain. | Not evaluated. |
| | Exposure to chemicals released to land or groundwater. | Not evaluated. |
| Ecological | Exposure to chemicals released to surface water. | Evaluated qualitatively in the Human Health and Ecological Hazards Summary (Section 3.3). |
| | Exposure to chemicals released to air or land. | Not evaluated. |

### 3.2.3 Exposure-Point Concentrations

The term exposure-point concentration refers to a chemical concentration in its transport or carrier medium, at the point of contact (or potential point of contact) with a human or environmental receptor. Sources of data for the Exposure Assessment include monitoring data, publicly-available bath chemistry data, some proprietary bath chemistry data, and fate and transport models to estimate air releases and air concentrations. Concentrations for dermal exposure in the baths are those estimated from publicly-available bath chemistry data, as described in Section 2.1.4, and from disclosed proprietary ingredient information. Fate and transport modeling were performed to estimate air concentrations for workplace and surrounding population exposures as described in this section.

**Monitoring Data**

Table 3.8 presents a summary of all available Federal Occupational Safety and Health Administration (OSHA) data for PWB manufacturers (standard industrial code [SIC] 3672). California OSHA was also consulted for monitoring data; they referred to the Federal OSHA database. In addition, one facility submitted results of monitoring for formaldehyde at 0.06 ppm (8 hr. time-weighed average [TWA]) along with their response to the IPC Workplace Practices Questionnaire.

It should be noted that OSHA monitoring is typically performed only for those chemicals which are regulated by OSHA (i.e., chemicals with permissible exposure limits [PELs]). Monitoring also does not distinguish between the MHC process and other parts of the PWB process that may be located in the same area.

**Table 3.8 Summary of Federal OSHA Monitoring Data for PWB Manufacturers (SIC 3672)**

| Chemical | No. of Data Points/ No. of Facilities | Range (ppm) | Average (ppm)[a] | Standard Deviation (ppm) |
|---|---|---|---|---|
| Ammonia | 26 / 6 | 0 - 27 | 6.9 | 8.24 |
| Copper Sulfate, as Copper | 11 / 2 | 0 - 0 | 0 | 0 |
| Ethanolamine | 5 / 1 | 0 - 0.09 | 0.02 | 0.04 |
| Formaldehyde | 43 / 11 | 0 - 4.65 | 0.44 | 0.75 |
| Hydrochloric Acid | 26 / 5 | 0 - 0 | 0 | 0 |
| Isopropanol | 16 / 4 | 0 - 215 | 41.7 | 57.6 |
| Methanol | 6 / 1 | 0 - 0 | 0 | 0 |
| Phosphoric Acid | 3 / 1 | 0 - 0 | 0 | 0 |
| Sodium Hydroxide | 33 / 6 | 0 - 2.3 | 0.359 | 0.614 |
| Stannous Chloride, as Tin | 26 / 10 | 0 - 0.113 | 0.006 | 0.023 |
| Sulfuric Acid | 28 / 11 | 0 - 0.24 | 0.045 | 0.070 |

[a] Zeros were included in averages; detection limits were not reported.

## Modeling Workplace Air Concentrations

Bath concentrations estimated from publicly-available chemistry data and disclosed proprietary chemical data, as well as process configurations from the IPC Workplace Practices Questionnaire, were used to estimate workplace and ambient air concentrations using fate and transport models (Robinson et al., 1997). This section describes air transport models to estimate worker inhalation exposure to chemicals from PWB MHC lines. Three air transport models are used to estimate worker exposure:

1. Volatilization of chemicals induced by air sparging.
2. Aerosol generation induced by air sparging.
3. Volatilization of chemicals from the open surface of MHC tanks.

For models 1 and 3, volatilization was modeled only for those chemicals with a vapor pressure above $10^{-3}$ torr (a vapor pressure less than $10^{-3}$ torr was assumed for inorganic salts even if vapor pressure data were not available). Aerosol generation and volatilization from air-sparged baths were modeled only for those baths that are mixed by air sparging as indicated in the Workplace Practices and Performance Demonstration data; this includes the electroless copper baths and some cleaning tanks. The total transport of chemicals from the air-sparged baths was determined by summing the releases from each of the three models. The third model was applied to determine volatilization of chemicals from un-sparged baths. A review of the relevant literature, descriptions of the models, and examples demonstrating the use of the models are available in the December 22, 1995 Technical Memorandum, *Modeling Worker Inhalation*

*Exposure* (Appendix D). Modeled emission rates and workplace air concentrations are presented in Table 3.9. Proprietary chemical results are not presented in order to protect proprietary chemical identities.

**Table 3.9 Results of Workplace Air Modeling**

| Chemical[a] | Emission Rate (mg/min) | Air Conc. ($mg/m^3$) | Federal OSHA and/or NIOSH Permissible Inhalation Exposure Limits ($mg/m^3$)[b] |
|---|---|---|---|
| **Electroless Copper, non-conveyorized** | | | |
| Ammonium Chloride | NA | NA | 10 (NIOSH) |
| Benzotriazole | 1.24e-01 | 5.54e-03 | |
| Boric Acid | 1.71e-01 | 7.64e-03 | |
| Copper (I) Chloride | 7.56e-02 | 3.38e-03 | 1 (as Cu dust and mist; OSHA/NIOSH) |
| Copper Sulfate; or Cupric Sulfate | 8.31e-02 | 3.71e-03 | 1 (as Cu dust and mist; OSHA/NIOSH) |
| Dimethylaminoborane | 1.94e+00 | 8.66e-02 | |
| Dimethylformamide | 1.42e+00 | 6.33e-02 | 30 (OSHA/NIOSH) |
| 2-Ethoxyethanol | 1.46e+03 | 6.51e+01 | 740 (OSHA); 1.8 (NIOSH) |
| Ethanolamine | 9.92e+00 | 4.44e-01 | 6 (OSHA) |
| Ethylene Glycol | 3.33e+00 | 1.49e-01 | |
| Ethylenediaminetetraacetic Acid (EDTA) | 5.11e-01 | 2.29e+02 | |
| Fluoroboric Acid | 2.20e+00 | 9.82e-02 | |
| Formaldehyde | 1.37e+01 | 6.15e-01 | 0.94 (0.75 ppm)[c] (OSHA) |
| Formic Acid | 3.51e+01 | 1.57e+00 | 9 (OSHA/NIOSH) |
| Hydrochloric Acid | 5.43e-03 | 2.43e-04 | 7 (NIOSH) |
| Hydrogen Peroxide | 1.66e-01 | 7.41e-03 | 1.4 (OSHA/NIOSH) |
| Hydroxyacetic Acid | 3.14e-02 | 1.40e-03 | |
| Isopropyl Alcohol; or 2-Propanol | 5.24e+02 | 2.34e+01 | 980 (OSHA) |
| m-Nitrobenzene Sulfonic Acid | 9.14e-04 | 4.09e-05 | |
| Magnesium Carbonate | 9.99e-03 | 4.47e-04 | |
| Methanol | 2.31e+02 | 1.03e+01 | 260 (OSHA/NIOSH) |
| p-Toluene Sulfonic Acid | NA | NA | |
| Palladium | NA | NA | |
| Peroxymonsulfuric Acid | 2.15e-01 | 9.60e-03 | |
| Potassium Bisulfate | 1.15e-01 | 5.14e-03 | |
| Potassium Cyanide | 2.52e-03 | 1.13e-04 | 5 (as CN; OSHA/NIOSH) |
| Potassium Hydroxide | 2.33e-03 | 1.04e-04 | 2 (NIOSH) |
| Potassium Persulfate | 8.16e-02 | 3.65e-03 | |
| Potassium Sulfate | 1.60e-01 | 7.15e-03 | |
| Potassium-Sodium Tartrate | 3.55e-01 | 1.59e-02 | |
| Sodium Bisulfate | NA | NA | |
| Sodium Carbonate | 5.65e-04 | 2.53e-05 | |
| Sodium Chlorite | NA | NA | |

| Chemical[a] | Emission Rate (mg/min) | Air Conc. ($mg/m^3$) | Federal OSHA and/or NIOSH Permissible Inhalation Exposure Limits ($mg/m^3$)[b] |
|---|---|---|---|
| Sodium Cyanide | 2.61e-03 | 1.17e-04 | 5 (as CN; OSHA/NIOSH) |
| Sodium Hydroxide | 1.18e-01 | 5.26e-03 | 2 (OSHA/NIOSH) |
| Sodium Hypophosphite | NA | NA | |
| Sodium Sulfate | NA | NA | |
| Stannous Chloride | NA | NA | 2 (as Sn; OSHA) |
| Sulfuric Acid | 1.24e+00 | 5.57e-02 | 1 (OSHA) |
| Tartaric Acid | 1.17e-02 | 5.21e-04 | |
| Triethanolamine; or 2,2',2"-Nitrilotris Ethanol | NA | NA | |
| **Non-Formaldehyde Electroless Copper, non-conveyorized** | | | |
| Copper Sulfate; or Cupric Sulfate | 2.74e-01 | 1.22e-02 | 1 (as Cu dust and mist; OSHA/NIOSH) |
| Hydrochloric Acid | NA | NA | 7 (NIOSH) |
| Hydrogen Peroxide | 9.36e-02 | 4.19e-03 | 1.4 (OSHA/NIOSH) |
| Isopropyl Alcohol; or 2-Propanol | 7.34e+01 | 3.28e+00 | 980 (OSHA) |
| Potassium Hydroxide | 1.49e-03 | 6.67e-05 | 2 (NIOSH) |
| Potassium Persulfate | 5.68e-02 | 2.54e-03 | |
| Sodium Chlorite | NA | NA | |
| Sodium Hydroxide | 1.74e-03 | 7.78e-05 | 2 (OSHA/NIOSH) |
| Stannous Chloride | NA | NA | 2 (as Sn; OSHA) |
| Sulfuric Acid | 1.48e-01 | 6.63e-03 | 1 (OSHA) |
| **Organic-Palladium, non-conveyorized** | | | |
| Hydrochloric Acid | NA | NA | 7 (NIOSH) |
| Sodium Bisulfate | NA | NA | |
| Sodium Carbonate | NA | NA | |
| Sodium Hypophosphite | NA | NA | |
| Sodium Persulfate | NA | NA | |
| Trisodium Citrate 5.5-Hydrate; or Sodium Citrate | NA | NA | |
| **Tin-Palladium, non-conveyorized** | | | |
| 1,3-Benzenediol | NA | NA | |
| Copper (I) Chloride | NA | NA | 1 (as Cu dust and mist; OSHA/NIOSH) |
| Copper Sulfate; or Cupric Sulfate | 7.38e-02 | 3.30e-03 | 1 (as Cu dust and mist; OSHA/NIOSH) |
| Ethanolamine | 2.00e+01 | 8.92e-01 | 6 (OSHA) |
| Fluoroboric Acid | 1.76e+00 | 7.89e-02 | |
| Hydrochloric Acid | NA | NA | 7 (NIOSH) |
| Hydrogen Peroxide | 9.71e-02 | 4.34e-03 | 1.4 (OSHA/NIOSH) |
| Isopropyl Alcohol; or 2-Propanol | 2.94e+02 | 1.32e+01 | 980 (OSHA) |
| Lithium Hydroxide | NA | NA | |
| Palladium | NA | NA | |

| Chemical[a] | Emission Rate (mg/min) | Air Conc. ($mg/m^3$) | Federal OSHA and/or NIOSH Permissible Inhalation Exposure Limits ($mg/m^3$)[b] |
|---|---|---|---|
| Palladium Chloride | NA | NA | |
| Potassium Carbonate | NA | NA | |
| Sodium Bisulfate | NA | NA | |
| Sodium Chloride | NA | NA | |
| Sodium Hydroxide | NA | NA | 2 (OSHA/NIOSH) |
| Sodium Persulfate | 8.38e-01 | 3.75e-02 | |
| Stannous Chloride | NA | NA | 2 (as Sn; OSHA) |
| Sulfuric Acid | 1.16e-01 | 5.19e-03 | 1 (OSHA) |
| Triethanolamine; or 2,2',2"-Nitrilotris Ethanol | NA | NA | |
| Vanillin | 8.09e-02 | 3.62e-03 | |

[a] Proprietary chemical results are not presented in order to protect proprietary chemical identities.
[b] Source: NIOSH, 1994 and 29 CFR 1910.1000, Table Z-1.
[c] OSHA has set an "action level" of 0.5 ppm for formaldehyde. At or above that level, people working in the area of exposure must be monitored, and the area must be segregated. From 0.1 - 0.5 ppm, workers must be notified that formaldehyde is present (but not that it is suspected of being a carcinogen).
NA: Not Applicable. A number was not calculated because the chemical's vapor pressure is below the $1 \times 10^{-3}$ torr cutoff and is not used in any air-sparged bath. Therefore, air concentrations are expected to be negligible.
Note: The numeric format used in these tables is a form of scientific notation, where the "e" replaces the " x $10^{x}$" in scientific notation. Scientific notation is typically used to present very large or very small numbers. For example, 1.2e-04 is the same as $1.2 \times 10^{-4}$, which is the same as 0.00012 in common decimal notation.

**Volatilization of Chemicals from Air-Sparged MHC Tanks.** Mixing in plating tanks (e.g., the electroless copper plating tank) is commonly accomplished by sparging the tank with air. The equation used for predicting the mass transfer rate from an aerated system is based on volatilization models used in research of aeration in wastewater treatment plants:

$$F_{y,s} = Q_G H_y c_{L,y} \left[ 1 - \exp\left( - \frac{K_{OL,y} a V_L}{H_y Q_G} \right) \right]$$

where:

$F_{y,s}$ = mass transfer rate of chemical *y* out of the system by sparging (mg/min)
$Q_G$ = gas flow rate (L/min)
$H_y$ = dimensionless Henry's Law Constant ($H_C$) for chemical *y*
$c_{L,y}$ = concentration of chemical *y* in bulk liquid (mg/L)
$K_{OL,y}$ = overall mass transfer coefficient for chemical *y* (cm/min)
a = interfacial area of bubble per unit volume of liquid ($cm^2/cm^3$)
$V_L$ = volume of liquid ($cm^3$)

**Aerosol Generation from Baths Mixed by Sparging with Air.** Aerosols or mists are also a potential source of contaminants from electroless baths. The rate of aerosol generation has been found to depend on the air sparging rate, bath temperature, air flow rate above the bath, and the distance between bath surface and the tank rim. The following equation is used to estimate the rate of aerosol generation (Berglund and Lindh, 1987):

$$R_A = \left[5.5x10^{-5}\left(Q_G / A\right)+0.01\right] F_T F_A F_D$$

where:

$R_A$ = aerosol generation rate (ml/min/m$^2$)
$Q_G$ = air sparging rate (cm$^3$/min)
A = bath area (m$^2$)
$F_T$ = temperature correction factor
$F_A$ = air velocity correction factor
$F_D$ = distance between the bath surface and tank rim correction factor.

The emission of contaminants resulting from aerosols depends on both the rate of aerosol generation and the concentration of contaminants in the aerosol. The following equation is used to estimate contaminant emission (flux) from aerosol generation:

$$F_{y,a} = \frac{M_I}{M_b} f_{IE} F_{y,s}$$

where:

$F_{y,a}$ = rate of mass transfer from the tank to the atmosphere by aerosols (mg/min)
$f_{IE}$ = fraction of bubble interface ejected as aerosols (dimensionless)
$M_I$ = mass of contaminant at the interface (mg)
$M_b$ = mass of contaminant in gas bubble (mg)

The literature on aerosol generation indicates that the typical size of aerosols is one to ten microns; this is important to note because particles in this range are more inhalable. Larger sized particles tend to fall back into baths rather than remaining airborne and dispersing throughout the room.

**Volatilization of Chemicals from the Open Surface of MHC Tanks.** Most plating tanks have a free liquid surface from which chemicals can volatilize into the workplace air. Air currents across the tank will accelerate the rate of volatilization. The EPA's Chemical Engineering Branch (CEB) Manual (EPA, 1991a) suggests the following model for evaporation of chemicals from open surfaces:

$$F_{y,o} = 1200\ c_{L,y}\ H_y\ A\ [D_{y,air} v_z/(\pi z)]^{0.5}$$

where:

$F_{y,o}$ = volatilization rate of chemical *y* from open tanks (mg/min)
$c_{L,y}$ = concentration of chemical *y* in bulk liquid (mg/L)
$H_y$ = dimensionless Henry's Law Constant ($H_c$) for chemical y
$D_{y,air}$ = molecular diffusion coefficient of chemical *y* in air (cm$^2$/sec)
$v_z$ = air velocity (m/sec)
z = distance along the pool surface (m)
A = bath area (m$^2$)

Some limitations of the model should be pointed out. The model was developed to predict the rate of volatilization of pure chemicals, not aqueous solutions. The model was also

derived using pure chemicals. As a result, the model implicitly assumes that mass transfer resistance on the gas side is the limiting factor. The model may overestimate volatilization of chemicals from solutions when liquid-side mass transfer is the controlling factor.

**Calculation of Chemical Concentration in Workplace Air from Emission Rates.** The indoor air concentration is estimated from the following equation (EPA, 1991a):

$$C_y = F_{y,T}/(V_R R_V k)$$

where:

$C_y$ = workplace contaminant concentration ($mg/m^3$)
$F_{y,T}$ = total emission rate of chemical from all sources (mg/min)
$V_R$ = room volume ($m^3$)
$R_V$ = room ventilation rate ($min^{-1}$)
k = dimensionless mixing factor

The mixing factor accounts for slow and incomplete mixing of ventilation air with room air. A value of 1.0 was used for this factor. The CEB Manual commonly uses values of the ventilation rate Q from 500 $ft^3$/min to 3,500 $ft^3$/min. Ventilation rates for MHC lines were determined from the facility data. An air turnover rate of 0.021 per minute (1.26 per hour) was used, which is based on estimated air turnover rates that yield 90th percentile air concentrations from Monte Carlo analysis. (This is explained in detail in Appendix D.) An average room volume was used from questionnaire data assuming a ten foot room height.

Other assumptions pertaining to these air models include the following:

- Deposition on equipment, condensation of vapors, and photodegadation are negligible.
- Incoming air is contaminant-free.
- The concentration of contaminant at the beginning of the day is zero.
- As much air enters the room as exits through ventilation (mass balance).
- Room air and ventilation air mix ideally.

**Sensitivity Analysis.** Model sensitivity and uncertainty was examined using Monte Carlo analysis with the air transport equations outlined above and probability distributions for each parameter based on data from the IPC Workplace Practices Questionnaire (see Appendix D for details). This was done with a Monte Carlo software package (Crystal Ball™ [Decisioneering, Inc., 1993]) in conjunction with a spreadsheet program.

This analysis suggested that a few parameters are key to modeling chemical flux from PWB tanks. These key parameters are air turnover rate, bath temperature, chemical concentration in the bath, and Henry's Law Constant.

The air model's sensitivity to these parameters and their uncertainty provides a means of isolating them from less important variables. Isolating these variables allows for additional scrutiny to be placed upon the point estimate assumptions used for them in the volatilization models.

The air turnover rate assumption contributes most to overall model variance. The chemical bath concentration and bath temperature also contribute variance to the model, but are less important than air turnover rate. This statement is fortified by the fact that relatively accurate information is available on their distributions. $H_C$ appears to be least important of the four, but may have more variability associated with it. The models appear to be largely indifferent to small changes in most other parameters.

**Modeling Air Concentrations for Population Exposure**

The following approach was used for dispersion modeling of air emissions from a single facility:

- Model: Industrial Source Complex Long Term ISC(2)LT model from the Risk*Assistant™ software.
- Building (release) height: 3m.
- Area source: 10 x 10 m.
- Meteorological data: an average emission rate-to-air concentration factor of $2.18 \times 10^{-6}$ min/m$^3$ was determined using data for Oakland, California; Denver, Colorado; and Phoenix, Arizona. (These three areas give the highest modeled concentrations around a facility for any available city data in the model.)
- Other parameters: regulatory default values were used. (These are model defaults pertaining to plume rise, stack-tip downwash, buoyancy-induced dispersion, wind profile exponents, vertical temperature gradient, and buildings adjacent to the emission source.)
- Setting: urban mode. (The setting can be either rural or urban. The urban setting is appropriate for urban areas or for large facilities.)
- Chemical degradation in air: not included in modeling.
- Location for exposure point concentrations: a standard polar grid[3] with 36 vector directions and one distance ring (at 100m) was used; the highest modeled air concentration in any direction at 100 meters was used to estimate population exposure.

Because of the short time expected for chemical transport to nearby residents, chemical degradation is not taken into account. The emission rates calculated for workplace inhalation exposures are used for the source emission rates to ambient air. Ambient air concentrations were not modeled for those chemicals with facility emission rates less than 23 kg/year (44 mg/min), with the exception of formaldehyde, which was included because it is a potential carcinogen. Results of ambient air modeling are presented in Table 3.10. Proprietary chemical results are not presented to protect proprietary chemical identities.

[3] A polar grid is a coordinate system that describes the location of a point by means of direction and distance in relation to a central point (e.g., two miles northeast of the center). In the model, a series of regularly-spaced concentric distance rings are defined at chosen intervals along with a defined number of direction vectors (e.g., north, south, east, west, northeast, northwest, southeast, and southwest would be eight directions).

**Table 3.10 Results of Ambient Air Modeling**

| Chemical[a] | Emission Rate[b] (mg/min) | Air Conc. ($mg/m^3$) |
|---|---|---|
| **Electroless Copper, non-conveyorized** | | |
| 2-Ethoxyethanol | 1.46e+03 | 3.17e-03 |
| Formaldehyde | 1.37e+01 | 3.00e-05 |
| Isopropyl Alcohol; or 2-Propanol | 5.24e+02 | 1.14e-03 |
| Methanol | 2.31e+02 | 5.03e-04 |
| **Electroless Copper, conveyorized** | | |
| 2-Ethoxyethanol | 1.55e+03 | 3.38e-03 |
| Formaldehyde | 3.66e+01 | 7.97e-05 |
| Formic Acid | 7.90e+01 | 1.72e-04 |
| Isopropyl Alcohol; or 2-Propanol | 1.04e+03 | 2.26e-03 |
| Methanol | 4.28e+02 | 9.34e-04 |
| **Non-Formaldehyde Electroless Copper, non-conveyorized** | | |
| Isopropyl Alcohol; or 2-Propanol | 7.34e+01 | 1.60e-04 |
| **Tin-Palladium, non-conveyorized** | | |
| Isopropyl Alcohol; or 2-Propanol | 2.94e+02 | 6.42e-04 |
| **Tin-Palladium, conveyorized** | | |
| Ethanolamine | 5.23e+01 | 1.14e-04 |
| Isopropyl Alcohol; or 2-Propanol | 2.34e+02 | 5.11e-04 |

[a] Proprietary chemical results are not presented in order to protect proprietary chemical identities.

[b] Only those chemicals with an emission rate at least 23 kg/year (44 mg/min), plus formaldehyde, are listed. Carbon, conductive polymer, graphite, and organic-palladium had no modeled emission rates above this cut-off.

Note: The numeric format used in these tables is a form of scientific notation, where the "e" replaces the " x $10^{x}$" in scientific notation. Scientific notation is typically used to present very large or very small numbers. For example, 1.2e-04 is the same as $1.2 \times 10^{-4}$, which is the same as 0.00012 in common decimal notation.

## Surface Water

Environmental releases to surface water were not quantified because chemical constituents and concentrations in wastewater could not be adequately characterized for the MHC line alone. This is because PWB manufacturers typically combine wastewater effluent from the MHC process line with effluent from other PWB manufacturing processes prior to on-site wastewater pretreatment. The pretreated wastewater is then discharged to a POTW. Many PWB manufacturers measure copper concentrations in effluent from on-site pretreatment facilities in accordance with POTW discharge permits, but they do not measure copper concentrations in MHC line effluent prior to pretreatment. Because there are many sources of copper-contaminated wastewater in PWB manufacturing, the contribution of the MHC line to overall copper discharges could not be estimated. Furthermore, most of the MHC alternatives contain copper, but because these technologies are only now being implemented in the U.S., their influence on total copper discharges from a PWB facility cannot be determined. Finally, while data are available on copper discharges from PWB facilities, data are not available for some of the other metals found in alternatives to electroless copper. Although ecological hazards are assessed in Section 3.3, without exposure or release data ecological risk could not be addressed in the risk characterization.

### 3.2.4 Exposure Parameters and Potential Dose Rate Models

This section contains information on models and parameter values for workplace and population exposure estimates. First, more detailed data from the IPC Workplace Practices Questionnaire are presented, then the exposure models and parameter values used in those models are described.

**Workplace Exposure Parameter Values**

Data on the frequency and duration of activities indicate the amount of time a worker may be exposed through workplace activities. Questionnaire data pertaining to various worker activities follow.

**Line Operation.** The time per shift that an MHC line operates gives an indication of the daily exposure duration associated with line operation. Time per shift varies by process type and degree of automation. It is probably also influenced by the total amount of PWB processed at a facility and MHC line capacity. Because limited data do not allow differentiation between MHC line operation needs for the various process alternatives, the same period of time for line operation is assumed for all process alternatives. This time, for all processes, ranges from one to 12 hours per shift, with an average of 6.8 hours per shift and a 90th percentile value of eight hours per shift.

**Chemical Bath Sampling.** Table 3.11 presents questionnaire data pertaining to duration and frequency of chemical bath sampling. These parameters are assumed to vary by MHC technology, but not by equipment configuration (e.g., non-conveyorized or conveyorized).

**Chemical Additions.** Table 3.12 presents questionnaire and supplier data pertaining to duration and frequency of chemical additions. Duration data indicate the amount of time a worker may be exposed to the chemicals being added to the bath. Although duration data vary by process and bath type, greater variation may be due to differences in facility operating procedures than differences inherent to process alternatives. Therefore, the same duration is assumed for all facilities, regardless of process, equipment, or bath type. Frequency of chemical additions was determined from supplier-provided data, typically a supplier's Product Data Sheet, which recommends a schedule for chemical additions based on time, amount of PWB (ssf) processed, or bath concentrations determined through sampling. For the purposes of this assessment, schedules based on time or ssf of PWB processed were used.

**Chemical Bath Replacement.** Table 3.13 presents questionnaire data pertaining to duration of chemical bath replacement. Questionnaire data were combined regardless of process configuration for replacement duration. Bath replacement frequency for conveyorized lines was determined specifically for type of bath. The 90th percentile frequencies are presented in Table 3.14.

**Table 3.11 Duration and Frequency of Chemical Bath Sampling**

| Process Alternative (number responding)[a] | Duration of Sampling (minutes) | | Frequency of Sampling (occur./year) | | Total Responses for All Baths |
|---|---|---|---|---|---|
| | Average[b] | 90th Percentile | Average[b] | 90th Percentile | |
| Electroless Copper (32) | 0.44 - 5.4 | 3 | 217 - 996 | 720 | 212 |
| Carbon (2) | 2.0 | 2 | 220 | 220 | 8 |
| Conductive Polymer (1) | 1.0 | 1 | 100 - 460 | 414 | 3 |
| Graphite (4) | 1.0 - 5.5 | 10 | 213 - 255 | 260 | 13 |
| Non-Formaldehyde Electroless Copper (1) | 1.0 | 1 | 50 - 260 | 260 | 5 |
| Organic-Palladium (2) | 1.5 - 2 | 2 | 230 - 490 | 250 | 13 |
| Tin-Palladium (12) | 1.2 - 4.0 | 2 | 210 - 660 | 520 | 65 |

[a] Five facilities did not respond to this question.
[b] Range of averages for each bath type.

**Table 3.12 Duration and Frequency of Chemical Additions**

| Facility Type | Duration of Chemical Additions (minutes)[a] | | Frequency of Chemical Additions (times/year)[b] |
|---|---|---|---|
| | Average | 90th Percentile | |
| Electroless Copper | 3.6 - 10[c] | ND | 0.4 - 52[c] |
| Carbon | 2 - 10[c] | ND | 1 - 58[c] |
| Graphite | 2 - 19[c] | ND | 4 - 44[c] |
| Non-Formaldehyde Electroless Copper | 2, regardless of bath type | ND | |
| Organic-Palladium | 20 - 25[c] | ND | 11 - 52[c] |
| Tin-Palladium | 5 - 15[c] | ND | 0.7 - 12[c] |
| All Facilities, regardless of process type | 8.6 | 20 | ND |

[a] From IPC Workplace Practices Questionnaire and Performance Demonstration database.
[b] Based on supplier-provided information.
[c] Depending on bath type.
ND: Not Determined.

**Table 3.13 Duration of Chemical Bath Replacement**

| Process Alternative (number responding) | Duration (minutes) | | |
|---|---|---|---|
| | Average[a] | 90th Percentile | Total Responses for All Baths |
| Electroless Copper (36) | 41 - 147 | 180 | 205 |
| Carbon (2) | 15 - 180 | 180 | 8 |
| Conductive Polymer (1) | 60 - 240 | 228 | 3 |
| Graphite (3) | 18 - 240 | 219 | 10 |
| Non-Formaldehyde Electroless Copper (1) | 30 | 30 | 5 |
| Organic-Palladium (2) | 30 - 360 | 108 | 13 |
| Tin-Palladium (13) | 31 - 110 | 180 | 75 |
| All Facilities | 78 | ND | 350 |

[a] Range of averages for each bath type.
ND: Not Determined.

**Table 3.14 Frequency of Chemical Bath Replacement for Conveyorized Processes**

| Process Alternative | Bath Type | 90th Percentile Frequency (occur./year) | Bath Type | 90th Percentile Frequency (occur./year) |
|---|---|---|---|---|
| Electroless Copper | Conditioner/Cleaner<br>Microetch<br>Predip<br>Catalyst | 24<br>50<br>24<br>1 | Accelerator<br>Electroless<br>Copper<br>Acid Dip<br>Anti-Tarnish | 16<br>4<br>50<br>28 |
| Carbon | Cleaner<br>Conditioner | 30<br>30 | Carbon Black<br>Microetch | 1<br>145 |
| Conductive Polymer | Microetch<br>Cleaner/Conditioner | 20.5<br>13 | Catalyst<br>Conductive Polymer | 1<br>17 |
| Graphite | Cleaner/Conditioner<br>Graphite | 56<br>7.3 | Microetch | 145 |
| Organic-Palladium | Conditioner<br>Microetch<br>Predip | 32<br>1<br>230 | Conductor<br>Post-Dip | 1<br>20 |
| Tin-Palladium | Cleaner/Conditioner<br>Predip<br>Catalyst | 141<br>151<br>1 | Accelerator<br>Microetch<br>Acid Dip | 47<br>65<br>230 |

**Conveyor Equipment Cleaning.** For conveyor equipment cleaning, nine facilities responded out of a total of 11 conveyorized systems. For these facilities:

- Duration of conveyor equipment cleaning ranged from 0.5 to 480 minutes, with an average of 140 minutes and 90th percentile of 288 minutes.
- Frequency of conveyor equipment cleaning ranged from two to 260 times per year, with an average of 55 times per year and 90th percentile of 92 times per year.

**Bath Filter Replacement.** Table 3.15 presents data on duration and frequency of bath filter replacement. For filter replacement, depending on bath and process types, the average duration ranges from one to 31 minutes and the average frequency ranges from 12 to 300 times per year. The frequency data used for intake model parameters is process-specific. Again, the duration for all facilities is assumed, regardless of process alternative or bath type.

**Working in the Process Area.** Table 3.16 presents questionnaire data pertaining to the amount of time various types of workers spend working in the MHC process area. Frequency is considered to be the days/year the MHC line is in operation (an average of 250 days/year and 90th percentile of 306 days/year).

**Table 3.15 Filter Replacement**

| Process Alternative (number responding)[a] | Duration (minutes) | | Total Responses for All Baths | Frequency (occur./year) | | Total Responses for All Baths |
|---|---|---|---|---|---|---|
| | Average[b] | 90th Percentile | | Average[b] | 90th Percentile | |
| Electroless Copper (20) | 8 - 31 | ND | 82 | 37 - 200 | 100 | 76 |
| Carbon (2) | 5 | ND | 6 | 12 - 20 | 20 | 6 |
| Conductive Polymer (1) | 5 - 10 | ND | 4 | 12.5 - 115 | 74 | 4 |
| Graphite (4) | 7 - 10 | ND | 9 | 67 - 107 | 103 | 9 |
| Non-Formaldehyde Electroless Copper (1) | 1 - 5 | ND | 2 | 16.7 | 17 | 2 |
| Organic-Palladium (2) | 2 - 3.5 | ND | 10 | 12 - 38 | 50 | 10 |
| Tin-Palladium (3) | 5 - 11 | ND | 14 | 24 - 300 | 74 | 14 |
| All Facilities | 13 | 20 | 138 | ND | ND | 138 |

[a] Sixteen facilities did not respond to this question.
[b] Range of averages for each bath type.
ND: Not Determined.

**Table 3.16 Duration of Working in the Process Area**

| Worker Type | Range (hours/shift) | Average (hours/shift) | 90th Percentile (hours/shift) |
|---|---|---|---|
| Line Operators | 3.3 - 10 | 7.8 | 8 |
| Laboratory Technicians | 0.1 - 10 | 3.9 | 8 |
| Maintenance Workers | 0.15 - 10 | 3.1 | 8 |
| Supervisory Personnel | 0.23 - 10 | 4.7 | 8 |
| Wastewater Treatment Operators | 0.1 - 10 | 4.4 | 8 |
| Contract Workers | 0.25 | 0.25 | 0.25 |
| Other Employees | 0.18 - 8 | 3.4 | 5.6 |

## Workplace Exposure Models

The general models for calculating inhalation and dermal potential dose rates are discussed below.

**Daily Inhalation Exposures.** The general model for inhalation exposure to workers is from CEB (EPA, 1991a):

$$I = (Cm)(b)(h)$$

where:

- I = daily inhalation potential dose rate (mg/day)
- Cm = airborne concentration of substance ($mg/m^3$) (note: this term is denoted "$C_y$" in air modeling equation in Section 3.2.3)
- b = inhalation rate ($m^3/hr$)
- h = duration (hr/day)

Data for these parameters are in Table 3.17.

**Table 3.17 Parameter Values for Daily Workplace Inhalation Exposures**

| Parameter | Units | Value | Source of Data, Comments |
|---|---|---|---|
| Cm | $mg/m^3$ | Modeled from single or average bath concentrations | |
| b | $m^3/hr$ | 1.25 | EPA, 1991a (data from NIOSH, 1976). |
| Duration (h) | | | |
| Line Operation | hours/day | 8 | From IPC Workplace Practices Questionnaire, 90th percentile for hours of MHC line operation, all process types (assuming hours/shift = hours/day). |
| Working in Process Area | hours/day | 8 | From IPC Workplace Practices Questionnaire, 90th percentile for hours/shift for first shift, all process types. |

**Daily Workplace Dermal Exposures.** The general model for potential dose rate via dermal exposure to workers is from CEB (EPA, 1991a):

$$D = SQC$$

where:

D = dermal potential dose rate (mg/day)
S = surface area of contact ($cm^2$)
Q = quantity typically remaining on skin ($mg/cm^2$)
C = concentration of chemical (percent)

Because a line operator is expected to have dermal contact with the chemicals in a given bath several times a day in the course of normal operations, the total time of contact combined with a flux rate (rate of chemical absorption through the skin) is believed to give a more realistic estimate of dermal exposure. The flux of a material through the skin is estimated in terms of mg absorbed per $cm^2$ per unit of time. Using flux of material through the skin, (based on EPA, 1992a) the equation is modified to:

$$D = (S)(C)(f)(h)(0.001)$$

where:

D = dermal potential dose rate (mg/day)
S = surface area of contact ($cm^2$)
C = concentration of chemical (mg/L)
f = flux through skin (cm/hour)
h = duration (hours/day)
with a conversion factor of 0.001 $L/cm^3$

This second equation was used for all workplace dermal exposure estimates.

Data for duration of contact (h) from the IPC Workplace Practices Questionnaire are included in Table 3.18.

**Table 3.18 Parameter Values for Daily Workplace Dermal Exposures**

| Parameter | Units | Value | | Source of Data, Comments |
|---|---|---|---|---|
| C | % | Range of reported values and average determined from publicly-available chemistry data and from disclosed proprietary ingredient information (see Section 2.1.4 and Appendix B). | | |
| S | $cm^2$ | 1,300 | | CEB Table 4-13, routine immersion, 2 hands, assuming gloves not worn. |
| Flux Through Skin (f) | cm/hr | Default for inorganics: 0.001<br>estimate for organics by:<br>log f = -2.72+0.71 log $K_{ow}$ -0.0061(MW)<br>($K_{ow}$ = octanol/water partition coefficient, MW = molecular weight) | | EPA, 1992a. |
| Duration of Contact (h) | | | | |
| Line Operation | hours/day | 8 | | 90th percentile from IPC Workplace Practices Questionnaire, hours of MHC line operation, all process types excluding conveyorized processes. |
| | | *electroless copper* (19 baths) | 0.42 | Corrected for typical number of baths in a process, including rinse baths. |
| | | *non-formaldehyde electroless copper* (17 baths) | 0.47 | |
| | | *organic-palladium* (12 baths) | 0.67 | |
| | | *tin-palladium* (14 baths) | 0.57 | |
| Chemical Bath Replacement | min/occur | *carbon* | 180 | 90th percentile from IPC Workplace Practices Questionnaire. |
| | | *conductive polymer* | 228 | |
| | | *electroless copper* | 180 | |
| | | *graphite* | 219 | |
| | | *non-formaldehyde electroless copper* | 30 | |
| | | *organic-palladium* | 108 | |
| | | *tin-palladium* | 180 | |
| Conveyor Equipment Cleaning | min/occur | 288 | | 90th percentile from IPC Workplace Practices Questionnaire, conveyorized lines. |
| Filter Replacement | min/occur | 20 | | 90th percentile from IPC Workplace Practices Questionnaire, all process types. |
| Chemical Bath Sampling | min/occur | *carbon* | 2 | 90th percentile from IPC Workplace Practices Questionnaire, excluding automated sampling. |
| | | *conductive polymer* | 1 | |
| | | *electroless copper* | 5 | |
| | | *graphite* | 10 | |
| | | *non-formaldehyde electroless copper* | 1 | |
| | | *organic-palladium* | 2 | |
| | | *tin-palladium* | 2 | |

Daily exposures are averaged over a lifetime (70 years) for carcinogens, and over the exposure duration (e.g., 25 years working in a facility) for non-carcinogens[4] using the following equations. To estimate average daily doses for inhalation:

$$LADD = (I)(EF)(ED)/[(BW)(AT_{CAR})]$$
$$ADD = (I)(EF)(ED)/[(BW)(AT_{NC})]$$

where:

LADD = lifetime average daily dose (mg/kg-day) (for carcinogens)
ADD = average daily dose (mg/kg-day) (for non-carcinogens)
I = daily inhalation potential dose rate (mg/day)
EF = exposure frequency (days/year)
ED = exposure duration (years)
BW = body weight (kg)
$AT_{CAR}$ = averaging time for carcinogenic effects (days)
$AT_{NC}$ = averaging time for non-carcinogenic effects (days)

To estimate average daily doses from dermal contact:

$$LADD = (D)(EF)(ED)/[(BW)(AT_{CAR})]$$
$$ADD = (D)(EF)(ED)/[(BW)(AT_{NC})]$$

where:

D = dermal potential dose rate (mg/day)

Parameter values for estimating worker's potential dose rates are presented in Table 3.19. Results of estimating inhalation and dermal ADDs (and the inhalation LADD for formaldehyde) are presented in Table 3.20 and Appendix E. Proprietary chemical results are not presented in order to protect proprietary chemical identities. The frequency data for activities pertaining to operating an MHC line could apply to more than one line worker, although they are assumed here to apply to a single, typical line operator. For example, facilities reported from one to 18 line operators working at one time, with an average of three line operators working the first shift. Therefore, the frequency of various worker activities pertaining to a single line operator may be overestimated by about a factor of three.

[4] Different averaging times are used for characterizing risk for carcinogenic and non-carcinogenic effects. For carcinogenic agents, because even a single incidence of exposure is assumed to have the potential to cause cancer throughout an individual's lifetime, the length of exposure to that agent is averaged over a lifetime. An additional factor is that the cancer latency period may extend beyond the period of working years before it is discernible. For chemicals exhibiting non-cancer health effects from chronic (longer-term) exposure, where there is an exposure threshold (a level below which effects are not expected to occur); only the time period when exposure is occurring is assumed to be relevant and is used as the averaging time.

**Table 3.19 Parameter Values for Estimating Average Workplace Exposures (for line operators)**

| Parameter | Units | Value | | Source of Data, Comments |
|---|---|---|---|---|
| **Exposure Frequency (EF): Inhalation Exposure** | | | | |
| Line Operation & Working in Process Area | days/year | 306 | | 90th percentile, days/year MHC line operates from IPC Workplace Practices Questionnaire, all process types (average is 250 days/year). |
| **EF: Dermal Exposure** | | | | |
| Line Operation | days/year | 306 | | 90th percentile, days/year MHC line operates from IPC Workplace Practices Questionnaire, all process types. |
| Chemical Bath Replacement | occur/year | *electroless copper*<br>*carbon*<br>*conductive polymer*<br>*graphite*<br>*organic-palladium*<br>*tin-palladium* | 1 - 50<br>1 - 145<br>1 - 20.5<br>7.3 - 145<br>1 - 230<br>1 - 230 | 90th percentiles for conveyorized processes from IPC Workplace Practices Questionnaire (see Table 3.14). |
| Conveyor Equipment Cleaning | occur/year | 92 | | 90th percentile from IPC Workplace Practices Questionnaire, for conveyorized lines. |
| Filter Replacement | occur/year | *electroless copper*<br>*carbon*<br>*conductive polymer*<br>*graphite*<br>*non-formaldehyde electroless copper*<br>*organic-palladium*<br>*tin-palladium* | 100<br>20<br>74<br>103<br>17<br>50<br>74 | 90th percentiles from IPC Workplace Practices Questionnaire. |
| Chemical Bath Sampling | occur/year | *electroless copper*<br>*carbon*<br>*conductive polymer*<br>*graphite*<br>*non-formaldehyde electroless copper*<br>*organic-palladium*<br>*tin-palladium* | 720<br>220<br>414<br>260<br>260<br>250<br>520 | 90th percentiles from IPC Workplace Practices Questionnaire, excluding automated sampling. |
| **Parameters Pertaining to All Workplace Exposures (for Line Operators)** | | | | |
| Exposure Duration (ED) | years | 25 | | 95th percentile for job tenure (Bureau of Labor Statistics, 1990). (Median tenure for U.S. males is 4 years; Bureau of Labor Statistics, 1997.) |
| Body Weight (BW) | kg | 70 | | Average for adults (EPA, 1991b). |
| Averaging Time (AT)<br>$AT_{CAR}$<br>$AT_{NC}$ | days | <br>25,550<br>9,125 | | <br>70 yrs (average lifetime)*365 d/yr<br>25 yrs (ED)*365 d/yr |

**Table 3.20 Estimated Average Daily Dose (ADD) for Workplace Exposure - Inhalation and Dermal**

| Chemical[a] | ADD (mg/kg-day) | | |
|---|---|---|---|
| | Inhalation | Dermal | |
| | Line Operator | Line Operator | Laboratory Technician |
| **Electroless Copper, non-conveyorized** | | | |
| Ammonium Chloride | NA | 8.4e-02 | 2.1e-03 |
| Benzotriazole | 6.64e-04 | 2.5e-03 | 6.1e-05 |
| Boric Acid | 9.15e-04 | 3.3e-02 | 8.0e-04 |
| Copper (I) Chloride | 4.05e-04 | 4.4e-02 | 1.1e-03 |
| Copper Sulfate; or Cupric Sulfate | 4.45e-04 | 4.9e-02 | 1.2e-03 |
| Dimethylaminoborane | 1.04e-02 | 3.9e-03 | 9.6e-05 |
| Dimethylformamide | 7.58e-03 | 1.1e-03 | 2.8e-05 |
| Ethanolamine | 5.31e-02 | 1.0e-02 | 2.5e-04 |
| 2-Ethoxyethanol | 7.79e+00 | 1.4e-01 | 3.4e-03 |
| Ethylene Glycol | 1.78e-02 | 2.5e-03 | 6.0e-05 |
| Ethylenediaminetetraacetic Acid (EDTA) | 2.74e-03 | 1.7e-05 | 4.2e-07 |
| Fluoroboric Acid | 1.18e-02 | 3.9e-01 | 9.6e-03 |
| Formaldehyde | 7.36e-02 | 1.1e-02 | 2.6e-04 |
| Formaldehyde (LADD)[b] | 2.63e-02 | NA | NA |
| Formic Acid | 1.88e-01 | 3.5e-02 | 8.5e-04 |
| Hydrochloric Acid | 2.91e-05 | 9.0e-01 | 2.2e-02 |
| Hydrogen Peroxide | 8.87e-04 | 1.3e-01 | 3.2e-03 |
| Hydroxyacetic Acid | 1.68e-04 | 2.4e-02 | 5.9e-04 |
| Isopropyl Alcohol; or 2-Propanol | 2.81e+00 | 3.1e-02 | 7.7e-04 |
| Magnesium Carbonate | 5.35e-05 | 7.8e-03 | 1.9e-04 |
| Methanol | 1.24e+00 | 1.1e-02 | 2.8e-04 |
| m-Nitrobenzene Sulfonic Acid | 4.90e-06 | 8.8e-07 | 2.2e-08 |
| p-Toluene Sulfonic Acid | NA | 4.0e-03 | 9.8e-05 |
| Palladium | NA | 2.4e-03 | 5.8e-05 |
| Peroxymonosulfuric Acid | 1.15e-03 | 1.7e-01 | 4.2e-03 |
| Potassium Bisulfate | 6.15e-04 | 9.0e-02 | 2.2e-03 |
| Potassium Cyanide | 1.35e-05 | 1.5e-03 | 3.6e-05 |
| Potassium Hydroxide | 1.25e-05 | 5.4e-03 | 1.3e-04 |
| Potassium Persulfate | 4.37e-04 | 6.4e-02 | 1.6e-03 |
| Potassium Sulfate | 8.56e-04 | 1.3e-01 | 3.1e-03 |
| Potassium-Sodium Tartrate | 1.90e-03 | 2.1e-01 | 5.0e-03 |
| Sodium Bisulfate | NA | 4.6e-01 | 1.1e-02 |
| Sodium Carbonate | 3.03e-06 | 3.3e-04 | 8.03-06 |
| Sodium Chlorite | NA | 3.0e-02 | 7.2e-04 |

| Chemical[a] | ADD (mg/kg-day) | | |
|---|---|---|---|
| | Inhalation | Dermal | |
| | Line Operator | Line Operator | Laboratory Technician |
| Sodium Cyanide | 1.40e-05 | 1.5e-03 | 3.7e-05 |
| Sodium Hydroxide | 6.30e-04 | 8.5e-02 | 2.1e-03 |
| Sodium Hypophosphite | NA | 5.6e-02 | 1.4e-03 |
| Sodium Sulfate | NA | 8.3e-02 | 2.0e-03 |
| Stannous Chloride | NA | 6.7e-02 | 1.6e-03 |
| Sulfuric Acid | 6.67e-03 | 1.2e+00 | 2.9e-02 |
| Tartaric Acid | 6.24e-05 | 5.7e-05 | 1.4e-06 |
| Triethanolamine; or 2,2',2"-Nitrilotris Ethanol | NA | 3.5e-03 | 8.5e-05 |
| **Electroless Copper, conveyorized** | | | |
| Ammonium Chloride | NA | 2.1e-02 | 2.1e-03 |
| Benzotriazole | NA | 6.3e-04 | 6.1e-05 |
| Boric Acid | NA | 9.2e-03 | 8.0e-04 |
| Copper (I) Chloride | NA | 9.8e-03 | 1.1e-03 |
| Copper Sulfate; or Cupric Sulfate | NA | 1.1e-02 | 1.2e-03 |
| Dimethylaminoborane | NA | 1.1e-03 | 9.6e-05 |
| Dimethylformamide | NA | 2.8e-04 | 2.8e-05 |
| Ethanolamine | NA | 2.5e-03 | 2.5e-04 |
| 2-Ethoxyethanol | NA | 3.5e-02 | 3.4e-03 |
| Ethylene Glycol | NA | 6.5e-04 | 6.0e-05 |
| Ethylenediaminetetraacetic Acid (EDTA) | NA | 3.8e-06 | 4.2e-07 |
| Fluoroboric Acid | NA | 9.4e-02 | 9.6e-03 |
| Formaldehyde | NA | 2.4e-03 | 2.6e-04 |
| Formic Acid | NA | 8.6e-03 | 8.5e-04 |
| Hydrochloric Acid | NA | 2.1e-01 | 2.2e-02 |
| Hydrogen Peroxide | NA | 3.6e-02 | 3.2e-03 |
| Hydroxyacetic Acid | NA | 6.0e-03 | 5.9e-04 |
| Isopropyl Alcohol; or 2-Propanol | NA | 7.8e-03 | 7.7e-04 |
| Magnesium Carbonate | NA | 2.2e-03 | 1.9e-04 |
| Methanol | NA | 2.6e-03 | 2.8e-04 |
| m-Nitrobenzene Sulfonic Acid | NA | 2.2e-07 | 2.2e-08 |
| p-Toluene Sulfonic Acid | NA | 9.9e-04 | 9.8e-05 |
| Palladium | NA | 5.2e-04 | 5.8e-05 |
| Peroxymonosulfuric Acid | NA | 4.7e-02 | 4.2e-03 |
| Potassium Bisulfate | NA | 2.5e-02 | 2.2e-03 |
| Potassium Cyanide | NA | 3.3e-04 | 3.6e-05 |
| Potassium Hydroxide | NA | 1.4e-03 | 1.3e-04 |

| Chemical[a] | ADD (mg/kg-day) | | |
|---|---|---|---|
| | Inhalation | Dermal | |
| | Line Operator | Line Operator | Laboratory Technician |
| Potassium Persulfate | NA | 1.8e-02 | 1.6e-03 |
| Potassium Sulfate | NA | 3.5e-02 | 3.1e-03 |
| Potassium-Sodium Tartrate | NA | 4.6e-02 | 5.0e-03 |
| Sodium Bisulfate | NA | 1.0e-01 | 1.1e-02 |
| Sodium Carbonate | NA | 7.3e-05 | 8.0e-06 |
| Sodium Chlorite | NA | 7.0e-03 | 7.2e-04 |
| Sodium Cyanide | NA | 3.4e-04 | 3.7e-05 |
| Sodium Hydroxide | NA | 1.9e-02 | 2.1e-03 |
| Sodium Hypophosphite | NA | 1.3e-02 | 1.4e-03 |
| Sodium Sulfate | NA | 1.8e-02 | 2.0e-03 |
| Stannous Chloride | NA | 1.5e-02 | 1.6e-03 |
| Sulfuric Acid | NA | 3.2e-01 | 2.9e-02 |
| Tartaric Acid | NA | 1.3e-05 | 1.4e-06 |
| Triethanolamine; or 2,2',2"-Nitrilotris Ethanol | NA | 8.6e-04 | 8.5e-05 |
| **Carbon, conveyorized** | | | |
| Copper Sulfate; or Cupric Sulfate | NA | 1.7e-02 | 1.4e-04 |
| Ethanolamine | NA | 9.6e-03 | 1.3e-04 |
| Potassium Hydroxide | NA | 7.3e-02 | 1.2e-03 |
| Sodium Persulfate | NA | 7.0e-01 | 5.7e-03 |
| Sulfuric Acid | NA | 6.4e-03 | 5.3e-05 |
| **Conductive Polymer, conveyorized** | | | |
| 1H-Pyrrole | NA | 2.6e-02 | 3.3e-04 |
| Peroxymonosulfuric Acid; or Potassium Peroxymonosulfate | NA | 7.0e-01 | 8.8e-03 |
| Phosphoric Acid | NA | 1.0e-01 | 1.3e-03 |
| Sodium Carbonate | NA | 2.5e-02 | 3.3e-04 |
| Sodium Hydroxide | NA | 2.7e-03 | 4.0e-05 |
| Sulfuric Acid | NA | 1.4e-02 | 1.8e-03 |
| **Graphite, conveyorized** | | | |
| Ammonia | NA | 4.2e-03 | 3.3e-04 |
| Copper Sulfate; or Cupric Sulfate | NA | 1.1e-02 | 4.5e-04 |
| Ethanolamine | NA | 5.3e-03 | 3.2e-04 |
| Graphite | NA | 9.8e-02 | 7.7e-03 |
| Peroxymonosulfuric Acid; or Potassium Peroxymonosulfate | NA | 1.2e-01 | 5.1e-03 |
| Potassium Carbonate | NA | 2.1e-02 | 1.3e-03 |
| Sodium Persulfate | NA | 2.4e-01 | 9.7e-03 |
| Sulfuric Acid | NA | 2.4e-01 | 1.0e-02 |

| Chemical[a] | ADD (mg/kg-day) | | |
|---|---|---|---|
| | Inhalation | Dermal | |
| | Line Operator | Line Operator | Laboratory Technician |
| **Non-Formaldehyde Electroless Copper, non-conveyorized** | | | |
| Copper Sulfate; or Cupric Sulfate | 1.47e-03 | 1.7e-01 | 2.7e-04 |
| Hydrochloric Acid | NA | 2.2e-02 | 3.4e-05 |
| Hydrogen Peroxide | 5.01e-04 | 1.2e-01 | 1.9e-04 |
| Isopropyl Alcohol; or 2-Propanol | 3.93e-01 | 1.3e-02 | 2.1e-05 |
| Potassium Hydroxide | 7.99e-06 | 2.2e-03 | 3.5e-06 |
| Potassium Persulfate | 3.04e-04 | 7.2e-02 | 1.1e-04 |
| Sodium Chlorite | NA | 3.3e-02 | 5.2e-05 |
| Sodium Hydroxide | 9.31e-06 | 2.2e-03 | 3.5e-06 |
| Stannous Chloride | NA | 6.9e-02 | 1.1e-04 |
| Sulfuric Acid | 7.94e-04 | 1.7e-01 | 2.6e-04 |
| **Organic-Palladium, non-conveyorized** | | | |
| Hydrochloric Acid | NA | 6.4e-02 | 2.2e-04 |
| Sodium Bisulfate | NA | 7.8e-01 | 2.7e-03 |
| Sodium Carbonate | NA | 2.3e-01 | 7.8e-04 |
| Sodium Hypophosphite | NA | 3.2e-02 | 1.1e-04 |
| Sodium Persulfate | NA | 7.8e-01 | 2.7e-03 |
| Trisodium Citrate 5.5-Hydrate; or Sodium Citrate | NA | 6.7e-03 | 2.3e-05 |
| **Organic-Palladium, conveyorized** | | | |
| Hydrochloric Acid | NA | 1.8e-02 | 2.2e-04 |
| Sodium Bisulfate | NA | 1.5e-01 | 2.6e-03 |
| Sodium Carbonate | NA | 4.8e-02 | 7.8e-04 |
| Sodium Hypophosphite | NA | 6.1e-03 | 1.1e-04 |
| Sodium Persulfate | NA | 1.5e-01 | 2.6e-03 |
| Trisodium Citrate 5.5-Hydrate; or Sodium Citrate | NA | 1.4e-03 | 2.3e-05 |
| **Tin-Palladium, non-conveyorized** | | | |
| 1,3-Benzenediol | NA | 9.7e-03 | 9.7e-05 |
| Copper (I) Chloride | NA | 2.3e-02 | 2.3e-04 |
| Copper Sulfate; or Cupric Sulfate | 3.95e-04 | 1.3e-01 | 1.2e-03 |
| Ethanolamine | 1.07e-01 | 2.7e-02 | 2.7e-04 |
| Fluoroboric Acid | 9.45e-03 | 1.7e-01 | 1.7e-03 |
| Hydrochloric Acid | NA | 2.9e-01 | 2.9e-03 |
| Hydrogen Peroxide | 5.20e-04 | 1.6e-01 | 1.5e-03 |
| Isopropyl Alcohol; or 2-Propanol | 1.58e+00 | 1.6e-02 | 1.6e-04 |
| Lithium Hydroxide | NA | 1.8e-01 | 1.8e-03 |
| Palladium | NA | 8.5e-03 | 8.5e-05 |

| Chemical[a] | ADD (mg/kg-day) | | |
|---|---|---|---|
| | Inhalation | Dermal | |
| | Line Operator | Line Operator | Laboratory Technician |
| Palladium Chloride | NA | 5.3e-03 | 5.3e-05 |
| Potassium Carbonate | NA | 2.9e+00 | 2.9e-02 |
| Sodium Bisulfate | NA | 7.9e-01 | 7.9e-03 |
| Sodium Chloride | NA | 9.0e+00 | 9.0e-02 |
| Sodium Hydroxide | NA | 2.6e-01 | 2.6e-03 |
| Sodium Persulfate | 4.49e-03 | 1.3e+00 | 1.3e-02 |
| Stannous Chloride | NA | 2.8e-01 | 2.8e-03 |
| Sulfuric Acid | 6.21e-04 | 1.9e+00 | 1.9e-02 |
| Triethanolamine; or 2,2',2"-Nitrilotris Ethanol | NA | 2.4e-03 | 2.4e-05 |
| Vanillin | 4.33e-04 | 3.0e-03 | 3.0e-05 |
| **Tin-Palladium, conveyorized** | | | |
| 1,3-Benzenediol | NA | 2.7e-03 | 9.7e-05 |
| Copper (I) Chloride | NA | 8.1e-03 | 2.3e-04 |
| Copper Sulfate; or Cupric Sulfate | NA | 4.9e-02 | 1.2e-03 |
| Ethanolamine | NA | 1.2e-02 | 2.7e-04 |
| Fluoroboric Acid | NA | 6.0e-02 | 1.7e-03 |
| Hydrochloric Acid | NA | 1.1e-01 | 2.9e-03 |
| Hydrogen Peroxide | NA | 6.1e-02 | 1.6e-03 |
| Isopropyl Alcohol; or 2-Propanol | NA | 8.4e-03 | 1.6e-04 |
| Lithium Hydroxide | NA | 6.5e-02 | 1.8e-03 |
| Palladium | NA | 2.4e-03 | 8.5e-05 |
| Palladium Chloride | NA | 1.5e-03 | 5.3e-05 |
| Potassium Carbonate | NA | 1.0e+00 | 2.9e-02 |
| Sodium Bisulfate | NA | 3.3e-01 | 7.9e-03 |
| Sodium Chloride | NA | 3.3e+00 | 9.0e-02 |
| Sodium Hydroxide | NA | 9.2e-02 | 2.6e-03 |
| Sodium Persulfate | NA | 5.2e-01 | 1.3e-02 |
| Stannous Chloride | NA | 7.9e-02 | 2.8e-03 |
| Sulfuric Acid | NA | 1.2e+00 | 1.9e-02 |
| Triethanolamine; or 2,2',2"-Nitrilotris Ethanol | NA | 1.2e-03 | 2.4e-05 |
| Vanillin | NA | 8.4e-04 | 3.0e-05 |

[a] Proprietary chemical results are not presented in order to protect proprietary chemical identities.

[b] LADD is calculated using a carcinogen averaging time ($AT_{CAR}$) of 70 years.

Note: The numeric format used in these tables is a form of scientific notation, where the "e" replaces the " x $10^{x}$" in scientific notation. Scientific notation is typically used to present very large or very small numbers. For example, 1.2e-04 is the same as 1.2 x $10^{-4}$, which is the same as 0.00012 in common decimal notation.

NA: Not Applicable. A number was not calculated because the chemical's vapor pressure is below the 1 x $10^{-3}$ torr cutoff and is not used in any sparged bath. Inhalation exposures are therefore expected to be negligible. LADDs were not calculated for dermal exposure.

## Population Exposure

The equation for estimating ADDs from inhalation for a person residing near a facility is:

$$LADD = (Ca)(IR)(EF)(ED)/[(BW)(AT_{CAR})]$$
$$ADD = (Ca)(IR)(EF)(ED)/[(BW)(AT_{NC})]$$

where:

LADD = lifetime average daily dose (mg/kg-day) (for carcinogens)
ADD = average daily dose (mg/kg-day) (for non-carcinogens)
Ca = chemical concentration in air ($mg/m^3$) (from air dispersion modeling, described in Section 3.2.3)
IR = inhalation rate ($m^3$/day)
EF = exposure frequency (day/yr)
ED = exposure duration (years)
BW = average body weight (kg)
$AT_{CAR}$ = averaging time for carcinogenic effects (days)
$AT_{NC}$ = averaging time for non-carcinogenic chronic effects (days)

Table 3.21 presents values used for these parameters.

**Table 3.21 Parameter Values for Estimating Nearby Residential Inhalation Exposure**

| Parameter | Units | Value | Source of Data, Comments |
|---|---|---|---|
| Ca | $mg/m^3$ | Modeled, varies by chemical and process type. | |
| IR | $m^3$/day | 15 | Total home exposures for adults based on activity patterns and inhalation rates (EPA, 1997). |
| EF | days/year | 350 | Assumes 2 weeks per year spent away from home (EPA, 1991b). |
| ED | years | 30 | National upper 90th percentile at one residence (EPA, 1990). |
| BW | kg | 70 | Average value for adults (EPA, 1991b). |
| AT<br>$AT_{CAR}$<br>$AT_{NC}$ | days | <br>25,550<br>10,950 | <br>70 yrs*365 days/year<br>ED * 365 days/year |

Results for general population inhalation exposure are presented in Table 3.22 and Appendix E. Proprietary chemical results are not presented in order to protect proprietary chemical identities.

**Table 3.22 Estimated Average Daily Dose (ADD) for General Population Inhalation Exposure**

| Chemical[a] | ADD (mg/kg-day) |
|---|---|
| **Electroless Copper, non-conveyorized** | |
| 2-Ethoxyethanol | 6.5e-04 |
| Formaldehyde | 7.4e-06 |
| Formaldehyde (LADD)[b] | 2.6e-06 |
| Isopropyl Alcohol; or 2-Propanol | 2.4e-04 |
| Methanol | 1.0e-04 |
| **Electroless Copper, conveyorized** | |
| 2-Ethoxyethanol | 7.0e-04 |
| Formaldehyde | 2.0e-05 |
| Formaldehyde (LADD)[b] | 7.0e-06 |
| Formic Acid | 3.5e-05 |
| Isopropyl Alcohol; or 2-Propanol | 4.6e-04 |
| Methanol | 1.9e-04 |
| **Non-Formaldehyde Electroless Copper, non-conveyorized** | |
| Isopropyl Alcohol; or 2-Propanol | 3.3e-05 |
| **Tin-Palladium, non-conveyorized** | |
| Isopropyl Alcohol; or 2-Propanol | 1.3e-04 |
| **Tin-Palladium, conveyorized** | |
| Ethanolamine | 2.3e-05 |
| Isopropyl Alcohol; or 2-Propanol | 1.0e-04 |

[a] Only those chemicals with an emission rate at least 23 kg/year (44 mg/min), plus formaldehyde, are listed. Carbon, conductive polymer, graphite, and organic-palladium had no modeled emission rates above this cut-off. Also, proprietary chemical results are not presented in order to protect proprietary chemical identities.

[b] LADD is calculated using a carcinogen averaging time ($AT_{CAR}$) of 70 years.

Note: The numeric format used in these tables is a form of scientific notation, where the "e" replaces the " x $10^{x}$" in scientific notation. Scientific notation is typically used to present very large or very small numbers. For example, 1.2e-04 is the same as 1.2 x $10^{-4}$, which is the same as 0.00012 in common decimal notation.

### 3.2.5 Uncertainty and Variability

Because of both the uncertainty inherent in the parameters and assumptions used in estimating exposure, and the variability that is possible within a population, there is no one number that can be used to describe exposure. In addition to data and modeling limitations, discussed in Sections 3.2.3, sources of uncertainty in assessing exposure include the following:

- Accuracy of the description of exposure setting: how well the model facility used in the assessment characterizes an actual facility; the likelihood of exposure pathways actually occurring (scenario uncertainty).

- Missing data and limitations of workplace practices data: this includes possible effects of any chemicals that may not have been included (e.g., minor ingredients in the formulations and proprietary chemical identities not disclosed by suppliers[5]); possible effects of side reactions in the baths, which were not considered; and questionnaire data with limited facility responses.
- Estimating exposure levels from averaged data and modeling in the absence of measured, site-specific data.
- Data limitations in the Source Release Assessment: releases to surface water and land could not be characterized quantitatively, as discussed in Section 3.1.
- Chemical fate and transport model applicability and assumptions: how well the models and assumptions represent the situation being assessed and the extent to which the models have been validated or verified (model uncertainty).
- Parameter value uncertainty, including measurement error, sampling error, parameter variability, and professional judgement.
- Uncertainty in combining pathways for an exposed individual.

A method typically used to provide information about the position an exposure estimate has in the distribution of possible outcomes is the use of exposure (or risk) descriptors. EPA's *Guidelines for Exposure Assessment* (EPA, 1992b) provides guidance on the use of risk descriptors, which include the following:

- *High-end*: approximately the 90th percentile of the actual (measured or estimated) distribution. This is a plausible estimate of individual risk for those persons at the upper end of the exposure distribution, and is not higher than the individual in the population who has the highest exposure.
- *Central tendency*: either an average estimate (based on average values for the exposure parameters) or a median estimate (based on 50th percentile or geometric mean values).
- *What-if*: represents an exposure estimate based on postulated questions (e.g., what if the air ventilation rates were ... ), in this case, making assumptions based on limited data so that the distribution is unknown. If any part of the exposure assessment qualifies as a "what-if" descriptor, then the entire exposure assessment is considered "what-if."

This exposure assessment uses whenever possible a combination of central tendency (either an average or median estimate) and high-end (90th percentile)[6] assumptions, as would be used for an overall high-end exposure estimate. The 90th percentile is used for:

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[5] Electrochemicals, LeaRonal, and Solution Technology Systems provided information on proprietary chemical ingredients to the project. Atotech provided information on one proprietary ingredient. W.R. Grace was making arrangements to transfer information on proprietary chemical ingredients in the conductive ink technology when it was determined that this information was no longer necessary because risk from the conductive ink technology could not be characterized. The other suppliers participating in the project (Enthone-OMI, MacDermid, and Shipley) declined to provide proprietary information on their MHC technologies. The absence of information on proprietary chemical ingredients is a significant source of uncertainty in the risk characterization. Risk information for proprietary ingredients is presented in this CTSA, but chemical identities, concentrations, and chemical properties are not listed.

[6] For exposure data from the IPC Workplace Practices Questionnaire, this means that 90 percent of the facilities reported a lower value, and ten percent reported a higher value.

- Hours per day of workplace exposure.
- Exposure frequency (days per year).
- Exposure duration in years (90th percentile for occupational and 95th percentile for residential exposures).
- The time and frequency of chemical bath and filter replacements, conveyor equipment cleaning and chemical bath sampling (minutes per occurrence and number of occurrences per year), and estimated workplace air concentrations.

Average values are used for:

- Body weight.
- Concentration of chemical in bath.
- The number of baths in a given process.

However, because some data, especially pertaining to bath concentrations and inhalation exposure are limited, and this exposure assessment does not apply to a specific facility, the entire exposure assessment should be considered "what-if."

### 3.2.6 Summary

This exposure assessment uses a "model facility" approach, with the goal of comparing the exposures and health risks of one MHC technology to the exposures and risks associated with switching to another technology. As much as possible, reasonable and consistent assumptions are used across alternatives. Data to characterize the model facility and exposure patterns for each MHC technology were aggregated from a number of sources, including PWB shops in the U.S. and abroad, supplier data, and input from PWB manufacturers at project meetings. Thus, the model facility is not entirely representative of any one facility, and actual exposure (and risk) could vary substantially, depending on site-specific operating conditions and other factors.

Chemical exposures to PWB workers and the general population from day-to-day MHC line operations were estimated by combining information gathered from industry (IPC Workplace Practices Questionnaire, MSDSs, and other available information) with standard EPA exposure assumptions for inhalation rate, surface area of dermal contact and other parameters, as discussed in the exposure assessment. The pathways identified for potential exposure from MHC process baths were inhalation and dermal contact for workers, and inhalation contact only for the general populace living near a PWB facility.

Environmental releases to surface water were not quantified due to a lack of data and the limited scope of this assessment. Chemical constituents and concentrations in wastewater could not be adequately characterized (see Section 3.2.3). Nor were the possible impacts of short-term exposures to high levels of hazardous chemicals addressed, such as those that could occur from chemical fires, spills, or other periodic releases.

Inhalation exposure could occur by breathing air containing vapor or aerosol-phase chemicals from the MHC process line. Inhalation exposures to workers are estimated only for non-conveyorized lines; inhalation exposure to workers from conveyorized MHC lines was assumed to be negligible because the lines are typically enclosed and vented to the outside.

The daily intake for inhalation exposure to workers was calculated by first modeling chemical emissions from MHC baths with three air-transport mechanisms: liquid surface diffusion (desorption), bubble desorption, and aerosol generation and ejection. This chemical emission rate was combined with information from the IPC Workplace Practices Questionnaire regarding process room size and air turnover rate to estimate an average indoor air concentration for the process area. General room ventilation was assumed, although the majority of shops have local ventilation on chemical tanks. An uncertainty and sensitivity analysis of the air transport models suggests that the air turnover (ventilation) rate assumption greatly influences the estimated air concentration in the process area because of its large variability.

Inhalation exposure to the human population surrounding PWB plants was estimated using the Industrial Source Complex - Long Term (ISCLT) air dispersion model. The modeled air concentrations of each contaminant were determined at 100 meters radially from a PWB facility, and the highest estimated air concentration was used. This model estimates air concentration from the process bath emission rates. These emissions were assumed to be vented to the ambient environment at the rate emitted from the baths, for all process alternatives. Inhalation exposures estimated for the public living 100 meters away from a PWB facility were very low (approximately 10,000 times lower than occupational exposures).

Dermal exposure could occur when skin comes in contact with the bath solution while dipping boards, adding replacement chemicals, etc. Although the data suggest that most MHC line operators do wear gloves, it was assumed in this evaluation that workers do not wear gloves to account for the fraction that do not. Otherwise, dermal exposure is expected to be negligible. For dermal exposure, the concentration of chemical in the bath and duration of contact for workers was obtained from the IPC Workplace Practices Questionnaire information. A permeability coefficient (rate of penetration through skin) was estimated for organics and a default rate assumption was used for inorganics. Another source of uncertainty in dermal modeling lies with the assumed duration of contact. The worker is assumed to have potential dermal contact for the entire time spent in the MHC area, divided equally among the baths. (This does not mean that a worker has both hands immersed in a bath for that entire time; but that the skin is in contact with bath solution, i.e., the hands may remain wet from contact.) This assumption may result in an overestimate of dermal exposure.

Assumptions and parameter values used in these equations are presented throughout this section. Complete results of the exposure calculations are presented in Appendix E, except proprietary chemical results are not presented in order to protect proprietary chemical identities. Exposure estimates are based on a combination of high end (90th percentile)[7] and average values, as would be used for a high-end exposure estimate. The 90th percentile was used for hours per day of workplace exposure, exposure frequency (days per year), exposure duration in years (90th percentile for occupational and 95th percentile for residential exposures), and the time and frequency of chemical bath and filter replacements, conveyor equipment cleaning and chemical bath sampling (minutes per occurrence and number of occurrences per year) and estimated workplace air concentrations. The average value was used for body weight, concentration of

[7] For exposure data from the IPC Workplace Practices Questionnaire, this means that 90 percent of the facilities reported a lower value, and ten percent reported a higher value.

chemical in bath, and the number of baths in a given process. However, because some data, especially pertaining to bath concentrations and inhalation exposure are limited, and this exposure assessment does not apply to a specific facility, the entire exposure assessment should be considered "what-if."

## 3.3 HUMAN HEALTH AND ECOLOGICAL HAZARDS SUMMARY

This section presents a summary of the human health and ecological hazards data that were used in the risk characterization.[8] This information is summarized from toxicity profiles prepared for non-proprietary chemicals identified as constituents in the baths for the MHC technologies evaluated. Table 3.23 lists these chemicals and identifies the MHC process or processes in which these chemicals are used. The electroless copper process is the predominant method now used in MHC. Section 2.1.4 includes more detailed information on bath constituents and concentrations. Throughout this section, toxicity data for proprietary chemicals are not presented in order to protect proprietary chemical identities.

**Table 3.23 Known Use Cluster Chemicals and Associated MHC Processes**

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

[8] Risk was not characterized for the conductive ink technology but human health and ecological hazards data are presented here.

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

| Chemical List | Electroless Copper | Carbon | Conductive Ink | Conductive Polymer | Graphite | Non-Formaldehyde Electroless Copper | Organic-Palladium | Tin-Palladium |
|---|---|---|---|---|---|---|---|---|
| Trisodium Citrate 5.5-Hydrate; Sodium Citrate | | | | | | | ✔ | |
| Vanillin | | | | | | | | ✔ |
| Proprietary Chemicals (no. known for alternative) | 12 | | | | 5 | | 1 | 5 |

### 3.3.1 Carcinogenicity

Table 3.24 summarizes the available information pertaining to carcinogenicity for the MHC chemicals, including classifications describing evidence of chemical carcinogenicity. Due to the large number of chemicals in commerce, including approximately 15,000 non-polymeric chemicals produced in significant amounts (i.e., > 10,000 lbs/year), many chemicals have not yet been tested or assigned carcinogenicity classifications. The classifications referenced in this risk assessment are defined below:

*EPA Weight-of-Evidence Classification*: In assessing the carcinogenic potential of a chemical, EPA classifies the chemical into one of the following groups, according to the weight-of-evidence from epidemiologic, animal and other supporting data, such as genotoxicity test results:

- Group A: Human Carcinogen (sufficient evidence of carcinogenicity in humans).
- Group B: Probable Human Carcinogen (B1 - limited evidence of carcinogenicity in humans; B2 - sufficient evidence of carcinogenicity in animals with inadequate or lack of evidence in humans).
- Group C: Possible Human Carcinogen (limited evidence of carcinogenicity in animals and inadequate or lack of human data).
- Group D: Not Classifiable as to Human Carcinogenicity (inadequate or no evidence).
- Group E: Evidence of Non-Carcinogenicity for Humans (no evidence of carcinogenicity in adequate studies).

EPA has proposed a revision of its guidelines that would eliminate the above discrete categories while providing a more descriptive classification.[9]

*International Agency for Research on Cancer (IARC) Classification*: This is a similar weight-of-evidence method for evaluating potential human carcinogenicity based on human data, animal data, and other supporting data. A summary of the IARC carcinogenicity classification system includes:

[9] The "Proposed Guidelines for Carcinogen Risk Assessment" (EPA, 1996a) propose use of weight-of-evidence descriptors, such as "Likely" or "Known," "Cannot be determined," and "Not likely," in combination with a hazard narrative, to characterize a chemical's human carcinogenic potential; rather than the classification system described above.

- Group 1: Carcinogenic to humans.
- Group 2A: Probably carcinogenic to humans.
- Group 2B: Possibly carcinogenic to humans.
- Group 3: Not classifiable as to human carcinogenicity.
- Group 4: Probably not carcinogenic to humans.

Both of these classification schemes represent judgements regarding the likelihood of human carcinogenicity. Table 3.24 lists all MHC chemicals which have been classified by EPA or IARC. The National Toxicology Program (NTP) is an additional source used to classify chemicals, but its classifications are based only on animal data from NTP studies.

**Table 3.24 Available Carcinogenicity Information**

| Chemical Name[a] | Cancer Slope Factor $(mg/kg\text{-}day)^{-1}$ | Comments/Classifications |
|---|---|---|
| Formaldehyde | 0.046[b] | EPA Group B1 (EPA, 1995b)[c]; IARC Group 2A (IARC, 1995)[c] |
| Carbon Black | ND | IARC Group 2B (IARC, 1996)[d] |
| Dimethylformamide | ND | IARC Group 2B (IARC, 1989)[d] |
| 1,3-Benzenediol | ND | IARC Group 3 (IARC, 1987)[e] |
| Hydrochloric Acid | ND | IARC Group 3 (HSDB, 1995)[e] |
| Hydrogen Peroxide | ND | IARC Group 3 (IARC, 1987)[e] |
| Copper (I) Chloride | ND | EPA Group D (EPA, 1995c)[f] |
| Copper (II) Chloride | ND | EPA Group D (EPA, 1995c)[f] |
| Palladium; Palladium Chloride | ND | No classification; rats developed respiratory tumors and leukemia at 5 ppm in water (Schroeder & Mitchener, 1971) |
| Sodium Sulfate | ND | No classification; "equivocal evidence" of tumorigenicity in mice (RTECS, 1995) |
| Triethanolamine; or 2,2',2"-Nitrilotris Ethanol | ND | No classification; equivocal carcinogenic evidence in animals (NTP, 1994) |
| Cyclic Ether[g] | not reported[h] | Possible/probable human carcinogen[i] |
| Alkyl Oxide[g] | not reported[h] | Probable human carcinogen[i] |
| Trisodium Acetate Amine B[j] | ND | Possible human carcinogen[i] |

[a] Only those chemicals with available data or classifications are listed.
[b] Unit risk units were converted from $1.3 \times 10^{-5}$ $\mu g/m^3$ $^{-1}$ to slope factor units of $(mg/kg\text{-}day)^{-1}$ using 20 $m^3$/day inhalation (breathing) rate and 70 kg body weight.
[c] EPA Group B: Probable Human Carcinogen (B1 - limited evidence of carcinogenicity in humans); IARC Group 2A: Possibly carcinogenic to humans.
[d] IARC Group 2B: Possibly carcinogenic to humans.
[e] IARC Group 3: Not classifiable as to human carcinogenicity.
[f] EPA Group D: Not classifiable as to human carcinogenicity (inadequate or no evidence).
[g] In graphite and electroless copper technologies.
[h] Cancer slope factors are available but not reported in order to protect proprietary chemical identities.
[I] Specific EPA and/or IARC groups not reported in order to protect proprietary chemical identities.
[j] In electroless copper technology.
ND: No Data. A cancer slope factor has not been determined for this chemical.

For carcinogenic effects, there is presumably no level of exposure that does not pose a small, but finite, probability of causing a response. This type of mechanism is referred to as "non-threshold." When the available data are sufficient for quantification, EPA develops an estimate of the chemical's carcinogenic potency expressed as a "slope factor." The slope factor ($q_1$*) is a measure of an individual's excess risk or increased likelihood of developing cancer if exposed to a chemical (expressed in units of $[mg/kg\text{-}day]^{-1}$). More specifically, $q_1$* is an approximation of the upper bound of the slope of the dose-response curve using the linearized multistage procedure at low doses. "Unit risk" is an equivalent measure of potency for air or drinking water concentrations and is expressed as the upper bound excess lifetime cancer risk per $\mu g/m^3$ in air, or as risk per $\mu g/L$ in water, for continuous lifetime exposures. (Unit risk is simply a transformation of slope factor into the appropriate scale.) Slope factors and unit risks can be viewed as quantitatively derived judgements of the magnitude of carcinogenic effect. These estimates will continue to be used whether the current EPA weight-of-evidence guidelines are retained or the new proposals are adopted. Their derivation, however, may change for future evaluations.

EPA risk characterization methods require a slope factor or unit risk to quantify the upper bound excess cancer risk from exposure to a known or suspected carcinogen. Therefore, formaldehyde is the only non-proprietary chemical for which cancer risk was characterized (see Section 3.4, Risk Characterization).

### 3.3.2 Chronic Effects (Other than Carcinogenicity)

Adverse effects other than cancer and gene mutations are generally assumed to have a dose or exposure threshold. Therefore, a different approach is needed to evaluate toxic potency and risk for these "systemic effects." Systemic toxicity means an adverse effect on any organ system following absorption and distribution of a toxicant to a site in the body distant from the toxicant's entry point. A reference dose (RfD) is an estimate (with uncertainty spanning perhaps an order of magnitude) of the daily exposure through ingestion to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious non-cancer effects during a lifetime (in mg/kg-day). Similarly, a reference concentration (RfC) is an estimate (with uncertainty spanning perhaps an order of magnitude) of the daily inhalation exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious non-cancer effects during a lifetime (in $mg/m^3$) (Barnes and Dourson, 1988). RfDs and RfCs can also be derived from developmental toxicity studies. However, this was not the case for any of the MHC chemicals evaluated. RfDs and RfCs are derived from EPA peer-reviewed study results (for values appearing in EPA's Integrated Risk Information System [IRIS]), together with uncertainty factors regarding their applicability to human populations. Table 3.25 presents a summary of the available RfC and RfD information obtained from IRIS and EPA's Health Effects Assessment Summary Tables (HEAST). One proprietary chemical, in the tin-palladium alternative, has an RfD available; this is not reported to protect the identity of the proprietary chemical.

**Table 3.25 Summary of RfC and RfD Information**

| Chemical Name[a] | Inhalation RfC ($mg/m^3$) | Comments[c] (Inhalation) | Oral/Dermal RfD (mg/kg-day) | Comments[b] (Oral/Dermal) |
|---|---|---|---|---|
| 2-Butoxyethanol Acetate | 0.02 | Rat, 13 weeks, hematological and liver effects (EPA, 1995d)[c, d] | ND | |
| 2-Ethoxyethanol | 0.2 | Rabbit, 13 weeks, reduced spleen, testicular weights, and white blood cell counts (EPA, 1996b) | 0.4 | Gavage, rat and mouse, 103 weeks, reduced body weight, testicular degeneration, and enlargement of adrenal gland (EPA, 1995d) |
| Ammonia | 0.1 | Occupational study, lack of irritation to workers exposed to 9.2 ppm concentration (EPA, 1997) | ND | |
| Diethylene Glycol Ethyl Ether and Acetate | ND | | 2 | Oral, rat, 3-generation study (chronic reproductive), kidney and bladder damage (EPA, 1995d) |
| Diethylene Glycol n-Butyl Ether | 0.02 | Inhalation, rat, 7 hours (EPA, 1995c,d)[d] | ND | |
| Dimethylformamide | 0.03 | Inhalation, human, 5+ years, 54 workers for hepatoxicity effects (EPA, 1996b) | ND | |
| Ethylene Glycol | ND | | 2 | Oral, rat, 2 years, decreased growth, renal calculi (EPA, 1995c) |
| Formaldehyde | ND | | 0.2 | Oral, rat, 2 years, GI tract and histopathological changes (EPA, 1995b) |
| Hydrochloric Acid | 0.007 | Rat, respiratory tract hyperplasia, lifetime exposure (EPA, 1995c) | ND | |
| Isophorone | ND | | 0.2 | Oral, dog, 90 days, no signs of cellular changes (EPA, 1995d) |
| Methanol | ND | | 0.5 | Gavage, rat, 90 days, decreased brain weights (EPA, 1995c) |
| Potassium Cyanide | ND | | 0.05 | Oral, rat, 2 years, no treatment effects on weight gain (EPA, 1995c) |
| Silver | ND | | 0.005 | Oral, human, 2 - 9.75 years, argyria of skin, eyes, mouth, and throat (EPA, 1996b) |
| Sodium Cyanide | ND | | 0.04 | Oral, rat, 2 years (EPA, 1995c) |

| Chemical Name[a] | Inhalation RfC ($mg/m^3$) | Comments[c] (Inhalation) | Oral/Dermal RfD (mg/kg-day) | Comments[b] (Oral/Dermal) |
|---|---|---|---|---|
| Stannous Chloride | ND | | 0.62 | Rat, 105 weeks (EPA, 1994a)[e] |

[a] Only those chemicals with available data are listed. Proprietary chemical data are not presented in order to protect proprietary chemical identities.
[b] Comments may include exposure route, test animal, duration of test, effects, and source of data.
[c] Based on data for 2-butoxyethanol.
[d] Provisional RfC or RfD.
[e] Based on data for tin.
ND: No data. An RfD or RfC has not been determined for this chemical.

When an RfD or RfC was not available for a chemical, other toxicity values were used, preferably in the form of a no-observed-adverse-effect level (NOAEL) or lowest-observed-adverse-effect level (LOAEL). These toxicity values were obtained from the published scientific literature as well as unpublished data submitted to EPA on chemical toxicity in chronic or subchronic studies. Typically, the lowest NOAEL or LOAEL value from a well-conducted study was used. (If study details were not presented or the study did not appear to be valid, the reported NOAEL/LOAELs were not used.) But unlike the majority of RfD/RfCs, NOAEL/LOAELs have not received EPA peer-review of the studies on which the values are based, and uncertainty factors have not been considered.

The LOAEL is the lowest dose level in a toxicity test at which there are statistically or biologically significant increases in frequency or severity of adverse effects in the exposed population over its appropriate control group (in mg/kg-day, or $mg/m^3$ for inhalation). The NOAEL is the highest dose level in a toxicity test at which there is no statistically or biologically significant increase in the frequency or severity of adverse effects in the exposed population over its appropriate control (in mg/kg-day, or $mg/m^3$ for inhalation). LOAEL values are presented only where NOAELs were not available. Table 3.26 presents a summary of the available NOAEL and LOAEL values.

**Table 3.26 NOAEL/LOAEL Values**

| Chemical Name[a] | Inhalation NOAEL/ LOAEL[b] ($mg/m^3$) | Comments (Inhalation) | Oral/Dermal NOAEL/ LOAEL[b] (mg/kg-day) | Comments (Oral/Dermal) |
|---|---|---|---|---|
| 1,3-Benzenediol | ND | | 100 (N)[c] | Gavage, rat/mouse, 2 years (NTP, 1992) |
| Ammonium Chloride | ND | | 1,691 (N) | Oral, mouse, developmental study in drinking water (Shepard, 1986) |
| Benzotriazole | ND | | 109 (L) | Oral, rat, 26 weeks, induced anemia, endocrine effects (RTECS, 1995) |
| Boric Acid | ND | | 62.5 (L) | Gavage, rabbit, developmental study showed cardiovascular defects (U.S. Borax Co., 1992) |

| Chemical Name[a] | Inhalation NOAEL/ LOAEL[b] ($mg/m^3$) | Comments (Inhalation) | Oral/Dermal NOAEL/ LOAEL[b] (mg/kg-day) | Comments (Oral/Dermal) |
|---|---|---|---|---|
| Carbon Black | 7.2 (L) | Human, 14 years, decrease in lung function: vital capacity (IARC, 1984) | ND | |
| Copper (I) Chloride | 0.6 (L) | Human, dust caused leukocytosis/anemia, respiratory irritant (U.S. Air Force, 1990) | 0.07 (L) | Oral, human, 1.5 years, GI tract effects (ATSDR, 1990a) |
| Diethylene Glycol Methyl Ether | ND | | 1,000 (N) | Oral, rat, 13 weeks, kidney damage, (HSDB, 1995) |
| Diethylene Glycol n-Butyl Ether | NA | | 191 | Dermal, rat, 90 days, hemolytic effects (RM1, 1992) |
| Dimethylformamide | NA | | 125 (L) | Oral, rat, 100 days, liver weight increases and body weight gains (Trochimowicz et al., 1994) |
| Ethanolamine | 12.7 (L) | Rat, dog, guinea pig, 90 days, skin irritation/ weight loss (ACGIH, 1991) | 320 (N) | Oral, rat, 90 days, altered liver/kidney weights at higher concentrations (ACGIH, 1991) |
| Ethylene Glycol | 31 | Human, headache, respiratory tract irritation, lymphocytosis (ATSDR, 1993) | NA | |
| Fluoroboric Acid | ND | | 0.77 | Human, 2 years, bone disease, GI problems & osteoarticular pain in women (HSDB, 1995; based on 50-100 mg/d, for fluorides, adjusted for 65 kg body weight) |
| Formaldehyde | 0.1 ppm (L) | Human, eye and upper respiratory tract irritation (EPA, 1991c)[d] | NA | |
| Formic Acid | 59.2 (N) | Rat/mouse, 2 weeks, respiratory epithelial lesions (Katz and Guest, 1994) | ND | |
| Graphite | 56 (L) | Human effect level for pneumoconiosis, nuisance from dust (Pendergrass, 1983) | ND | |

| Chemical Name[a] | Inhalation NOAEL/ LOAEL[b] ($mg/m^3$) | Comments (Inhalation) | Oral/Dermal NOAEL/ LOAEL[b] (mg/kg-day) | Comments (Oral/Dermal) |
|---|---|---|---|---|
| Hydrogen Peroxide | 79 | Mouse, 7/9 died from 79 $mg/m^3$ in 6 weeks (EPA, 1988) | 630 (N) | Oral, developmental and reproductive studies for 5 weeks (rat) and 3 months (mouse), respectively (IARC, 1985) |
| Hydroxyacetic Acid | ND | | 250 (N) | Gavage, developmental rat study showed lung noise, reduced weight gain (DuPont, 1995) |
| Isopropyl Alcohol, 2-Propanol | 980 (N) | Rat, 13 weeks (SIDS, 1995) | 100 (N) | Oral, rat, 2-generation study (CMA, 1995; RM2, 1996) |
| Magnesium Carbonate | Generally regarded as safe (U.S. FDA as cited in HSDB, 1995). | | | |
| Methanol | 1,596 - 10,640 (1,200 - 8,000 ppm) | Human, 4 year occupational study, vapor caused vision loss (ACGIH, 1991) | NA | |
| Palladium, Palladium Chloride | ND | | 0.95 (L) | Oral, rat, 180 days, decreased weight (Schroeder & Mitchener, 1971) |
| Potassium Hydroxide | 7.1 | Human, caused cough/bronchial effects, severe eye/skin irritant (Graham et al., 1984) | ND | |
| Potassium Sodium Tartrate | Generally regarded as safe (U.S. FDA as cited in HSDB, 1996). | | | |
| Potassium Sulfate | 15 ($TC_{LO}$)[e] | Rat, 4 hr/d for 17 weeks, metabolic effects (RTECS, 1995) | ND | |
| Sodium Carbonate | 10 (N) | Rat, 4 hr/d, 5 d/w for 3.5 months, decreased weight gain, lung effects (Pierce, 1994) | ND | |
| Sodium Chlorite | ND | | 10 (N) | Gavage, rat, 13 weeks, hematological effects (Harrington et al., 1995) |
| Sodium Hydroxide | 2 (L) | Human, dyspnea, irritant (ACGIH, 1991) | ND | |
| Sodium Sulfate | ND | | 420 (N) | Oral, rat, 16 weeks (Young, 1992) |
| Sulfuric Acid | 0.066 (N) | Human (EPA, 1994a) | ND | |

| Chemical Name[a] | Inhalation NOAEL/ LOAEL[b] ($mg/m^3$) | Comments (Inhalation) | Oral/Dermal NOAEL/ LOAEL[b] (mg/kg-day) | Comments (Oral/Dermal) |
|---|---|---|---|---|
| Tartaric Acid | ND | | 8.7 | Oral, dog study, 3/4 developed casts (color or tint) in urine, weight changes and advanced renal tubular degeneration, at 990 g/kg for 90-114 days (Informatics, Inc., 1974) |
| Triethanolamine; or 2,2',2"-Nitrilotris Ethanol | ND | | 32 (L) | Dermal, mouse, 105 weeks, irritation effects (NTP, 1994) |
| Vanillin | ND | | 64 (L) | Oral, rat, 10 weeks, growth depression and damage to kidney, myocardium, liver and spleen (Kirwin and Galvin, 1993) |

[a] Only those chemicals with available data are listed. Proprietary chemical data are not presented in order to protect proprietary chemical identities.
[b] When more than one NOAEL and/or LOAEL was available, only the lowest available NOAEL or LOAEL was used and is listed here. If both NOAEL and LOAEL data are available, the NOAEL is used and is listed here.
[c] (N) = NOAEL; (L) = LOAEL. If neither is indicated, the toxicity measure was not identified as a NOAEL or LOAEL in the available information.
[d] This value is highly uncertain; precise thresholds for these irritant effects of formaldehyde have not been established. Estimates based on a large number of clinical and non-clinical observations indicate that most people have irritant reaction thresholds over the range of 0.1 to 3.0 ppm formaldehyde (EPA, 1991c).
[e] $TC_{LO}$ = total concentration resulting in a sublethal effect.
ND: No Data. A NOAEL or LOAEL was not available for this chemical.
NA: Not Applicable. A NOAEL or LOAEL is not required because an RfD or RfD was available for this chemical.

Neither RfDs/RfCs nor LOAELs/NOAELs were available for several chemicals in each MHC process alternative. For these chemicals, no quantitative estimate of risk could be calculated. EPA's Structure-Activity Team (SAT)[10] has reviewed the chemicals without relevant toxicity data to determine if these chemicals are expected to present a toxicity hazard. This review was based on available toxicity data on structural analogues of the chemicals, expert judgement, and known toxicity of certain chemical classes and/or moieties. Chemicals received a concern level rank of high, medium, or low. Results of the SAT evaluation are presented in Table 3.27. A summary of the SAT results for proprietary chemicals is presented in Table 3.28. An overview of chemicals and available toxicity data is presented in Table 3.29.

[10] The SAT is a group of expert scientists at EPA who evaluate the potential health and environmental hazards of new and existing chemicals.

**Table 3.27 Summary of Health Effects Information (from Structure-Activity Team Reports)**

| Chemical | SAT Health Effects (pertaining to dermal or inhalation exposure) | Overall Concern Level |
|---|---|---|
| Dimethylaminoborane | Absorption is expected to be good via all routes of exposure. This compound is corrosive when handled in concentrated form. There is concern for developmental toxicity and reproductive effects for the boron. | High concern |
| EDTA, Sodium Salt | Expect no absorption by skin, but expect absorption by lungs and GI tract. Compound is a chelator and is expected to chelate Ca and Mg. Concerns for developmental toxicity and cardiac arrhythmia due to ability to chelate Ca. Arrhythmia expected to occur only at high doses. | Low moderate concern |
| Fluoroboric Acid | Expect absorption via the skin following irritation. Expect good absorption via the lungs and GI tract. This compound is a severe skin irritant and may be corrosive. There is uncertain concern for developmental toxicity based on information for fluoride. | High concern |
| Graphite | Expect absorption to be nil by all routes. There is concern for lung effects through lung overall (fibrosis) with repeated inhalation exposure of respirable particles. | Low moderate concern |
| Magnesium Carbonate | Absorption is expected to be nil through the skin and good through the lungs and GI tract. This compound is used as an antacid. | Low moderate concern |
| m-Nitrobenzene Sulfonic Acid, Sodium Salt | Absorption is expected to be nil through the skin and good through the lungs and GI tract. The nitro group can be reduced to anamine. There is concern for methemoglobinemia as an aromatic amine compound. As a nitrobenzene derivative, there is concern for neutrotoxicity and developmental toxicity. Serious brain damage was noted at 125 ppm in a 2-week inhalation study with nitrobenzene. It is expected to be irritating to mucous membranes and the upper respiratory tract. | Moderate concern |
| Monopotassium Peroxymonosulfate | Absorption is expected to be nil through the skin and good through the lungs and GI tract. The peroxymonosulfate moiety is reactive with moisture (oxidizing agent). This material will be an irritant as a concentrated solution. | Moderate concern |
| Palladium Chloride | Absorption is expected to be nil through the skin and good through the lungs and GI tract. It is an irritant and is reported to be a dermal sensitizer in humans (HSDB). | Moderate high concern |
| Phosphoric Acid | Expect absorption by all routes. Compound is corrosive. | Moderate concern for corrosive effects to all tissues |

| Chemical | SAT Health Effects (pertaining to dermal or inhalation exposure) | Overall Concern Level |
|---|---|---|
| Potassium Bisulfate | Absorption is expected to be nil through the skin as the neat material and good through the lungs and GI tract. Expect absorption via the skin in solution because of damage to the skin. This compound is expected to be a severe irritant and/or corrosive to the skin, eyes, and mucous membranes because of its acidity. | Moderate concern |
| Potassium Carbonate | Absorption is expected to be nil through the skin and good through the lungs and GI tract. This material is an alkaline solution and is irritating to the skin, mucous membranes, and upper respiratory tract. | Low moderate concern |
| Potassium Persulfate | Absorption may occur through the skin following irritation of the skin. Absorption is expected to be good via the lungs and GI tract with reaction of the persulfate (oxidizing agent). This compound is irritating and/or corrosive to the skin, eyes, and mucous membranes. It may also be a dermal and respiratory sensitizer. | Moderate concern |
| Potassium Sulfate | Absorption is expected to be nil through the skin and good through the lungs and GI tract. No significant adverse effects expected. | Low concern |
| p-Toluene Sulfonic Acid | Expect no absorption by skin, moderate absorption by GI tract, and good absorption by lungs. TSCA Section 8e-10286 report that this chemical is a severe skin irritation. No other health concern identified. | Low moderate concern |
| Sodium Bisulfate | Absorption is expected to be nil through the skin as the neat material and good through the lungs and GI tract. Expect absorption via the skin in solution because of damage to the skin. This compound is expected to be a severe irritant and/or corrosive to the skin, eyes, and mucous membranes because of its acidity. | Moderate concern |
| Sodium Hypophosphite | Absorption is expected to be nil through the skin and good through the lungs and GI tract. It is irritating to mucous membranes and may cause dermal sensitization (HSDB). | Low moderate concern |
| Sodium Persulfate | Absorption may occur through the skin following irritation of the skin. Absorption is expected to be good via the lungs and GI tract with reaction of the persulfate (oxidizing agent). This compound is irritating and/or corrosive to the skin, eyes, and mucous membranes. It may also be a dermal and respiratory sensitizer. In an inhalation sensory irritation study in mice, mortality occurred at 0.77 mg/l and greater (TSCA Section 8e-12867 Report). Sodium peroxysulfate is positive for dermal sensitization in a human patch test (TSCA Section 8e-2767 Report). Ocular opacity was also reported. | Moderate concern |

**Table 3.28 Summary of EPA Structure-Activity Team Results for Proprietary Chemicals**

| Technology | No. of Additional Trade Secret Chemicals[a] | No. of Additional Trade Secret Chemicals With No Human Health Toxicity Data[b] | SAT Human Health Concern Rank (no. of proprietary chemicals) | | |
|---|---|---|---|---|---|
| | | | Low | Low-Moderate | Moderate |
| Electroless Copper | 9 | 4 | 1 | 2 | 1 |
| Graphite | 5 | 3 | 0 | 2 | 1 |
| Tin-Palladium | 5 | 4 | 2 | 1 | 1 |
| Organic-Palladium | 1 | 0 | 0 | 0 | 0 |

[a] New chemical for this process alternative.
[b] The toxicity data required to calculate cancer risk, hazard quotient, and MOE were not available.

**Table 3.29 Available Toxicity Data for Non-Proprietary Chemicals**

| Chemical | Cancer: Slope Factor (SF), Weight-of-Evidence (WOE) Classification | Inhalation: RfC, NOAEL, or LOAEL | Oral/Dermal: RfD, NOAEL, or LOAEL | SAT |
|---|---|---|---|---|
| 2-Ethoxyethanol | | **RfC** | **RfD** | |
| 1,3-Benzenediol | WOE | | NOAEL | |
| 2-Butoxyethanol Acetate; Butylcellusolve Acetate | | **RfC** | | |
| Ammonia | | **RfC** | | |
| Ammonium Chloride | | | NOAEL | |
| Benzotriazole | | | LOAEL | |
| Boric Acid | | | LOAEL | |
| Carbon Black | WOE | LOAEL | | |
| Copper (I) Chloride; Copper | WOE | LOAEL | LOAEL | |
| Copper Sulfate; or Cupric Sulfate[a] | | | | |
| Diethylene Glycol n-Butyl Ether | | **RfC** | Other[b] | |
| Diethylene Glycol Ethyl Ether | | | **RfD** | |
| Diethylene Glycol Methyl Ether | | | NOAEL | |
| Dimethylaminoborane | | | | ✔ |
| Dimethylformamide | WOE | **RfC** | LOAEL | |
| Ethanolamine; Monoethanolamine; 2-Aminoethanol | | LOAEL | NOAEL | |
| Ethylene Glycol | | Other[b] | **RfD** | |
| Ethylenediaminetetraacetic Acid (EDTA) | | | | ✔ |
| Fluoroboric Acid; Sodium Bifluoride | | | Other[b] | ✔ |
| Formaldehyde | **SF**, WOE | LOAEL | **RfD** | |
| Formic Acid | | NOAEL | | |
| Graphite | | LOAEL | | ✔ |
| Hydrochloric Acid | WOE | **RfC** | | |

| Chemical | Cancer: Slope Factor (SF), Weight-of-Evidence (WOE) Classification | Inhalation: RfC, NOAEL, or LOAEL | Oral/Dermal: RfD, NOAEL, or LOAEL | SAT |
|---|---|---|---|---|
| Hydrogen Peroxide | WOE | Other[b] | NOAEL | |
| Hydroxyacetic Acid | | | NOAEL | |
| Isophorone | | | **RfD** | |
| Isopropyl Alcohol; 2-Propanol | | NOAEL | NOAEL | |
| Lithium Hydroxide | | | | ✔ |
| m-Nitrobenzene Sulfonic Acid; Sodium m-Nitrobenzenesulfonate | | | | ✔ |
| Magnesium Carbonate | | | | ✔ |
| Methanol | | Other[b] | **RfD** | |
| p-Toluene Sulfonic Acid; Tosic Acid | | | | ✔ |
| Palladium | | | LOAEL | |
| Palladium Chloride | | | LOAEL | ✔ |
| Peroxymonosulfuric Acid; Potassium Peroxymonosulfate | | | | ✔ |
| Phenol-Formaldehyde Copolymer | | | | |
| Phosphoric Acid | | | | ✔ |
| Potassium Bisulfate | | | | ✔ |
| Potassium Carbonate | | | | ✔ |
| Potassium Cyanide | | | **RfD** | |
| Potassium Hydroxide | | Other[b] | | |
| Potassium Persulfate | | | | ✔ |
| Potassium Sulfate | | Other[b] | | ✔ |
| Potassium-Sodium Tartrate[c] | | | | |
| Silver | | | **RfD** | |
| Sodium Bisulfate | | | | ✔ |
| Sodium Carbonate | | NOAEL | | |
| Sodium Chloride[d] | | | | |
| Sodium Chlorite | | | NOAEL | |
| Sodium Cyanide | | | **RfD** | |
| Sodium Hydroxide | | LOAEL | | |
| Sodium Hypophosphite | | | | ✔ |
| Sodium Persulfate | | | | ✔ |
| Sodium Sulfate | | | NOAEL | |
| Stannous Chloride; Tin (II) Chloride | | | **RfD** | |
| Sulfuric Acid | | NOAEL | | |
| Tartaric Acid | | | Other[b] | |

| Chemical | Cancer: Slope Factor (SF), Weight-of-Evidence (WOE) Classification | Inhalation: RfC, NOAEL, or LOAEL | Oral/Dermal: RfD, NOAEL, or LOAEL | SAT |
|---|---|---|---|---|
| Triethanolamine; or 2,2',2"-Nitrilotris Ethanol | | | LOAEL | |
| Trisodium Citrate 5.5-Hydrate; Sodium Citrate | | | | ✔ |
| Vanillin | | | LOAEL | |

[a] The toxicity data for copper (I) chloride was used to evaluate copper sulfate and cupric sulfate.
[b] Toxicity data other than an RfC, RfD, NOAEL, or LOAEL was used. See Table 3.26 for description of the toxicity data.
[c] Potassium-sodium tartrate added directly to human food is affirmed as generally regarded as safe when meeting specified food manufacturing requirements (U.S. FDA as cited in HSDB, 1996).
[d] Sodium chloride (table salt) is a necessary mineral and electrolyte in humans and animals, and under normal conditions the body efficiently maintains a systemic concentration of 0.9 percent by retaining or excreting dietary sodium chloride. It is not generally considered poisonous to humans or animals, its main systemic effect being blood pressure elevation.

Chemicals having potential developmental toxicity were identified based on the data provided in the toxicity profiles. The data are summarized in Table 3.30. The values listed in the table included the no-observable-effect level (NOEL) or, in the absence of a NOEL, the lowest-observable-effect level (LOEL) concentrations. Chemicals which have inconclusive data concerning the developmental toxicity, as a result of multiple studies having conflicting conclusions, are identified as possible developmental toxicants. The chemical is listed as a possible toxicant given the uncertainty in the data.

**Table 3.30 Developmental Hazards Summary**

| Chemical Name | Oral NOEL (mg/kg/day)[a] | Comments | Inhalation NOEL ($mg/m^3$)[a] | Comments |
|---|---|---|---|---|
| Ammonium Chloride | 1,691 | Drinking water, mice, after day 7 of gestation. No congenital effects (Shepard, 1986). | NA | |
| Boric Acid | 125 | Oral, rabbits, gestation days 6-19. Prenatal mortality, interventricular septal defect, unspecified malformations (U.S. Borax Co., 1992). | NA | |
| 2-Butoxyethanol - **possible inhalation** | 100 | Oral, rats, gestation days 9-11 or 11-13. Reduced prenatal viability noted (Gingell et al., 1994). | 50 ppm | Rats exposed 6 hours/day on gestation days 6-15 to 100 and 200 ppm. Maternal toxicity noted and increased resorbed litters, decreased pup viability, and delayed ossification (Rohm and Haas, 1992). In another study, rats exposed 7 hours/day to 150 and 200 ppm on gestation days 7-15 had maternal toxicity (transient hemoglobinuria), but no developmental toxicity (Gingell et al., 1994). |
| Copper | 51.7 | Food, mice, 30 days before mating through day 19 of gestation. Malformations (EPA, 1984a). | NA | |
| Diethylene Glycol Methyl Ether | 150 (LOEL) | Oral, mice, gestation days 6-15. Malformation of neural tube, heart, renal and skeletal systems (Price et al., 1987). | NA | |
| 2-Ethoxyethanol | 93.1 | Oral, rats, gestation days 1-21. Increase major skeletal malformations (EPA, 1984b). | 369 (LOEL) | Mice, exposure of 6 hours/day, days 6-15 of gestation. Developmental neurotoxicity (EPA, 1996b; 1985a). |

| Chemical Name | Oral NOEL (mg/kg/day)[a] | Comments | Inhalation NOEL ($mg/m^3$)[a] | Comments |
|---|---|---|---|---|
| Ethanolamine | 50 (LOEL) | Oral, rats, gestation days 6-15. Increases in intrauterine deaths, malformations, and increased fetal weight (Mankes, 1986 as reported in TOXLINE, 1995). | NA | |
| Ethylene Glycol | 500 | Oral, mice, gestation days 6-15. Lower body weights and craniofacial and skeletal malformations (Shell Oil, 1992a). | 150 | Rats and mice, exposure of 6 hours/day, days 6-15 of gestation. Fetal malformations in mice (exencephaly, cleft palate, and abnormal rib and facial bones) (Shell Oil, 1992b; Union Carbide, 1991). |
| Ethylenediaminetetraacetic Acid (EDTA) | 954 - LOEL | Diet, rats, gestation days 7-14. Maternal-toxicity and reduced litters, reduced fetal weight and malformations (EPA, 1987). | NA | |
| Hydrazine | NA | Subcutaneous, rats, gestation days 11-21. Injection of 8 mg/kg/day resulted in reduced ratio of fetal survivors to implantation sites, reduced fetal weight, and 100% mortality of pups within 24 hrs of birth (Lee and Aleyassine, 1970). | NA | |
| Hydrochloric Acid | NA | | 450 (LOEL) | Rats, exposure of 1 hour/day for 12-16 days prior to mating or on gestation day 9. Adults exhibited mortality. Increased fetal mortality, decreased fetal weight and increased fetal lung weights (EPA, 1995c). |
| Hydroxylamine Sulfate | NA | Mice. No details given for type of exposure, duration, or dose. Resulted in early fetal deaths and pre-implantation losses (Gross, 1985). | NA | |

| Chemical Name | Oral NOEL (mg/kg/day)[a] | Comments | Inhalation NOEL ($mg/m^3$)[a] | Comments |
|---|---|---|---|---|
| Isopropanol | 480 | Oral, rabbits, gestation days 6-18. Reduced fetal body weights noted in oral exposure of rats, but at concentrations with maternal toxicity. No teratogenic effects noted (Tyl, et al., 1995, as cited in CMA, 1995). | 3,000 ppm (LOEL) | Rats, exposure of 7 hours/day, gestation days 1-19. Reduced fetal weight (Nelson et al., 1943 as cited in ACGIH, 1991). |
| Isophorone | NA | | 50 ppm | Rats, exposure of 6 hours/day, gestation days 6-15. Reduction in mean crown-rump length, significant decrease in maternal body weight noted (Bio/Dynamics Inc., 1984). |
| Lithium Hydroxide | NA | Studies indicate that the risk of major congenital malformations in offspring from women receiving lithium during early pregnancy is slightly higher (4-12%) than that among control groups (2-4%) (Cohen et al., 1994 as cited in Opresko, 1995). Lithium chloride has been shown to cause cleft palate in rats and mice, but lithium carbonate was negative for developmental effects in monkeys, rabbits, and rats (Beliles, 1994). However other studies have shown an increase incidence of cleft palate in mice (Szabo, 1970 as cited in Opresko, 1995). | NA | |
| Methanol | NA | Drinking water, folate-deficient rats, gestation days 6-15. Maternal toxicity (decreased weight gain) and developmental toxicity (increased resorption) observed at drinking water concentrations of 1% and 2% (Lington and Bevan, 1994). | 6,650 (LOEL) | Mice, exposure of 7 hours/day, gestation days 7-9. Increased exencephaly (Lington and Bevan, 1994). |

| Chemical Name | Oral NOEL (mg/kg/day)[a] | Comments | Inhalation NOEL ($mg/m^3$)[a] | Comments |
|---|---|---|---|---|
| N,N-Dimethylformamide | 200 | Dermal, rats, gestation days 8-16 (EPA, 1986). Hydrocephalus, growth retardation, post-implantation losses, and increase mortality in offspring (IARC, 1989). | 0.05 (LOEL) | Rabbits, exposure of 4 hours/day, days 1-19 of gestation. Reduced fetal growth (IARC, 1989). |
| Phenol | 60 | Oral, rats, gestation days 6-15. Reduced fetal body weights (EPA, 1996c). | NA | |
| Potassium Carbonate | NA | Epidemiology study of 226 males employed at potash mine. After starting work underground, mean birth weights increased slightly and there was a decrease in male/female ratio (Wiese and Skipper, 1986). | NA | |
| Potassium and Sodium Cyanide | NA (276.6 mg CN/kg diet) | Oral, pigs, through gestation and lactation. Fetuses had reduced thyroid, spleen, and heart weights. Sows showed hyperplasia of kidney glomeruli and histological changes in thyroid (Tewe and Maner, 1981). | NA | |
| Silver - **Possible** | NA | Silver concentrations in 12 anencephalic human fetuses was higher than silver concentrations in livers of 12 therapeutically aborted fetuses and 14 fetuses aborted spontaneously. Could not be determined if high silver concentrations were associated with the anencephalic malformation or with fetal age (ATSDR, 1990b). | NA | |
| Sodium Chloride | 56,400 ($TD_{LO}$)[b] | Oral, rats, day 5 or 7 pre-conception and one or more days post-conception. Unspecified toxic effects noted (RTECS, 1996). | NA | |

| Chemical Name | Oral NOEL (mg/kg/day)[a] | Comments | Inhalation NOEL ($mg/m^3$)[a] | Comments |
|---|---|---|---|---|
| Sodium Chlorite | 1.4 (LOEL) | Drinking water, rats, 2.5 months prior to mating through gestational day 20. Increase in variation of sternum and increase in crown-rump length. Same study, oral dose 200 mg/kg/day and 2,800 mg/kg/day via drinking water, gestational days 8-15, no developmental effects (Perry et al., 1994). | NA | |
| Sodium Sulfate | 2,800 | Oral, mice, gestation days 8-12. No effect on body weights or litter sizes (Young, 1992). Parentally administered dose of 60 mg/kg on day 8 of gestation produced developmental abnormalities of the musculosketal system (RTECS, 1995). | NA | |
| Stannous Chloride | 50 | Oral, mice, 10 consecutive days, no effect on gestation of fetal survival (Gitilitz and Moran, 1983). Method of exposure unknown, rats, gestation days 7-12. 500 mg/kg resulted in teratogenic effects (Wu, 1990, as reported in TOXLINE, 1995). | NA | |

[a] Unless otherwise noted.

[b] $TD_{Lo}$ = The lowest dose of a chemical that is expected to cause a defined toxic effect.

NA: Not applicable. Data for calculating a dose were not available.

### 3.3.3 Ecological Hazard Summary

Table 3.31 presents a summary of the available ecological hazard information. Concern concentrations (CCs) were determined only for aquatic species (e.g., *Daphnia*, algae, and/or fish) using standard EPA methodology. Methods for determining CCs are summarized below. (*Cleaner Technologies Substitutes Assessment: A Methodology and Resources Guide* [Kincaid et al., 1996] presents the methods in more detail.)

**Table 3.31 Aquatic Toxicity Information**

| Chemical Name[a] | $LC_{50}$ (mg/L)[b] | Test Information | Species | CC (mg/L)[c] | Source |
|---|---|---|---|---|---|
| 1,3-Benzenediol | > 100<br>0.25<br>88.6<br>262<br>> 100 | all 96 hr | rainbow trout<br>water flea<br>minnow<br>zebra fish<br>snail | AsF = 100[(2)]<br>0.0025 | AQUIRE, 1995 |
| 2-Butoxyethanol Acetate | 150<br>960<br>> 500 | 48 hr<br>17 hr<br>72 hr | water flea<br>protozoa<br>green algae | AsF = 100[(2)]<br>1.5 | Verschueren, 1996 |
| 2-Ethoxyethanol | > 5,000<br>> 10,000<br><br>7,660 | 24 hr<br>96 hr<br><br>48 hr $IC_{50}$[d] | goldfish<br>bluegill & silversides<br>water flea | AsF = 1,000[(3)]<br>5.0 | AQUIRE, 1996; EPA, 1985a |
| Ammonia | 0.42-0.84<br>1.74<br>1.58 | 8 hr<br>24 hr<br>24 hr | rainbow trout<br>water flea<br>snail | AsF = 100[(2)]<br>CC = 0.0042 | AQUIRE, 1995 |
| Ammonium Chloride | 640<br>139<br>50 | 24 hr TLm[e]<br>24-96 hr TLm<br>96 hr TLm | carp<br>bluegill<br>water flea | AsF = 1,000[(3)]<br>0.05 | Verscheuren, 1983 |
| Boric Acid | 46-75<br>22-155<br>79-100 | 7 day<br>9 day<br>28 day | goldfish<br>catfish<br>rainbow trout | AsF = 1,000[(3)]<br>0.022 | AQUIRE, 1995 |
| Carbon Black | No information found in literature | | | | |
| Copper | 0.8-1.9<br>0.0885-21<br>0.13-0.5<br>0.125<br>10-33 | 96 hr<br>96 hr<br>96 hr<br>96 hr<br>24 hr | carp<br>minnow<br>rainbow trout<br>salmon<br>shrimp | AsF = 100[(2)]<br>0.00088 | AQUIRE, 1995 |
| Copper Chloride (Cuprous) | 0.40-2.3 | 96 hr | mummichog (fish) | AsF = 1,000[(3)]<br>0.0004 | AQUIRE, 1995 |
| Copper Sulfate | 0.18-12<br>0.096-0.12<br>0.036-1.38<br>0.002-160<br>0.10-0.24<br>0.002-23.6<br>0.56-40 | 96 hr<br>96 hr<br>96 hr<br>96 hr<br>96 hr<br>96 hr<br>96 hr | bullhead<br>zebrafish<br>goldfish<br>carp<br>salmon<br>minnow<br>oyster | AsF = 100[(2)]<br>0.00002 | AQUIRE, 1995 |
| Diethylene Glycol Methyl Ether | > 5,000<br>7,500 | 24 hr<br>96 hr | goldfish<br>minnow | AsF = 1,000[(3)]<br>5.0 | AQUIRE, 1995 |

| Chemical Name[a] | $LC_{50}$ (mg/L)[b] | Test Information | Species | CC (mg/L)[c] | Source |
|---|---|---|---|---|---|
| Diethylene Glycol<br>Ethyl Ether | 9,650-26,500<br>12,900-13,400<br>15,200<br>6,010<br>1,982-4,670 | 96 hr<br>96 hr<br>96 hr<br>96 hr<br>48 hr | minnow<br>rainbow trout<br>mosquito fish<br>catfish<br>water flea | AsF = 100[(2)]<br>CC = 20 | AQUIRE, 1996 |
| Diethylene Glycol<br>n-Butyl Ether | 1,300<br>3,200<br>1,000 | 96 hr<br>$EC_{50}$[f]<br>decreased cell multiplication | bluegill<br>water flea<br>blue-green algae | AsF = 100[(2)]<br>10 | AQUIRE, 1995 |
| Dimethylformamide | 1.2-2.5<br>1,300<br>> 1,000<br>9,860<br>18,800 | MATC[g], chronic<br>24 hr<br>48 hr<br>96 hr<br>48 hr $EC_{50}$ | water flea<br>guppy<br>medaka<br>rainbow trout<br>water flea | AsF = 10[(4)]<br>CC = 0.12 | EPA, 1986 |
| Ethanolamine | 170<br>40 & 70<br>140<br>0.75 | 96 hr<br>24 hr $LC_0$[h] & $LC_{100}$[i]<br>24 hr<br>8 day, toxicity threshold | goldfish<br>creek chub<br>water flea<br>green algae | AsF = 10[(1)]<br>CC = 0.075 | AQUIRE, 1995 |
| Ethylene Glycol | 41,000<br>49,000-57,000<br>41,000-57,600<br>> 5,000<br>330 | 96 hr<br>96 hr<br>48 hr<br>24 hr<br>48 hr | rainbow trout<br>minnow<br>water flea<br>goldfish<br>African frog | AsF = 100[(2)]<br>CC = 3.3 | AQUIRE, 1995 |
| Ethylenediaminetetraacetic Acid (EDTA) | 129<br>625<br>59.8<br>41-532<br>280 | 96 hr<br>24 hr<br>96 hr<br>96 hr, varying pH<br>24 hr | catfish<br>water flea<br>minnow<br>bluegill<br>shrimp | AsF = 100[(2)]<br>CC = 0.41 | AQUIRE, 1995 |
| Fluoroboric Acid | 125<br>(as fluoride) | 48 hr | brown trout | AsF = 1,000[(3)]<br>CC = 0.125 | Woodiwiss & Fretwell, 1974 |
| Formaldehyde | 25.2-40<br>47.2<br>6.7<br>25.5-26.3 | 96 hr<br>96 hr<br>96 hr<br>96 hr | bluegill<br>rainbow trout<br>striped bass<br>catfish | AsF = 1,000[(3)]<br>CC = 0.0067 | EPA, 1985b |
| Formic Acid | 175<br>80-90<br>151 | 24 hr<br>48 hr<br>48 hr | bluegill<br>green crab<br>water flea | AsF = 1,000[(3)]<br>CC = 0.08 | AQUIRE, 1995 |
| Hydrochloric Acid | 282<br>100<br><br>180 | 24-96 hr<br>96 hr produced no stress effects<br><br>96 hr | mosquito fish<br>green crab<br><br>goldfish | AsF = 1,000[(3)]<br>CC = 0.1 | AQUIRE, 1995 |
| Hydrogen Peroxide | 89<br>12<br>155 | 24 hr<br>228 hr $LT_{50}$[j]<br>24 hr | mackerel<br>zebra mussel<br>gobi | AsF = 10[(1)]<br>CC = 1.2 | AQUIRE, 1995 |
| Isophorone | 12.9<br>79<br>228 | 96 hr<br>NOEC[k]<br>96 hr | mysid shrimp<br>green algae<br>minnow | AsF = 100[(2)]<br>CC = 0.13 | AQUIRE, 1996 |

| Chemical Name[a] | $LC_{50}$ (mg/L)[b] | Test Information | Species | CC (mg/L)[c] | Source |
|---|---|---|---|---|---|
| Isopropanol | > 1,400<br>900-1,100<br>1,150<br>1,800 | 96 hr<br>24 hr<br>96 hr<br>toxicity threshold | mosquito fish<br>creek chub<br>shrimp<br>green algae | AsF = 100[(2)]<br>CC = 9.0 | AQUIRE, 1995 |
| Lithium Hydroxide | No aquatic toxicity information available | | | | |
| m-Nitrobenzene Sulfonic Acid | 8,600<br>> 500 | 24 &48 hr<br>48 & 96 hr | water flea<br>trout, guppy, bluegill, minnow | AsF = 100[(2)]<br>CC = 5 | AQUIRE, 1995; Greim et al., 1994 |
| Methanol | 28,200<br>20,100<br>1,700<br>2.6-3.1%<br>> 10,000 | 96 hr<br>96 hr<br>48 hr<br>10-14 day $EC_{50}$<br>24 hr $LC_{50}$ | minnow<br>rainbow trout<br>goldfish<br>algae<br>brine shrimp | AsF = 100[(2)]<br>CC = 17 | AQUIRE, 1995 |
| Palladium, Palladium Chloride | 0.237<br>0.142 | 24 hr $EC_{50}$<br>48 hr $EC_{50}$ | tubificid worm | AsF = 1,000[(3)]<br>CC = 0.00014 | AQUIRE, 1995 |
| Phenol-Formaldehyde Copolymer | No aquatic toxicity information available. Once cured, PF copolymer is highly insoluble and is not expected to be toxic to aquatic life. | | | | |
| Phosphoric Acid | 138 | TLm | mosquito fish | AsF = 1,000[(3)]<br>CC = 0.138 | HSDB, 1995 |
| Potassium Cyanide, Sodium Cyanide | 0.052<br>0.057<br>0.0079 | 96 hr<br>96 hr<br>chronic value | brook trout<br>rainbow trout<br>brook trout | AsF = 10[(1)]<br>CC = 0.79 | EPA, 1980 |
| Potassium Hydroxide | 85<br>80<br>80 | 24 hr<br>48 hr<br>96 hr | mosquito fish<br>mosquito fish<br>guppy | AsF = 1,000[(3)]<br>CC = 0.08 | AQUIRE, 1995 |
| Potassium Persulfate | 1,360<br>234<br>845<br>92-251 | 48 hr<br>48 hr<br>48 hr<br>48 hr | carp<br>rainbow trout<br>guppy<br>water flea | AsF = 100[(2)]<br>CC = 0.92 | AQUIRE, 1995 |
| Potassium-Sodium Tartrate | No aquatic toxicity information available. | | | | |
| Potassium Sulfate | 112<br>1,180<br>3,550<br>2,380 | all 96 hr | mussel<br>adult snail<br>bluegill<br>bleak | AsF = 1,000[(3)]<br>CC = 0.11 | AQUIRE, 1995 |
| 1H-Pyrrole | 210<br>856 | 96 hr<br>72 hr $EC_{50}$ | minnow<br>protozoan | AsF = 1,000[(3)]<br>CC = 0.21 | AQUIRE, 1996 |
| Silver | 0.0514<br>0.064<br>0.036<br>58 | 96 hr<br>96 hr<br>96 hr<br>98 hr | rainbow trout<br>bluegill<br>minnow<br>minnow | AsF = 1,000[(3)]<br>CC = 0.000036 | AQUIRE, 1996 |
| Sodium Bisulfate | 58-80<br>190 | 24 & 48 hr<br>immobilized after 48 hrs | mosquito larvae<br>water flea | AsF = 1,000[(3)]<br>CC = 0.058 | AQUIRE, 1995 |
| Sodium Carbonate | 300-320<br>297<br>242<br>524 | 96 hr<br>50 hr<br>5 day<br>96 hr | bluegill<br>guppy<br>diatom (algae)<br>water flea | AsF = 100[(2)]<br>CC = 2.4 | AQUIRE, 1995 |

| Chemical Name[a] | $LC_{50}$ (mg/L)[b] | Test Information | Species | CC (mg/L)[c] | Source |
|---|---|---|---|---|---|
| Sodium Chloride | 4,324-13,750 | 24 hr-10 day | goldfish | AsF = 100[(2)] | AQUIRE, |
| | 17,550-18,100 | 25-96 hr | mosquito fish | CC = 2.8 | 1996 |
| | 23,000-32,000 | 24-96 hr | damsel fly | | |
| | 280-1,940 | ≥ 24 hr | water flea | | |
| | 1,500-5,000 | 24-96 hr | striped bass | | |
| Sodium Chlorite | 75 | 96 hr | minnow | AsF = 1,000[(3)] | TR-Metro, |
| | 0.65 | 96 hr | mysid shrimp | CC = 0.00016 | 1994; Albright |
| | 0.161 | 48 hr | water flea | | & Wilson, |
| | | | | | 1992a,b |
| Sodium Citrate | 3,330 | 24 hr | water flea | AsF = 1,000[(3)] | AQUIRE, |
| | | | | CC = 3.3 | 1995 |
| Sodium Hydroxide | 125 | 96 hr | mosquito fish | AsF = 10[(1)] | AQUIRE, |
| | 30 | 24 hr $LC_{40}$[l] | pikeperch | CC = 2.5 | 1995; |
| | 33-100 | 48 hr | poacher | | HSDB, 1995 |
| | ≥ 25 | chronic | guppy | | |
| Sodium Persulfate | 1,667 | 48 hr | carp | AsF = 1,000[(3)] | AQUIRE, |
| | 64.6 | 48 hr | water flea | CC = 0.065 | 1995 |
| | 388 | 48 hr | rainbow trout | | |
| | 631 | 48 hr | guppy | | |
| Sodium Sulfate | 200-290 | 96 hr | amphipoda | AsF = 100[(2)] | AQUIRE, |
| | 81 | 96 hr | bass larvae | CC = 0.81 | 1995 |
| | 204 | 96 hr | water flea | | |
| | 4,380 | 96 hr | bluegill | | |
| | 3,360 | 32 day | *Myriophyllum spicatum* | | |
| Stannous Chloride[m] | 0.6 | 30 day lethal conc | green algae | AsF = 100[(2)] | AQUIRE, |
| | 2.1 | 7 day | goldfish eggs | CC = 0.0009 | 1995 |
| | 0.09 | 7 day | toad eggs | | |
| | 0.4 | 28 day | rainbow trout eggs | | |
| Sulfuric Acid | 80-90 | 48 hr | poacher | AsF = 10[(1)] | AQUIRE, |
| | 42 | 96 hr | mosquito fish | CC = 2.0 | 1995 |
| | 42.5 | 48 hr | prawn | | |
| | 20 | 7 day, no mortality | water flea | | |
| Tartaric Acid | 250-320 | $LD_0$[n] | paramecium | AsF = 10[(1)] | Verschueren, |
| | 200 | $LD_0$ longtime hardwater exp. | goldfish | CC = 1.0 | 1983 |
| | 10 | $LD_0$ longtime softwater exp. | | | |
| Tetrasodium EDTA | 360 | 72 hr | protozoa | AsF = 10[(1)] | AQUIRE, |
| | 663 | 48 hr | cryptomonad | CC = 1.1 | 1995 |
| | 1,033 | $EC_{50}$ | water flea | | |
| | 11 | 8 day, decreased cell multiplication | green algae | | |
| | 1,030-2,070 | 96 hr | bluegill | | |

| Chemical Name[a] | $LC_{50}$ (mg/L)[b] | Test Information | Species | CC (mg/L)[c] | Source |
|---|---|---|---|---|---|
| Triethanolamine; or 2,2',2"-Nitrilotris Ethanol | > 5,000<br>11,800<br>176-213 mg/kg<br>1.8 | 24 hr<br>96 hr<br>48 hr, $LD_0$<br>8 day, decreased cell multiplication | goldfish<br>minnow<br>carp<br>green algae | AsF = 10(1)<br>CC = 0.18 | AQUIRE, 1995 |
| Vanillin | 112-121<br>57-123 | 96 hr<br>96 hr | minnow<br>minnow | AsF = 1,000(3)<br>CC = 0.057 | AQUIRE, 1996; Verschueren, 1996 |

[a] Only those chemicals with data are listed. Proprietary chemical data are not presented in order to protect proprietary chemical identities.
[b] Lethal concentration ($LC_{50}$) = the concentration of a chemical in water that causes death or complete immobilization in 50 percent of the test organisms at the end of the specified exposure period. $LC_{50}$ values typically represent acute exposure periods, usually 48 or 96 hours but up to 14 days for fish. Units are mg/L unless otherwise noted.
[c] Concern concentration (CC) = most sensitive toxicity value (mg/L) ÷ AsF. AsF = Assessment (uncertainty) factor.
[d] Concentration that immobilizes 50 percent of the test population.
[e] TLm = Median threshold limit value, or tolerance limit median - equivalent to an $LC_{50}$ value.
[f] $EC_{50}$ = Effective concentration to 50 percent of a test population.
[g] MATC = Maximum acceptable toxicant concentration. It is generally defined as the geometric mean of the highest concentration tested at which no significant deleterious effect was observed and the lowest concentration tested at which some significant deleterious effect was observed.
[h] $LC_0$ = Estimated maximum concentration that would not result in death of the exposed organisms.
[i] $LC_{100}$ = Lethal concentration to 100 percent of a test population.
[j] $LT_{50}$ = Time for 50 percent of the test population to die at a preselected concentration.
[k] NOEC = No-observed effect concentration.
[l] $LC_{40}$ = Lethal concentration to 40 percent of a test population.
[m] Stannous chloride is expected to rapidly dissociate in water under environmental conditions, followed by formation of tin complexes and precipitation out of the water column. This process would make stannous chloride much less available for toxic effects to aquatic organisms.
[n] $LD_0$ = Estimated maximum dose that would not result in death of the exposed organisms.
(1) Chronic data available and was most sensitive endpoint, AsF = 10.
(2) Acute data available for multiple species and trophic levels, AsF = 100.
(3) Limited acute data available, AsF = 1,000.
(4) AsF of 10 used for MATC data.

The CC for each chemical in water was calculated using the general equation:

CC = acute or chronic toxicity value ÷ AsF

where:

CC = aquatic toxicity concern concentration, the concentration of a chemical in the aquatic environment below which no significant risk to aquatic organisms is expected.

AsF = assessment factor (an uncertainty factor), the adjustment value used in the calculation of a CC that incorporates the uncertainties associated with: 1) toxicity data (e.g., laboratory test versus field test, measured versus estimated data); 2) acute exposures versus chronic exposures; and 3) species sensitivity. This factor is expressed as an order of magnitude or as a power of ten (EPA, 1984c).

If several acute or chronic toxicity values are available, the lowest one is used (most sensitive tested species), unless poor or uncertain data quality disqualifies one or more of the values. The AQUIRE database, an extensive source of aquatic toxicity data, includes a numerical rating of study quality.

AsFs are dependent on the amount and type of toxicity data contained in a toxicity profile and reflect the amount of uncertainty about the potential effects associated with a toxicity value. In general, the more complete the toxicity profile and the greater the quality of the toxicity data, the smaller the AsF used.

The following approach was used, depending on availability and type of data:

- If the toxicity profile only contained one or two acute toxicity values (no chronic values), AsF = 1,000 and the CC was calculated by using the lower acute value.
- If the toxicity profile contained three or more acute values (no chronic values), AsF = 100 and the CC was calculated by using the lowest acute value.
- If the toxicity profile contained at least one chronic value, and the value was for the most sensitive species, AsF = 10 and the CC was calculated by using the lowest chronic value. Otherwise, AsF = 100 and the CC was calculated with the acute value for the most sensitive species.
- If the toxicity profile contained field toxicity data, AsF = 1 and CC was calculated by using the lowest value.

Aquatic toxicity values were estimated using the ECOSAR program (EPA, 1994b) for chemicals without available measured acute or chronic aquatic toxicity data. These values are presented in Table 3.32. An AsF of 1,000 was used to calculate all CCs based on such estimates.

Table 3.33 presents chemicals with aquatic toxicity CCs. The chemicals are listed in ascending order (i.e., the chemical with the lowest CC to the chemical with the highest CC for each of the alternatives). The lowest CC is for copper sulfate, based on fish toxicity data. The table also presents aquatic hazard concern levels; chemicals were assigned to aquatic toxicity concern levels according to the following EPA criteria:

For chronic values:

≤ 0.1 mg/L.....High concern
> 0.1 to ≤ 10 mg/L.....Moderate concern
> 10 mg/L.....Low concern

For acute values:

≤ 1 mg/L.....High concern
> 1 to ≤ 100 mg/L.....Moderate concern
> 100 mg/L.....Low concern

Chronic toxicity ranking takes precedence over the acute ranking.

It should be noted that aquatic hazard concern levels are derived from the lowest toxicity value available. Therefore, these rankings are derived separately from the CCs which are derived based on the amount of toxicity data available for a given chemical. A summary of the aquatic toxicity results for the known proprietary chemicals is presented in Table 3.34.

These rankings are based only on chemical toxicity to aquatic organisms, and are not an expression of risk. The number of chemicals with a high aquatic hazard concern level include two in carbon, two in conductive ink, none in the conductive polymer process, nine in the electroless copper process, three in graphite, three in non-formaldehyde electroless copper, two in organic-palladium, and nine in tin-palladium.

**Table 3.32 Estimated Ecological (Aquatic)Toxicity Information for Non-Proprietary Chemicals**

| Chemical | Acute Toxicity (mg/L) | | | Chronic Toxicity (mg/L) | | | AsF, CC (mg/L) |
|---|---|---|---|---|---|---|---|
| | Fish (FW) 96 hr $LC_{50}$ | Daphnid 48 hr $LC_{50}$ | Green Algae 96 hr $EC_{50}$ | Fish 14 day $LC_{50}$ | Daphnid 16 day $EC_{50}$ | Green Algae >96 hr ChV | |
| Benzotriazole[1] | 45.3 | 378.1 | 23.4 | ND | ND | ND | 1,000<br>0.023 |
| Dimethylaminoborane[2] | 10 | 0.7 | 3.0 | 1.0 | 0.070 | 0.3 | 10<br>0.007 |
| Graphite[2] | * | * | * | * | * | * | |
| Hydroxyacetic Acid[1] | > 1,000 * | > 1,000 * | > 1,000 * | ND | ND | ND | 1,000<br>1 |
| Magnesium Carbonate[2] | > 100 | 140 | > 100 | > 10 | 82 | > 10 | 10<br>> 1.0 |
| Peroxymonosulfuric Acid[2] | ≤ 3.0 | ≤ 3.0 | ≤ 3.0 | ≤ 0.30 | ≤ 0.30 | ≤ 1.0 | 10<br>0.030 |
| Potassium Bisulfate[2] | > 1,000 | > 100 | > 100 | > 100 | > 10 | > 10 | 10<br>> 1.0 |
| Potassium Carbonate[2] | 1,300 | 330 | 100 | 100 | 190 | > 30 | 10<br>> 3.0 |
| p-Toluene Sulfonic Acid[2] | Predicted toxicity values of environmental base set all > 100 mg/L, chronic values all > 10.0 mg/L based on SARs for anionic LAS surfactants. | | | | | | 10<br>1.0 |
| Sodium Hypophosphite[2] | > 100 | > 100 | 0.030 | > 10 | > 10 | 0.060 | 10<br>0.006 |

[1] ECOSAR Program.
[2] SAT Report.
* No adverse effects expected in a saturated solution.
ND: No Data. ECOSAR (EPA, 1994b) did not include an estimating component for this endpoint for the chemical class.

**Table 3.33 Aquatic Hazard Concern Concentrations (CCs) and Hazard Concern Levels by MHC Technology for Non-Proprietary Chemicals**

| Chemicals in MHC Processes[a] | CCs (mg/L) | Aquatic Hazard Concern Level[b] |
|---|---|---|
| **Electroless Copper** | | |
| Copper Sulfate | 0.00002[(2)] | High[(A)] |
| Palladium; Palladium Chloride | 0.00014[(3)] | High[(A)] |
| Sodium Chlorite | 0.00016[(3)] | High[(A)] |
| Copper Chloride | 0.0004[(3)] | High[(A)] |
| Stannous Chloride[c] | 0.0009[(2)] | High[(A)] |
| Sodium Hypophosphite | 0.006[(5)] | Low[(A)] |
| Formaldehyde | 0.0067[(3)] | Moderate[(A)] |
| Dimethylaminoborane | 0.007[(5)] | High[(C)] |
| Boric Acid | 0.022[(3)] | Moderate[(A)] |
| Benzotriazole | 0.023[(5)] | Moderate[(A)] |
| Peroxymonosulfuric Acid | 0.030[(5)] | Moderate[(C)] |
| Ammonium Chloride | 0.05[(3)] | Moderate[(A)] |
| Sodium Bisulfate | 0.058[(3)] | Moderate[(A)] |
| Ethanolamine | 0.075[(1)] | High[(A)] |
| Potassium Hydroxide | 0.08[(3)] | Moderate[(A)] |
| Formic Acid | 0.08[(3)] | Moderate[(A)] |
| Potassium Hydroxide | 0.08[(3)] | Moderate[(A)] |
| Hydrochloric Acid | 0.1[(3)] | Moderate[(A)] |
| Potassium Sulfate | 0.11[(3)] | Low[(A)] |
| Dimethylformamide | 0.12[(4)] | Moderate[(C)] |
| Fluoroboric Acid | 0.125[(3)] | Low[(A)] |
| Triethanolamine; or 2,2',2"-Nitrilotris Ethanol | 0.18[(1)] | Moderate[(C)] |
| Ethylenediaminetetraacetic Acid (EDTA) | 0.41[(2)] | Moderate[(A)] |
| Sodium Cyanide | 0.79[(1)] | High[(C)] |
| Potassium Cyanide | 0.79[(1)] | High[(C)] |
| Sodium Sulfate | 0.81[(2)] | Moderate[(A)] |
| Potassium Persulfate | 0.92[(2)] | Moderate[(A)] |
| Hydroxyacetic Acid | 1[(5)] | Low[(A)] |
| Magnesium Carbonate | 1.0[(5)] | Low[(C)] |
| p-Toluene Sulfonic Acid | 1.0[(5)] | Low[(C)] |
| Tartaric Acid | 1.0[(1)] | Moderate[(C)] |
| Potassium Bisulfate | >1.0[(5)] | Low[(C)] |
| Hydrogen Peroxide | 1.2[(1)] | Low[(C)] |
| Sulfuric Acid | 2.0[(1)] | Low[(C)] |

| Chemicals in MHC Processes[a] | CCs (mg/L) | Aquatic Hazard Concern Level[b] |
|---|---|---|
| Sodium Carbonate | 2.4[(2)] | Low[(A)] |
| Sodium Hydroxide | 2.5[(1)] | Low[(C)] |
| Ethylene Glycol | 3.3[(2)] | Low[(A)] |
| m-Nitrobenzene Sulfonic Acid | 5[(2)] | Low[(A)] |
| 2-Ethoxyethanol | 5.0[(3)] | Low[(A)] |
| Isopropanol | 9.0[(2)] | Low[(A)] |
| Methanol | 17[(2)] | Low[(A)] |
| Potassium-Sodium Tartrate | no data available | |
| **Carbon** | | |
| Copper Sulfate | 0.00002[(2)] | High[(A)] |
| Sodium Persulfate | 0.065[(3)] | Moderate[(A)] |
| Ethanolamine | 0.075[(1)] | High[(A)] |
| Potassium Hydroxide | 0.08[(3)] | Moderate[(A)] |
| Sulfuric Acid | 2.0[(1)] | Low[(C)] |
| Potassium Carbonate | > 3.0[(5)] | Low[(C)] |
| Ethylene Glycol | 3.3[(2)] | Low[(A)] |
| Carbon Black | no data available | |
| **Conductive Ink** | | |
| Silver | 0.000036[(3)] | High[(A)] |
| Copper | 0.00088[(2)] | High[(A)] |
| Isophorone | 0.13[(2)] | Moderate[(A)] |
| 2-Butoxyethanol Acetate | 1.5[(2)] | Low[(A)] |
| Diethylene Glycol Methyl Ether | 5.0[(3)] | Low[(A)] |
| Diethylene Glycol n-Butyl Ether | 10[(2)] | Low[(A)] |
| Methanol | 17[(2)] | Low[(A)] |
| Diethylene Glycol Ethyl Ether | 20[(2)] | Low[(A)] |
| Graphite | not expected to be toxic[(5)] | Low |
| Phenol-Formaldehyde Copolymer | not expected to be toxic[(5)] | Low |
| Carbon Black | no data available | |
| **Conductive Polymer** | | |
| Peroxymonosulfuric Acid | 0.030[(5)] | Moderate[(C)] |
| Phosphoric Acid | 0.138[(3)] | Low[(A)] |
| 1H-Pyrrole | 0.21[(3)] | Low[(A)] |
| Sulfuric Acid | 2.0[(1)] | Low[(C)] |
| Sodium Carbonate | 2.4[(2)] | Low[(A)] |
| Sodium Hydroxide | 2.5[(1)] | Low[(C)] |

| Chemicals in MHC Processes[a] | CCs (mg/L) | Aquatic Hazard Concern Level[b] |
|---|---|---|
| **Graphite** | | |
| Copper Sulfate | 0.00002[(2)] | High[(A)] |
| Ammonia | 0.0042[(2)] | High[(A)] |
| Peroxymonosulfuric Acid | 0.030[(5)] | Moderate[(C)] |
| Sodium Persulfate | 0.065[(3)] | Moderate[(A)] |
| Ethanolamine | 0.075[(1)] | High[(A)] |
| Sulfuric Acid | 2.0[(1)] | Low[(C)] |
| Potassium Carbonate | > 3.0[(5)] | Low[(C)] |
| Graphite | not expected to be toxic[(5)] | Low |
| **Non-Formaldehyde Electroless Copper** | | |
| Copper Sulfate | 0.00002[(2)] | High[(A)] |
| Sodium Chlorite | 0.00016[(3)] | High[(A)] |
| Stannous Chloride[c] | 0.0009[(2)] | High[(A)] |
| Potassium Hydroxide | 0.08[(3)] | Moderate[(A)] |
| Hydrochloric Acid | 0.1[(3)] | Moderate[(A)] |
| Potassium Persulfate | 0.92[(2)] | Moderate[(A)] |
| Hydrogen Peroxide | 1.2[(1)] | Low[(C)] |
| Sulfuric Acid | 2.0[(1)] | Low[(C)] |
| Sodium Hydroxide | 2.5[(1)] | Low[(C)] |
| Isopropanol | 9.0[(2)] | Low[(A)] |
| **Organic-Palladium** | | |
| Sodium Hypophosphite | 0.006[(5)] | High[(C)] |
| Sodium Bisulfate | 0.058[(3)] | Moderate[(A)] |
| Sodium Persulfate | 0.065[(3)] | Moderate[(A)] |
| Hydrochloric Acid | 0.1[(3)] | Moderate[(A)] |
| Sodium Carbonate, Sodium Bicarbonate | 2.4[(2)] | Low[(A)] |
| Sodium Citrate | 3.3[(3)] | Low[(A)] |
| **Tin-Palladium** | | |
| Copper Sulfate | 0.00002[(2)] | High[(A)] |
| Palladium Chloride, Palladium | 0.00014[(3)] | High[(A)] |
| Copper | 0.00088[(2)] | High[(A)] |
| Stannous Chloride[c] | 0.0009[(2)] | High[(A)] |
| 1,3-Benzenediol | 0.0025[(2)] | High[(A)] |
| Dimethylaminoborane | 0.007[(5)] | High[(C)] |
| Vanillin | 0.057[(3)] | Moderate[(A)] |
| Sodium Bisulfate | 0.058[(3)] | Moderate[(A)] |
| Sodium Persulfate | 0.065[(3)] | Moderate[(A)] |

| Chemicals in MHC Processes[a] | CCs (mg/L) | Aquatic Hazard Concern Level[b] |
|---|---|---|
| Ethanolamine | 0.075(1) | High(A) |
| Hydrochloric Acid | 0.1(3) | Moderate(A) |
| Fluoroboric Acid | 0.125(3) | Low(A) |
| Phosphoric Acid | 0.14(3) | Low(A) |
| Triethanolamine; or 2,2',2"-Nitrilotris Ethanol | 0.18(1) | Moderate(C) |
| Hydrogen Peroxide | 1.2(1) | Low(C) |
| Sulfuric Acid | 2.0(1) | Low(C) |
| Sodium Hydroxide | 2.5(1) | Low(C) |
| Sodium Chloride | 2.8(2) | Low(A) |
| Potassium Carbonate | > 3.0(5) | Low(C) |
| Isopropanol | 9.0(2) | Low(A) |
| Lithium Hydroxide | no data available | |

[a] Different supplier's product lines do not necessarily include all of the chemicals listed for a process alternative.

[b] Based on lowest available toxicity data:

(A) indicates the lowest acute value was used for hazard ranking.

(C) indicates the hazard ranking is based on a chronic value, if available and lower than any acute value.

[c] Stannous chloride is expected to rapidly dissociate in water under environmental conditions, followed by tin forming complexes and precipitating out of the water column. This process would make stannous chloride much less available for toxic effects to aquatic organisms.

Basis of Concern Concentrations:

(1) Chronic data.

(2) Acute data for multiple species and taxonomic groups.

(3) Limited acute data.

(4) Chronic MATC.

(5) Structure-activity relationship estimate using the ECOSAR program or SAT report.

**Table 3.34 Summary of Aquatic Toxicity for Proprietary Chemicals**

| Technology | No. of Additional Trade Secret Chemicals[a] | Aquatic Toxicity Concern Rank | | | CC (mg/l) | | | |
|---|---|---|---|---|---|---|---|---|
| | | Low | Moderate | High | < 0.1 | 0.9 - 0.99 | 1 - 10 | > 10 |
| Electroless Copper | 9 | 6 | 3 | 0 | 1 | 2 | 5 | 1 |
| Graphite | 5 | 4 | 1 | 0 | 0 | 2 | 2 | 1 |
| Tin-Palladium | 5 | 2 | 1 | 2 | 2 | 1 | 1 | 1 |
| Organic-Palladium | 1 | 0 | 0 | 1 | 1 | 0 | 0 | 0 |

[a] Includes chemicals not previously identified in the publicly-available bath chemistry data for a technology.

### 3.3.4 Summary

For human health hazards, toxicity data in the form of RfDs, RfCs, NOAELs, LOAELs, and cancer slope (cancer potency) factors were compiled for inhalation and dermal pathways. Formaldehyde was the only non-proprietary chemical with an established cancer slope (cancer potency) factor. Other non-proprietary chemicals in the MHC processes are suspected carcinogens, but do not have established slope factors. Dimethylformamide and carbon black

have been determined by IARC to possibly be carcinogenic to humans (IARC Group 2B). Dimethylformamide is used by at least one supplier in the electroless copper process. Carbon black is used in the carbon and conductive ink processes. Two proprietary chemicals used in the graphite and electroless copper processes, cyclic ether and alkyl oxide, have cancer slope factors. Another proprietary chemical used in the electroless copper process, trisodium acetate amine B, is possibly carcinogenic to humans but does not have an established slope factor.

An ecological hazards assessment was performed based on chemical toxicity to aquatic organisms. Concern concentrations (CCs) were estimated for MHC chemicals using an established EPA method. A CC is an acute or chronic toxicity value divided by an assessment factor (AsF). AsFs are dependent on the amount and type of toxicity data contained in a toxicity profile and reflect the amount of uncertainty about the potential effects associated with a toxicity value. Concern concentrations were determined for aquatic species (e.g., *Daphnia*, algae, and/or fish). The lowest CC is for copper sulfate, based on fish toxicity data.

Chemicals were also ranked for aquatic toxicity concern levels using established EPA criteria (high, moderate, and low concern) based on the available toxicity data. The number of chemicals with a high aquatic hazard concern level include nine in the electroless copper process, two in carbon, two in conductive ink, none in conductive polymer, three in graphite, three in non-formaldehyde electroless copper, and nine in the tin-palladium process, and two in the organic palladium process.

## 3.4 RISK CHARACTERIZATION

Risk characterization is the summarizing step of a risk assessment, which integrates the hazard and exposure assessment components and presents overall conclusions. Risk characterization typically includes a description of the assumptions, scientific judgments, and uncertainties that are part of this process. There are several types of risk assessment ranging from screening level to comprehensive, and differing according to framework: site-specific, single chemical, or multiple chemical. This risk assessment is best described as a screening level assessment of multiple chemicals identified as belonging to a particular use cluster (MHC) in the PWB industry. This is a screening level, rather than a comprehensive risk characterization, both because of the predefined scope of the assessment and because of exposure and hazard data limitations. The intended audience of this risk characterization is the PWB industry and others with a stake in the practices of this industry.

The focus of this risk characterization is on chronic (long-term) exposure to chemicals that may cause cancer or other toxic effects rather than on acute toxicity from brief exposures to chemicals. The focus is also on those health effects from chronic exposures that could be used to measure risk. In addition, this risk characterization does not consider chemical persistence. The Process Safety Assessment (Section 3.5) includes further information on chemical safety concerns.

The goals of the PWB project risk characterization are:

- To present conclusions and uncertainties associated with a screening level health risk assessment of chemicals used in the MHC process of PWB manufacture.
- To integrate chemical hazard and exposure information to assess risks from ambient environment and occupational exposures from the MHC process.
- To use reasonable and consistent assumptions across alternatives, so health risks associated with one alternative can be compared to the health risks associated with other alternatives.
- To identify the areas of concern that differ among the substitutes in a manner that facilitates decision-making.

This section contains a summary of the exposure assessment (Section 3.4.1), the human health hazards assessment (Section 3.4.2), a description of methods used to calculate risk indicators (Section 3.4.3), results (Section 3.4.4), discussion of uncertainties (Section 3.4.5), and conclusions (Section 3.4.6). Detailed exposure data are presented separately in the Exposure Assessment (Section 3.2) and in Appendix E.

### 3.4.1 Summary of Exposure Assessment

The exposure assessment uses a "model facility" approach, where as much as possible, reasonable and consistent assumptions are used across alternatives. Data to characterize the model facility and exposure patterns for each process alternative were aggregated from a number of sources, including PWB shops in the U.S. and abroad, supplier data, and input from PWB manufacturers at project meetings. Thus, the model facility is not entirely representative of any

one facility, and actual exposure (and risk) could vary substantially, depending on site-specific operating conditions and other factors.

Chemical exposures to PWB workers and the general population were estimated by combining information gathered from industry (IPC Workplace Practices Questionnaire and Performance Demonstration data, MSDSs, and other available information) with standard EPA exposure assumptions (e.g., for inhalation rate, surface area of dermal contact, and other parameters). The pathways identified for potential exposure from MHC process baths were inhalation and dermal contact for workers, and inhalation contact only for the general populace living near a PWB facility.

The possible impacts from chemical spills are not addressed due to the pre-defined scope of this assessment. In addition, environmental releases to surface water were not quantified because chemical constituents and concentrations in wastewater could not be adequately characterized for the MHC line alone. This is because PWB manufacturers typically combine wastewater effluent from the MHC process line with effluent from other PWB manufacturing processes prior to on-site wastewater pretreatment. The pretreated wastewater is then discharged to a POTW. Many PWB manufacturers measure copper concentrations in effluent from on-site pretreatment facilities in accordance with POTW discharge permits, but they do not measure copper concentrations in MHC line effluent prior to pretreatment. Because there are many sources of copper-contaminated wastewater in PWB manufacturing, the contribution of the MHC line to overall copper discharges could not be estimated. Furthermore, most of the MHC alternatives contain copper, but because these technologies are only now being implemented in the U.S., their influence on total copper discharges from a PWB facility cannot be determined. Finally, while data are available on copper discharges from PWB facilities, data are not available for some of the other metals found in alternatives to electroless copper. Although ecological hazards are assessed in Section 3.3, without exposure or release data a comparative evaluation of ecological (aquatic) risk could not be performed.

Inhalation exposure could occur by breathing air containing vapor or aerosol-phase chemicals from the MHC process line. Inhalation exposures to workers from non-conveyorized lines are estimated in the exposure assessment. Inhalation exposure to workers from conveyorized MHC lines is assumed to be negligible because the lines are typically enclosed and vented to the outside. The model used to estimate daily inhalation exposure is from the EPA *Chemical Engineering Branch Manual for the Preparation of Engineering Assessments* (EPA, 1991a):

$$I = (Cm)(b)(h)$$

where:

- $I$ = daily inhalation potential dose rate (mg/day)
- $Cm$ = airborne concentration of substance ($mg/m^3$)
- $b$ = inhalation rate ($m^3/hr$)
- $h$ = duration (hr/day)

Daily exposures are then averaged over a lifetime (70 years) for carcinogens, and over the exposure duration (e.g., 25 years working in a facility) for non-carcinogens,[11] using the following equations:

For carcinogens:

$$LADD = (I)(EF)(ED)/[(BW)(AT_{CAR})]$$

For non-carcinogens:

$$ADD = (I)(EF)(ED)/[(BW)(AT_{NC})]$$

where:

| | | |
|---|---|---|
| LADD | = | lifetime average daily dose (mg/kg-day) |
| ADD | = | average daily dose (mg/kg-day) |
| EF | = | exposure frequency (days/year) |
| ED | = | exposure duration (years) |
| BW | = | body weight (kg) |
| $AT_{CAR}$ | = | averaging time for carcinogenic effects (days) |
| $AT_{NC}$ | = | averaging time for non-carcinogenic chronic effects (days) |

The daily intake for inhalation exposure to workers was calculated by first modeling chemical emissions from MHC baths with three air-transport mechanisms: liquid surface diffusion (desorption), bubble desorption, and aerosol generation and ejection. This chemical emission rate was combined with data from the IPC Workplace Practices Questionnaire and Performance Demonstration regarding process room size and air turnover rate to estimate an average indoor air concentration for the process area. An uncertainty and sensitivity analysis of the air transport models suggests that the air turnover (ventilation) rate assumption greatly influences the estimated air concentration in the process area because of its large variability (see the Exposure Assessment, Section 3.2.3).

Inhalation exposure to a hypothetical population located near a model PWB facility was estimated using the Industrial Source Complex - Long Term (ISCLT) air dispersion model. The modeled air concentrations of each contaminant were determined at 100 meters radially from a PWB facility, and the highest estimated air concentration was used. This model estimates air concentrations from the process bath emission rates for all processes. These emissions were assumed to be vented to the ambient environment at the rate emitted from the baths. Inhalation exposures estimated for the public living 100 meters away from a PWB facility were very low (approximately 10,000 times lower than occupational exposures).

[11] Different averaging times are used for characterizing risk for carcinogenic and non-carcinogenic effects. For carcinogenic agents, because even a single incidence of exposure is assumed to have the potential to cause cancer throughout an individual's lifetime, the length of exposure to that agent is averaged over a lifetime. An additional factor is that the cancer latency period may extend beyond the period of working years before it is discernible. For chemicals exhibiting non-cancer health effects from chronic (longer-term) exposure, where there is an exposure threshold (a level below which effects are not expected to occur), only the time period when exposure is occurring is assumed to be relevant and is used as the averaging time.

Dermal exposure could occur when skin comes in contact with the bath solution while dipping boards, adding bath replacement chemicals, etc. Although the data suggest that most MHC line operators do wear gloves, it was assumed in this evaluation that workers do not wear gloves to account for the fraction that do not. Otherwise, dermal exposure is expected to be negligible. For dermal exposures, the flux of a material through the skin was estimated based on EPA, 1992a:

$$D = (S)(C)(f)(h)(0.001)$$

where:

- D = dermal potential dose rate (mg/day)
- S = surface area of contact ($cm^2$)
- C = concentration of chemical in the bath (mg/L)
- f = flux through skin (cm/hour)
- h = duration (hours/day)

  with a conversion factor of 0.001 ($L/cm^3$)

It should be noted that the above equation was developed for exposures with an infinite volume of liquid or boundary layer contacting the skin, such as swimming or bathing. Occupational conditions of dermal contact are likely to be more finite in comparison, resulting in possible overestimates of flux through the skin.

As for inhalation, daily dermal exposures were then averaged over a lifetime for carcinogens, and over the exposure duration for non-carcinogens, using the following equations:

For carcinogens:

$$LADD = (D)(EF)(ED)/[(BW)(AT_{CAR})]$$

For non-carcinogens:

$$ADD = (D)(EF)(ED)/[(BW)(AT_{NC})]$$

For dermal exposure, the concentration of chemical in the bath and duration of contact for workers was obtained from publicly-available bath chemistry data, disclosed proprietary chemical information, and IPC Workplace Practices Questionnaire information, respectively. A permeability coefficient (rate of penetration through skin) was estimated for organics and a default rate assumption was used for inorganics. Reliance on such estimates in the absence of data is a source of uncertainty in the exposure assessment.

Key assumptions in the exposure assessment include the following:

- For dermal exposure, it was assumed that line operators do not wear gloves. Although the data suggests that most MHC line operators do wear gloves, it was assumed for this evaluation that workers do not wear gloves to account for the subset of workers who do not wear proper personal protective equipment.
- For dermal exposure, it was assumed that all non-conveyorized lines are manual hoist.

- The worker is assumed to have potential dermal contact for the entire time spent in the MHC area, divided equally among the baths. This does not mean that a worker has both hands immersed in a bath for that entire time; but that the skin is in contact with bath solution (i.e., the hands may remain wet from contact). This assumption may result in an overestimate of dermal exposure.
- For estimating ambient (outdoor) air concentrations, it was assumed that no air pollution control technologies are used to remove airborne chemicals from facility air prior to venting it to the outside.
- For inhalation exposure to workers, it was assumed that chemical emissions to air in the process room from conveyorized lines are negligible, and that no vapor control devices (e.g., bath covers) are used on baths in non-conveyorized lines.
- For air concentrations, the model assumes complete mixing in the process room and that concentrations do not change with time (steady state).
- For all exposures, it was assumed that there is one MHC process line and one line operator per shift in a process area.
- For characterizing the chemical constituents in the MHC process baths, it was assumed that the form (speciation) and concentration of all chemicals in the baths are constant over time, and that MSDSs accurately reflect the concentrations in product lines. If reported constituent weight percents on an MSDS total less than 100 percent, the remainder is assumed to be water. These assumptions are discussed further below.

The exposure assessment does not account for any side reactions occurring in the baths (e.g., the Cannizarro side reaction, which involves the reaction of formaldehyde in electroless copper baths). A study performed by Merix Corporation found that for every one mole of formaldehyde reacting in the intended copper deposition process, approximately one mole was reacting with hydroxide in a Cannizarro side reaction to produce formate ion and methanol (Williamson, 1996). Other studies have found that the Cannizarro reaction tendency increases with the alkalinity of the bath. The exposure assessment assumed that the formaldehyde in the bath is not reacted, and is available to be emitted as formaldehyde. This assumption could tend to overestimate formaldehyde exposures, and thus risk. However, if side reactions are occurring with other chemicals that result in the formation of other toxic chemicals (such as methanol), risk from these chemicals could be underestimated. A search for literature references to studies of side reactions occurring in PWB baths did not produce sufficient information to quantify the risk of reaction products in this risk characterization.

Chemical concentrations in baths are based on publicly-available chemistry data, including MSDSs, partial proprietary chemical information, and supplier Product Data Sheets that describe how to mix and maintain chemical baths. Many MSDSs provided concentration ranges for chemical constituents instead of absolute concentrations, in which case it was assumed that a chemical is present at the mid-point of the reported concentration range. This assumption may either overestimate or underestimate risk for chemicals, depending on their actual concentrations.

Using MSDS data for an exposure assessment can also lead to an underestimate of overall risk from using a process because the identities of many proprietary ingredients are not included

in the MSDSs. Efforts were made to obtain this information from suppliers of MHC bath formulations and proprietary information has been received from three of the seven suppliers.[12]

Assumptions and parameter values used in these equations and results of the exposure calculations are presented in the Exposure Assessment (Section 3.2). In order to provide information about the position an exposure estimate has in the distribution of possible outcomes, exposure (or risk) descriptors are used following EPA's (EPA, 1992b) *Guidelines for Exposure Assessment*. For this risk characterization, the exposure assessment uses whenever possible a combination of central tendency (either an average or median estimate) and high-end (90th percentile)[13] assumptions, as would be used for an overall high-end exposure estimate. The 90th percentile is used for:

- Hours per day of workplace exposure.
- Exposure frequency (days per year).
- Exposure duration in years (90th percentile for occupational and 95th percentile for residential exposures).
- The time and frequency of chemical bath and filter replacements, conveyor equipment cleaning and chemical bath sampling (minutes per occurrence and number of occurrences per year).
- Estimated workplace air concentrations.

Average values are used for:

- Body weight.
- Concentration of chemical in bath.
- The number of baths in a given process.

Some values used in the exposure calculations, however, are better characterized as "what-if," especially pertaining to bath concentrations, use of gloves, and process area ventilation rates for the model facility. ("What-if" represents an exposure estimate based on postulated questions, making assumptions based on limited data where the distribution is unknown.) Because some part of the exposure assessment for both inhalation and dermal exposures qualifies as a "what-if" descriptor, the entire assessment should be considered "what-if."

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[12] Electrochemicals, LeaRonal, and Solution Technology Systems provided information on proprietary chemical ingredients to the project. Atotech provided information on one proprietary ingredient. W.R. Grace was preparing to transfer information on proprietary chemical ingredients in the conductive ink technology when it was determined that this information was no longer necessary because risk from the conductive ink technology could not be characterized. The other suppliers participating in the project (Enthone-OMI, MacDermid, and Shipley) declined to provide proprietary information on their MHC technologies. The absence of information on proprietary chemical ingredients is a significant source of uncertainty in the risk characterization. Risk information for proprietary ingredients, as available, is presented in this CTSA, but chemical identities, concentrations, and chemical properties are not listed.

[13] For exposure data from the IPC Workplace Practices Questionnaire, this means that 90 percent of the facilities reported a lower value, and ten percent reported a higher value.

### 3.4.2 Summary of Human Health Hazards Assessment

Toxicity data in the form of RfDs, RfCs, NOAELs, LOAELs, and cancer slope (cancer potency) factors were compiled for inhalation and dermal pathways. CCs and aquatic toxicity hazard ranks for aquatic species were calculated from aquatic toxicity data on PWB chemicals, but ecological risk characterization was not carried out because the aquatic exposure could not be estimated.

Formaldehyde was the only non-proprietary chemical with an established cancer slope (cancer potency) factor. Other non-proprietary chemicals in the MHC processes are suspected carcinogens, but do not have established slope factors. Dimethylformamide and carbon black have been determined by IARC to possibly be carcinogenic to humans (IARC Group 2B). Dimethylformamide is used by at least one supplier in the electroless copper process. Carbon black is used in the carbon and conductive ink processes. Because slope factors (cancer potency values) are needed for quantitative estimates of cancer risk, cancer risk results are only presented for formaldehyde. Two proprietary chemicals used in the graphite and electroless copper processes, cyclic ether and alkyl oxide, have cancer slope factors. One proprietary chemical used in the electroless copper process, trisodium acetate amine B, was determined to possibly be carcinogenic to humans but does not have an established slope factor.

### 3.4.3 Methods Used to Calculate Human Health Risks

Estimates of human health risk from chemical exposure are characterized here in terms of excess lifetime cancer risk, hazard quotient (HQ), and margin of exposure (MOE). This section defines these risk indicators and discusses the methods for calculating each of them.

**Cancer Risk**

Cancer risks are expressed as the excess probability of an individual developing cancer over a lifetime from chemical exposure. For chemicals classified as carcinogens, an upper bound excess lifetime cancer risk, expressed as a unitless probability, was estimated by the following equation:

cancer risk = LADD x slope factor

where:

Cancer Risk = the excess probability of developing cancer over a lifetime as a result of exposure to a potential carcinogen. The estimated risks are the upper bound excess lifetime cancer risks for an individual. (*Upper bound* refers to the method of determining a slope factor, where the upper bound value for the slope of the dose-response curve is used. *Excess* means the estimated cancer risk is in addition to the already-existing background risk of an individual contracting cancer from all other causes.)

LADD = the lifetime average daily dose, the estimated potential daily dose rate received during the exposure duration, averaged over a 70-year lifetime (in mg/kg-day). LADDs were calculated in the Exposure Assessment (Section 3.2).

Slope factor ($q_1$ *) is defined in Section 3.3.1.

## Non-Cancer Risk Indicators

Non-cancer risk estimates are expressed either as a HQ or as a MOE, depending on whether or not RfDs and RfCs are available. There is generally a higher level of confidence in the HQ than the MOE, especially if the HQ is based on an RfD or RfC that has been peer-reviewed by EPA. If an RfD or RfC is available, the HQ is calculated to estimate risk from chemicals that exhibit chronic, non-cancer toxicity. (RfDs and RfCs are defined in Section 3.3.2.) The HQ is the unitless ratio of the RfD (or RfC) to the potential dose rate. For MHC chemicals that exhibit non-cancer toxicity, the HQ was calculated by:

$$HQ = ADD/RfD$$

where:

ADD = average daily dose rate, the amount of a chemical ingested, inhaled, or applied to the skin per unit time, averaged over the exposure duration (in mg/kg-day). ADDs were calculated in the Exposure Assessment (Section 3.2).

The HQ is based on the assumption that there is a level of exposure (i.e., the RfD or RfC) below which it is unlikely, even for sensitive subgroups, to experience adverse health effects. Unlike cancer risk, the HQ does not express *probability* and is not necessarily linear; that is, an HQ of ten does not mean that adverse health effects are ten times more likely to occur than for an HQ of one. However, the ratio of estimated dose to RfD/RfC reflects level of concern.

For chemicals where an RfD or RfC was not available, a MOE was calculated by:

$$MOE = NOAEL/ADD \text{ or } LOAEL/ADD$$

As with the HQ, the MOE is not a probabilistic statement of risk. The ratio for calculating MOE is the inverse of the HQ, so that a high HQ (exceeding one) indicates a potential concern, whereas a high MOE (exceeding 100 for a NOAEL-based MOE or 1,000 for a LOAEL-based MOE) indicates a low concern level. (NOAELS and LOAELs are defined in Section 3.3.2.) As the MOE increases, the level of concern decreases. (As the HQ increases, the level of concern also increases.)

Both the exposure estimates and toxicity data are specific to the route of exposure (i.e., inhalation, oral, or dermal). Very few RfDs, NOAELs, or LOAELs were available for dermal exposure. If oral data were available, the following adjustments were made to calculate dermal values:

$$RfD_{DER} = (RfD_{ORAL})(\text{GI absorption})$$
$$NOAEL/LOAEL_{DER} = (NOAEL \text{ or } LOAEL_{ORAL})(\text{GI absorption})$$
$$SF_{DER} = (SF_{ORAL})/\text{GI absorption})$$

where:

$RfD_{DER}$ = reference dose adjusted for dermal exposure (mg/kg-day)
$NOAEL/LOAEL_{DER}$ = NOAEL or LOAEL adjusted for dermal exposure (mg/kg-day)

$SF_{DER}$ = cancer slope factor adjusted for dermal exposure $(mg/kg\text{-}day)^{-1}$
GI absorption = gastrointestinal absorption efficiency

This adjustment is made to account for the fact that the oral RfDs, NOAELs, and LOAELs are based on an applied dose, while dermal exposure represents an estimated absorbed dose. The oral RfDs, NOAELs, and LOAELs used to assess dermal risks were therefore adjusted using gastro-intestinal (GI) absorption to reflect an absorbed dose. Table 3.35 lists the GI absorption data used in calculating risk from dermal exposure.

**Table 3.35 Absorption Percentages**

| Chemicals[a] | GI Tract Absorption (%) | Source of Data |
|---|---|---|
| 1,3-Benzenediol | 100 | NTP, 1992 |
| 2-Ethoxyethanol | 100 | assumption[b] |
| Ammonium Chloride | 97 | Reynolds, 1982 |
| Benzotriazole | 20 | assumption[b] |
| Boric Acid | 90 | EPA, 1990 |
| Copper (I) Chloride | 60 | EPA, 1994a |
| Diethylene Glycol Ethyl Ether | 20 | assumption[b] |
| Diethylene Glycol Methyl Ether | 20 | assumption[b] |
| Diethylene Glycol n-Butyl Ether | 20 | assumption[b] |
| Dimethylformamide | 20 | assumption[b] |
| Ethanolamine | 20 | assumption[b] |
| Ethylene Glycol | 100 | ATSDR, 1993 |
| Fluoroboric Acid | 100 | Stokinger, 1981 |
| Formaldehyde | 1 | EPA, 1995b |
| Hydrogen Peroxide | 5 | default (EPA, 1989) |
| Hydroxyacetic Acid | 20 | assumption[b] |
| Isopropyl Alcohol, 2-Propanol | 20 | assumption[b] |
| Methanol | 100 | Lington & Bevan, 1994 |
| Palladium | 5 | Beliles, 1994 |
| Palladium Chloride | 5 | Beliles, 1994 |
| Phenol | 20 | assumption[b] |
| Potassium Cyanide | 5 | default (EPA, 1989) |
| Silver | 21 | ATSDR, 1990b |
| Sodium Chlorite | 5 | default (EPA, 1989) |
| Sodium Cyanide | 5 | default (EPA, 1989) |
| Sodium Sulfate | 100 | HSDB, 1995 |
| Stannous Chloride | 3 | ATSDR, 1992 |
| Vanillin | 6 | Kirwin and Galvin, 1993 |

[a] Includes only those chemicals where dermal HQs or MOEs were calculated. Proprietary chemical data are not presented in order to protect proprietary chemical identities.
[b] An assumption of 20 percent was made for organic chemicals when no other data were available.

### 3.4.4 Results of Calculating Risk Indicators

This section presents the results of calculating risk indicators for both the occupational setting and the ambient (outdoor) environment. When considering these risk characterization results, it should be remembered that the results are intended for use in relative risk comparisons between processes based on a model PWB facility, and should not be used as absolute indicators for potential health risks to MHC line workers or to the public.

**Occupational Setting**

Estimated cancer risks and non-cancer risk indicators from occupational exposure to MHC chemicals are presented below. It should be noted that no epidemiological studies of health effects among PWB workers were located.

**Inhalation Cancer Risk.** The electroless copper and graphite processes are the only processes containing chemicals for which a cancer slope (cancer potency) factor is available. Formaldehyde, in the electroless copper process, is the only non-proprietary chemical for which an inhalation cancer risk has been estimated. Formaldehyde has an EPA weight-of-evidence classification of Group B1, a Probable Human Carcinogen. The EPA Group B1 classification is typically based on limited evidence of carcinogenicity in humans, sufficient evidence of carcinogenicity in animals, and additional supporting evidence. The cancer slope factor for formaldehyde is based exclusively on animal data, and is associated with nasal cancer.

Inhalation exposure estimates are based on the assumptions that emissions to indoor air from conveyorized lines are negligible, that the air in the process room is completely mixed and chemical concentrations are constant over time, and that no vapor control devices (e.g., bath covers) are used in non-conveyorized lines. The exposure estimates use 90th percentile modeled air concentrations (0.62 $mg/m^3$ for formaldehyde in the non-conveyorized electroless copper process), which means that, based on the IPC Workplace Practices Questionnaire data and publicly-available information on bath concentrations, approximately 90 percent of the facilities are expected to have lower air concentrations and, therefore, lower risks. Using 90th percentile data is consistent with EPA policy for estimating upper-bound exposures.

With regard to formaldehyde cancer risk, EPA in 1987 issued a risk assessment in which formaldehyde was classified as a Group B1 Probable Human Carcinogen; in addition it was determined to be an irritant to the eyes and respiratory tract. A quantitative risk assessment for cancer was presented using available exposure data and a cancer slope (cancer potency) factor of 0.046 per milligram formaldehyde per kilogram body weight per day. In 1991, EPA proposed a modification of this assessment using additional animal testing and exposure data that had become available. Incorporation of this new data would result in an estimated cancer slope factor of 0.00094 per milligram formaldehyde per kilogram body weight per day, a 50-fold reduction from the current cancer slope factor. However, EPA's Science Advisory Board recommended that formaldehyde cancer risk be presented as a range of risk estimates using data from both the 1987 and 1991 assessments, due to the many uncertainties and data gaps that preclude the use of one assessment to the exclusion of the other. Therefore, upper bound maximum individual cancer risk over a lifetime is presented as a range from $1 \times 10^{-3}$ (one in 1,000) to $2 \times 10^{-5}$ (two in 100,000 or one in 50,000) based on a workplace concentration of 0.62 milligrams formaldehyde

per cubic meter of air (over an 8 hour-day) for line operators using the non-conveyorized electroless copper process. It should be pointed out that intensity of exposures to formaldehyde (air concentration) may be more important than average exposure levels over an 8-hour day in increasing cancer risk (Hernandez et al., 1994). The use of modeled, steady state, workplace air concentrations instead of actual monitoring data of average and peak concentrations thus emerges as a significant source of uncertainty in estimating cancer risk to workers exposed to formaldehyde in this industry. The available toxicological data do not indicate that dermal exposure to formaldehyde increases cancer risk, but no dermal cancer studies were located.

To provide further information on the possible variation in occupational formaldehyde exposure and risk estimates, formaldehyde cancer risk is also estimated using average and median values, as would be done for a central tendency exposure estimate.[14] The following median or average parameter values are used:

- The 50th percentile air concentration estimated from the quantitative uncertainty analysis (Section 3.2.3) of 0.055 $mg/m^3$ (compared to the high-end point estimate of 0.62 $mg/m^3$).
- The median job tenure for men in the U.S. of 4.0 years (Bureau of Labor Statistics, 1997) (compared to the 95th percentile of 25 years).
- The average value of 6.8 hrs/day for a line operator from the IPC Workplace Practices Questionnaire (compared to the 90th percentile of 8 hrs/day).
- The average exposure frequency of 250 days/year from the IPC Workplace Practices Questionnaire (compared to the 90th percentile of 306 days/year).

Using these values, there is approximately a 100-fold reduction in estimated exposure with the estimated "central tendency" LADD of $2.6 \times 10^{-4}$ mg/kg-day. Combined with the slope factor of 0.046 per mg/kg-day, this results in a cancer risk of $1 \times 10^{-5}$ (one in 100,000). Considering the 50-fold reduction in cancer potency (with a slope factor of 0.00092 per mg/kg-day) the cancer risk would be $2 \times 10^{-9}$ (one in five million).

Inhalation cancer risk was also estimated for one proprietary chemical, alkyl oxide, in the non-conveyorized electroless copper process. This is discussed to a limited extent, however, to protect proprietary ingredient identity. The line operator inhalation exposure estimate for alkyl oxide[15] results in an estimated upper bound excess individual lifetime cancer risk of $3 \times 10^{-7}$ based on high end exposure.

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[14] This "central tendency" estimate should also be considered a "what-if" exposure estimate, because of the uncertainty of the process area ventilation rate data.

[15] It should be noted that alkyl oxide is present in the electroless copper and graphite baths at trace concentrations (less than one part per million) and it has a relatively high tendency to evaporate. Based on air modeling estimates, and assuming 100 liter baths, all of this chemical would be released to air within one hour. The assumption that chemical concentration in the baths remains constant over time would result, in this case, in large over-estimates of inhalation exposure. A correction factor was applied to the calculated cancer risks to reflect exposure from the chemical being present for one hour in the baths, at a yearly frequency equal to the bath replacement frequency.

Risks to other workers were assumed to be proportional to the amount of time spent in the process area. Based on the IPC Workplace Practices Questionnaire data, the average line operator spends 1,900 hours per year in the MHC process area. Annual average exposure times (i.e., time spent in the process area) for various worker types from the workplace practices database are listed below. The number in parenthesis is the ratio of average time for that worker type to the average time for a line operator.

- Contract worker: 62 hours per year (0.033).
- Laboratory technician: 1,100 hours per year (0.58).
- Maintenance worker: 930 hours per year (0.49).
- Supervisor: 1,150 hours per year (0.61).
- Wastewater treatment operator: 1,140 hours per year (0.60).
- Other: 1,030 hours per year (0.54).

**Dermal Cancer Risk.** Dermal cancer risks were estimated for two proprietary chemicals, alkyl oxide and cyclic ether, in the graphite and electroless copper processes. These results are only discussed to a limited extent, however, in order to protect the identity of the proprietary ingredients. Both chemicals have oral cancer slope factors, which were converted for dermal exposure as described in Section 3.4.3. Worker dermal exposure estimates for cyclic ether result in the following estimated upper bound excess individual lifetime cancer risks:

- For conveyorized electroless copper, $8 \times 10^{-8}$ for a line operator and $9 \times 10^{-9}$ for a laboratory technician.
- For non-conveyorized electroless copper, $4 \times 10^{-7}$ for a line operator and $9 \times 10^{-9}$ for a laboratory technician.
- For graphite, $1 \times 10^{-7}$ for a line operator and $9 \times 10^{-9}$ for a laboratory technician.

All of these cancer risk estimates are below the concern level of $1 \times 10^{-6}$. Worker dermal exposure estimates for alkyl oxide result in the following estimated upper bound excess individual lifetime cancer risks:[16]

- For conveyorized electroless copper, $4 \times 10^{-9}$ for a line operator and $1 \times 10^{-10}$ for a laboratory technician.
- For non-conveyorized electroless copper, $1 \times 10^{-8}$ for a line operator and $1 \times 10^{-10}$ for a laboratory technician.
- For graphite, $8 \times 10^{-8}$ for a line operator and $6 \times 10^{-9}$ for a laboratory technician.

**Other Potential Cancer Risks.** Slope factors (cancer potency values) are needed to calculate estimates of cancer risk. In addition to the chemicals discussed above,

[16] It should be noted that alkyl oxide is present in the electroless copper and graphite baths at trace concentrations (less than one part per million) and it has a relatively high tendency to evaporate. Based on air modeling estimates, and assuming 100 liter baths, all of this chemical would be released to air within one hour. The assumption that chemical concentration in the baths remains constant over time would result in this case, in large over-estimates of dermal exposure. A correction factor was applied to the calculated cancer risks to reflect exposure from the chemical being present for one hour in the baths, at a yearly frequency equal to the bath replacement frequency.

dimethylformamide and carbon black are classified as probable human carcinogens (IARC Group 2B). Like formaldehyde, the evidence for carcinogenic effects is based on animal data. However, unlike formaldehyde, slope factors are not available for either chemical. There are potential cancer risks to workers from both chemicals, but they cannot be quantified. Dimethylformamide is used in the electroless copper process. Workplace exposures have been estimated but cancer potency and cancer risk are unknown. Carbon black is used in the carbon and conductive ink processes. Occupational exposure due to air emissions from the carbon baths is expected to be negligible because the carbon process is typically conveyorized and enclosed. There may be some airborne carbon black, however, from the drying oven steps, which was not quantified in the exposure assessment. Carbon black is also used in one product line of the conductive ink process; exposures from conductive ink were not characterized. One proprietary chemical used in the electroless copper process, trisodium acetate amine B, was determined to possibly be carcinogenic to humans but does not have an established slope factor.

**Non-Cancer Risk.** HQs and MOEs for line operators and laboratory technicians from workplace exposures are presented in Appendix E. An HQ exceeding one indicates a potential concern. Unlike cancer risk, HQ does not express probability, only the ratio of the estimated dose to the RfD or RfC, and it is not necessarily linear (an HQ of ten does not mean that adverse health effects are ten times more likely than an HQ of one).

EPA considers high MOE values, such as values greater than 100 for a NOAEL-based MOE or 1,000 for a LOAEL-based MOE, to pose a low level of concern (Barnes and Dourson, 1988). As the MOE decreases, the level of concern increases. Chemicals are noted here to be of potential concern if a NOAEL-based MOE is lower than 100, a LOAEL-based MOE is lower than 1,000, or a MOE based on an effect level that was not specified as a LOAEL is less than 1,000. As with HQ, it is important to remember that the MOE is not a probabilistic statement of risk.

Inhalation risk indicators of concern for non-proprietary chemicals are presented in Table 3.36, and for the known proprietary chemicals in Table 3.37. This includes chemicals of potential concern based on MOE and/or HQ results, as well as cancer risk results for any chemical with a cancer slope factor. Inhalation exposure estimates are based on the assumptions that emissions to air from conveyorized lines are negligible, that the air in the process room is completely mixed and chemical concentrations are constant over time, and that no vapor control devices (e.g., bath covers) are used in non-conveyorized lines.

Dermal risk indicators of concern for non-proprietary chemicals are presented in Table 3.38 and for the known proprietary chemicals in Table 3.39. This includes chemicals of potential concern based on MOE and/or HQ results, as well as cancer risk results for any chemical with a cancer slope factor. Dermal exposure estimates are based on the assumption that both hands are routinely immersed in the bath and that the worker does not wear gloves.

It should be noted that Tables 3.36 through 3.39 do not include chemicals for which toxicity data were unavailable.

**Table 3.36 Summary of Human Health Risk Results From Inhalation Exposure for Selected Non-Proprietary Chemicals**

| Chemical of Concern[a] | Risk Indicator[a,b] | | | Potential Health Effects |
|---|---|---|---|---|
| | Electroless Copper, non-conveyorized | Non-Formaldehyde Electroless Copper, non-conveyorized | Tin-Palladium, non-conveyorized | |
| Copper (I) Chloride | MOE[c] (1)<br>420, line operator<br>LOAEL | NA | NA | Long-term exposure to copper dust can irritate nose, mouth and eyes, and cause dizziness. Long-term exposure to high levels of copper may cause liver damage. Copper is not known to cause cancer. The seriousness of the effects of copper can be expected to increase with both level and length of exposure. |
| Ethanolamine | MOE (3)<br>68, line operator<br>LOAEL | NA | MOE (2,3)<br>34, line operator<br>LOAEL | Ethanolamine is a strong irritant. Animal studies showed that the chemical is an irritant to respiratory tract, eyes, and skin. No data were located for inhalation exposure in humans. |
| 2-Ethoxyethanol | HQ[c] (4)<br>140, line operator | NA | NA | In animal studies 2-ethoxyethanol caused harmful blood effects including destruction of red blood cells and resulting in the release of hemoglobin (hemolysis) and male reproductive effects at high exposure levels. The seriousness of the effects can be expected to increase with both level and length of exposure. No data were located for inhalation exposure in humans. |
| Ethylene Glycol | MOE (3,5)<br>500, line operator<br>Human Exposure Data | NA | NA | In humans, low levels of vapors produce throat and upper respiratory irritation. When ethylene glycol breaks down in the body, it forms chemicals that crystallize and that can collect in the body and prevent kidneys from working. The seriousness of the effects can be expected to increase with both level and length of exposure. |

| Chemical of Concern[a] | Risk Indicator[a, b] | | | Potential Health Effects |
|---|---|---|---|---|
| | Electroless Copper, non-conveyorized | Non-Formaldehyde Electroless Copper, non-conveyorized | Tin-Palladium, non-conveyorized | |
| Formaldehyde | cancer risk (1)<br>$2 \times 10^{-5}$ to $1 \times 10^{-3}$, line operator[d]<br><br>MOE<br>0.48, line operator<br>LOAEL | NA | NA | Formaldehyde in animals produces nasal cancer (from inhalation) at low levels. In humans, exposure at low levels in air produces skin irritation and throat and upper respiratory irritation. The seriousness of these effects can be expected to increase with both level and length of exposure. |
| Formic Acid | MOE<br>90, line operator<br>NOAEL | NA | NA | Formic acid is a strong irritant to the skin, eyes, and mucous membranes based on clinical evidence in humans and animal toxicity data. There is also clinical evidence to indicate adverse effects on kidney function in humans, as well as central nervous system effects, such as visual and mental disturbances, following repeated exposures to high concentrations of formic acid. |
| Methanol | MOE (1,4,6)<br>370, line operator<br>Human Exposure Data | NA | NA | Long-term exposure to methanol vapors can cause headache, irritated eyes and dizziness at high levels. No harmful effects were seen when monkeys were exposed to highly concentrated vapors of methanol. When methanol breaks down in the tissues, it forms chemicals that can collect in the tissues or blood and lead to changes in the interior of the eye causing blindness. |
| Sodium Hydroxide | MOE<br>910, line operator<br>LOAEL | NA | NA | Sodium hydroxide is corrosive by all routes of exposure, with numerous case reports of poisonings in humans. Contact with the skin begins to cause immediate damage but not immediate pain. Acute and repeated exposures both result in damage due to the corrosive properties of the chemical. Carcinomas of the esophagus, larynx, and trachea have been reported in humans several, years after ingestion of high concentrations of sodium hydroxide. |

| Chemical of Concern[a] | Risk Indicator[a,b] | | | Potential Health Effects |
|---|---|---|---|---|
| | Electroless Copper, non-conveyorized | Non-Formaldehyde Electroless Copper, non-conveyorized | Tin-Palladium, non-conveyorized | |
| Sulfuric Acid | MOE (1,2,3,4,5,7,8)<br>2.8, line operator<br>NOAEL | MOE (1,5)<br>24, line operator<br>NOAEL | MOE (2,5,8)<br>30, line operator<br>NOAEL | Sulfuric acid is a very strong acid and can cause structural damage to skin and eyes. Humans exposed to sulfuric acid mist at low levels in air experience a choking sensation and irritation of lower respiratory passages. |

[a] This table includes results for chemicals and pathways with a MOE less than 1,000 if based on LOAELs (or less than 100 if based on NOAELs), an HQ greater than one, or a calculated cancer risk. It does not include chemicals for which toxicity data were unavailable, chemicals which have not been identified or evaluated because of their proprietary status, or chemicals used in MHC process alternatives which were not included in this evaluation.

[b] How to read this table:

| A (B) |
|---|
| C, D |
| E |

A: Type of risk indicator for which results are reported (HQ, MOE, or cancer risk)

B: Process bath(s) in which the chemical is used. Numbers in parenthesis indicate the process bath(s) in which the chemical is used:

(1) electroless copper bath (2) accelerator bath (3) cleaner/conditioner bath (4) anti-tarnish bath
(5) microetch bath (6) catalyst bath (7) predip bath (8) acid dip bath

C: Value calculated for risk indicator (cancer risk, HQ, or MOE).

D: Type of worker for which risk results are presented (line operator or laboratory technician).

E: Type of toxicity data used for MOE: NOAEL, LOAEL or data from human exposures which do not provide a range of exposures but identify levels which have adverse effects on humans.

[c] There is generally a higher level of confidence in the HQ than the MOE because the HQ is based on an RfD or RfC that has been peer-reviewed by EPA. MOEs are calculated for chemicals without an available RfC or RfD.

[d] To provide further information on the possible variation of formaldehyde exposure and risk, an additional exposure estimate is provided using average and median values (rather than high-end) as would be done for a central tendency exposure estimate. This results in approximately a 35-fold reduction in occupational formaldehyde exposure and risk.

NA: Not Applicable.

**Table 3.37 Summary of Human Health Risk Results from Inhalation Exposure for Selected Proprietary Chemicals**

| Code Name for Chemical of Concern | Risk Indicator | Potential Health Effects |
|---|---|---|
| | Electroless Copper, non-conveyorized | |
| Alkyl Oxide | cancer risk<br>$3 \times 10^{-7}$, line operator | Probable human carcinogen. |
| Alkene Diol | MOE<br>97, line operator<br>LOAEL | Exposure to low levels may result in irritation of the throat and upper respiratory tract. |

Note: Baths not specified to protect proprietary chemical identities.

[a] This table includes results for chemicals and pathways with a MOE less than 1,000 if based on LOAELs (or less than 100 if based on NOAELs), an HQ greater than one, or a calculated cancer risk. It does not include chemicals for which toxicity data were unavailable, chemicals which have not been identified or evaluated because of their proprietary status, or chemicals used in MHC process alternatives which were not included in this evaluation.

[b] How to read this table:

| A |
|---|
| C, D |
| E |

A: Type of risk indicator for which results are reported (HQ, MOE, or cancer risk)
C: Value calculated for risk indicator (cancer risk, HQ, or MOE).
D: Type of worker for which risk results are presented (line operator or laboratory technician).
E: Type of toxicity data used for MOE: NOAEL, LOAEL or data from human exposures which do not provide a range of exposures but identify levels which have adverse effects on humans.

[c] There is generally a higher level of confidence in the HQ than the MOE because the HQ is based on an RfD or RfC that has been peer-reviewed by EPA. MOEs are calculated for chemicals without an available RfC or RfD.

For inhalation exposure, 2-ethoxyethanol is the only MHC chemical with an HQ greater than one; this is for a line operator in the non-conveyorized electroless copper process. Chemicals with MOEs below the above-mentioned levels for inhalation exposure include the following:

- For non-conveyorized electroless copper: copper (I) chloride, ethanolamine, ethylene glycol, formaldehyde, formic acid, methanol, sodium hydroxide, sulfuric acid, and one proprietary chemical for a line operator.
- For non-conveyorized tin-palladium: ethanolamine and sulfuric acid for a line operator.
- For non-conveyorized non-formaldehyde electroless copper: sulfuric acid for a line operator.

Dermal risk indicators of concern for non-proprietary chemicals are presented in Table 3.38 and for the known proprietary chemicals in Table 3.39. Dermal exposure estimates are based on the assumption that workers do not wear gloves and that all non-conveyorized lines are operated by manual hoist. Chemicals with HQs from dermal exposure greater than one include:

- Formaldehyde for a line operator in the non-conveyorized electroless copper and conveyorized electroless copper processes.
- Stannous chloride for a line operator in the non-conveyorized electroless copper, non-formaldehyde electroless copper (non-conveyorized), non-conveyorized tin-palladium, and conveyorized tin-palladium processes.
- One proprietary chemical for a line operator in the conveyorized electroless copper process.

## Table 3.38 Summary of Human Health Risk Results From Dermal Exposure for Selected Non-Proprietary Chemicals

| Chemical of Concern[a] | Risk Indicator[a, b] | | | | | Potential Health Effects |
|---|---|---|---|---|---|---|
| | Electroless Copper, non-conveyorized | Electroless Copper, conveyorized | Non-Formaldehyde Electroless Copper, non-conveyorized | Tin-Palladium, non-conveyorized | Tin-Palladium, conveyorized | |
| Copper (I) Chloride | MOE [c] (1)<br>0.96, line operator<br>39, laboratory tech.<br>LOAEL | MOE (1)<br>4.3, line operator<br>39, laboratory tech.<br>LOAEL | NA | MOE (2)<br>1.9, line operator<br>190, laboratory tech.<br>LOAEL | MOE (2)<br>5.2, line operator<br>190, laboratory tech.<br>LOAEL | No data were located for health effects from dermal exposure in humans. |
| Fluoroboric Acid | MOE (2)<br>2.0, line operator<br>80, laboratory tech.<br>Human Exposure Data | MOE (2)<br>8.5, line operator<br>80, laboratory tech.<br>Human Exposure Data | NA | MOE (2)<br>4.6, line operator<br>460, laboratory tech.<br>Human Exposure Data | MOE (2)<br>13, line operator<br>460, laboratory tech.<br>Human Exposure Data | In humans, fluoroboric acid produces strong caustic effects leading to structural damage to skin and eyes. |
| Formaldehyde | HQ (1)<br>15, line operator<br>LOAEL | HQ (1)<br>3.4, line operator<br>LOAEL | NA | NA | NA | In humans, exposure at low levels in air produces skin irritation. The seriousness of these effects can be expected to increase with both level and length of exposure. |
| Palladium | MOE (6)<br>20, line operator<br>820, laboratory tech.<br>LOAEL | MOE (6)<br>92, line operator<br>820, laboratory tech.<br>LOAEL | NA | MOE (6)<br>5.6, line operator<br>560, laboratory tech.<br>LOAEL | MOE (6)<br>20, line operator<br>560, laboratory tech.<br>LOAEL | No specific information was located for health effects from dermal exposure in humans. |
| Palladium Chloride | NA | NA | NA | MOE (6)<br>8.9 line operator<br>890, laboratory tech.<br>LOAEL | MOE (6)<br>32, line operator<br>890, laboratory tech.<br>LOAEL | Long-term dermal exposure in humans produces contact dermatitis. |
| Sodium Chlorite | MOE (2)<br>17, line operator<br>NOAEL | MOE (2)<br>73, line operator<br>NOAEL | MOE (2)<br>15, line operator<br>NOAEL | NA | NA | No specific information was located for health effects from dermal exposure to sodium chlorite in humans. Animal studies showed that the chemical produces moderate irritation of skin and eyes. |

| Chemical of Concern[a] | Risk Indicator[a,b] | | | | | Potential Health Effects |
|---|---|---|---|---|---|---|
| | Electroless Copper, non-conveyorized | Electroless Copper, conveyorized | Non-Formaldehyde Electroless Copper, non-conveyorized | Tin-Palladium, non-conveyorized | Tin-Palladium, conveyorized | |
| Stannous Chloride | HQ (6)<br>3.6, line operator | NA | HQ (6)<br>3.7, line operator | HQ (6)<br>15, line operator | HQ (6)<br>4.2, line operator | Mild irritation of the skin and mucous membrane has been shown from inorganic tin salts. However, no specific information was located for dermal exposure to stannous chloride in humans. Stannous chloride is only expected to be harmful at high doses; it is poorly absorbed and leaves the body rapidly. |

[a] This table includes results for chemicals and pathways with a MOE less than 1,000 if based on LOAELs (or less than 100 if based on NOAELs), an HQ greater than one, or a calculated cancer risk. It does not include chemicals for which toxicity data were unavailable, chemicals which have not been identified or evaluated because of their proprietary status, or chemicals used in MHC process alternatives which were not included in this evaluation.

[b] How to read this table:

| A (B) |
|---|
| C, D |
| E |

A: Type of risk indicator for which results are reported (HQ, MOE, or cancer risk).

B: Process bath(s) in which the chemical is used. Numbers in parenthesis indicate the process bath(s) in which the chemical is used:

(1) electroless copper bath (2) accelerator bath (3) cleaner/conditioner bath (4) anti-tarnish bath
(5) microetch bath (6) catalyst bath (7) predip bath (8) acid dip bath

C: Value calculated for risk indicator (cancer risk, HQ, or MOE).

D: Type of worker for which risk results are presented (line operator or laboratory technician).

E: Type of toxicity data used for MOE: NOAEL; LOAEL; or data from human exposures which do not provide a range of exposures but identify levels which have adverse effects on humans.

[c] There is generally a higher level of confidence in the HQ than the MOE because the HQ is based on an RfD or RfC that has been peer-reviewed by EPA. MOEs are calculated for chemicals without an available RfC or RfD.

NA: Not Applicable.

## Table 3.39 Summary of Human Health Risk Results from Dermal Exposure for Selected Proprietary Chemicals

| Code Name for Chemical of Concern | Risk Indicator[a] | | | | | Potential Health Effects |
|---|---|---|---|---|---|---|
| | Electroless Copper, non-conveyorized | Electroless Copper, conveyorized | Graphite, conveyorized | Organic-Palladium, non-conveyorized | Organic-Palladium, conveyorized | |
| Nitrogen Heterocycle | MOE<br>130, line operator | MOE<br>510, line operator | NA | NA | NA | No data were located for health effects from dermal exposure in humans. |
| Palladium Salt | NA | NA | NA | MOE<br>1.5, line operator<br>450, lab. tech. | MOE<br>8.0, line operator<br>450, lab. tech. | Exposure may result in skin irritation and sensitivity. |
| Sodium Carboxylate | MOE<br>71, line operator | MOE<br>320, line operator | NA | NA | NA | No data were located for health effects from dermal exposure in humans. |
| Cyclic Ether | cancer risk<br>$4 \times 10^{-7}$, line operator<br>$9 \times 10^{-9}$, lab. tech. | cancer risk<br>$8 \times 10^{-8}$, line operator<br>$9 \times 10^{-9}$, lab. tech. | cancer risk<br>$1 \times 10^{-7}$, line operator<br>$9 \times 10^{-9}$, lab. tech. | NA | NA | Possible/probable human carcinogen. |
| Alkyl Oxide | cancer risk<br>$1 \times 10^{-8}$, line operator<br>$1 \times 10^{-10}$, lab. tech. | cancer risk<br>$4 \times 10^{-9}$, line operator<br>$1 \times 10^{-10}$, lab. tech. | cancer risk<br>$8 \times 10^{-8}$, line operator<br>$6 \times 10^{-9}$, lab. tech. | NA | NA | Long-term dermal exposure in humans produces contact dermatitis; probable human carcinogen. |
| Tin Salt | NA | HQ<br>1.1, line operator | NA | NA | NA | No data were located for health effects from dermal exposure in humans. Inorganic tin compounds may irritate the eyes, nose, throat, and skin. |

[a] MOE based on LOAEL.

Note: Baths not specified to protect proprietary chemical identities.

[b] This table includes results for chemicals and pathways with a MOE less than 1,000 if based on LOAELs (or less than 100 if based on NOAELs), an HQ greater than one, or a calculated cancer risk. It does not include chemicals for which toxicity data were unavailable, chemicals which have not been identified or evaluated because of their proprietary status, or chemicals used in MHC process alternatives which were not included in this evaluation.

[c] How to read this table:

| |
|---|
| A |
| C, D |
| E |

A: Type of risk indicator for which results are reported (HQ, MOE, or cancer risk).
C: Value calculated for risk indicator (cancer risk, HQ, or MOE).
D: Type of worker for which risk results are presented (line operator or laboratory technician).
E: Type of toxicity data used for MOE: NOAEL; LOAEL; or data from human exposures which do not provide a range of exposures but identify levels which have adverse effects on humans.

[d] There is generally a higher level of confidence in the HQ than the MOE because the HQ is based on an RfD or RfC that has been peer-reviewed by EPA. MOEs are calculated for chemicals without an available RfC or RfD.

NA: Not Applicable.

Chemicals with NOAEL-based MOEs lower than 100, or LOAEL-based MOEs or other MOEs lower than 1,000 for dermal exposure include the following:

- For non-conveyorized electroless copper: copper (I) chloride, fluoroboric acid, palladium, sodium chlorite, and two proprietary chemicals for a line operator; copper (I) chloride, fluoroboric acid, and palladium for a laboratory technician.
- For conveyorized electroless copper: copper (I) chloride, fluoroboric acid, palladium, sodium chlorite, and two proprietary chemicals for a line operator; copper (I) chloride, fluoroboric acid, and palladium for a laboratory technician.
- For non-conveyorized non-formaldehyde electroless copper: sodium chlorite for a line operator.
- For non-conveyorized tin-palladium: copper (I) chloride, fluoroboric acid, palladium and palladium chloride for a line operator and laboratory technician.
- For conveyorized tin-palladium: copper (I) chloride, fluoroboric acid, palladium and palladium chloride for a line operator and laboratory technician.
- For non-conveyorized organic-palladium: one proprietary chemical for a line operator and laboratory technician.
- For conveyorized organic-palladium: one proprietary chemical for a line operator and laboratory technician.

## Ambient (Outdoor) Environment

**Cancer Risk.** As with the occupational setting, the electroless copper and graphite processes are the only processes for which a cancer risk to humans in the ambient (outdoor) environment has been estimated. Formaldehyde is the only non-proprietary chemical with cancer risks estimated for the general population. These results are for both conveyorized and non-conveyorized electroless copper processes, assuming that emissions from both process configurations are vented to the outside. The upper bound excess[17] individual lifetime cancer risk for nearby residents from the non-conveyorized electroless copper process from formaldehyde inhalation was estimated to range from $2 \times 10^{-9}$ to $1 \times 10^{-7}$. The risk for nearby residents from the conveyorized electroless copper process was estimated to range from $6 \times 10^{-9}$ to $3 \times 10^{-7}$. Again, the higher values ($3 \times 10^{-7}$ for conveyorized and $1 \times 10^{-7}$ for non-conveyorized) are based on a LADDs of $7.0 \times 10^{-6}$ mg/kg-day and $2.6 \times 10^{-6}$ mg/kg-day, respectively, and a slope (cancer potency) factor of 0.046 per mg/kg-day. The lower values ($6 \times 10^{-9}$ for conveyorized and $2 \times 10^{-9}$ for non-conveyorized) take into account a possible 50-fold reduction in inhalation unit risk.

The discussion of reduction in estimated cancer risk from Section 3.4.1 applies to these results as well. Formaldehyde has been classified as Group B1, a Probable Human Carcinogen based on limited evidence of carcinogenicity in humans, sufficient evidence of carcinogenicity in animals, and additional supportive evidence. These estimates indicate low concern and are

[17] *Upper bound* refers to the method of determining a slope factor, where the upper bound value (generated from a certain probability statement) for the slope of the dose-response curve is used. *Excess* means the estimated cancer risk is in addition to the already-existing background risk of an individual contracting cancer from all other causes.

interpreted to mean that, over a lifetime, an individual resident is expected to have no more than one excess chance in ten million of developing cancer from exposure to formaldehyde from a nearby facility using the non-conveyorized electroless copper process, or one excess chance in three million of developing cancer from exposure to formaldehyde from the conveyorized electroless copper process. The conveyorized electroless copper risk is slightly higher due to the larger surface areas of conveyorized baths, resulting in higher modeled air emission rates.

The graphite and electroless copper processes contain one known proprietary chemical, alkyl oxide, with an inhalation cancer slope factor. Inhalation exposure to cyclic ether, the other proprietary chemical with a cancer slope factor, is assumed negligible because the chemical is non-volatile and is not used in an air-sparged bath. The upper bound excess individual lifetime cancer risk for nearby residents from the (conveyorized) graphite process from inhalation of alkyl oxide was estimated to be $9 \times 10^{-11}$. This estimate indicates low concern and is interpreted to mean that, over a lifetime, an individual resident is expected to have no more than one excess chance in 11 billion of developing cancer from exposure to alkyl oxide from a conveyorized graphite process. The upper bound excess individual lifetime cancer risk for nearby residents from the electroless copper process from inhalation of alkyl oxide was estimated to be $1 \times 10^{-11}$ for the non-conveyorized process and $3 \times 10^{-11}$ for the conveyorized electroless copper process.[18] These estimates also indicate low concern and are interpreted to mean that, over a lifetime, an individual resident is expected to have no more than one excess chance of developing cancer in 100 billion for non-conveyorized electroless copper, and no more than one excess chance in 33 billion for conveyorized electroless copper from inhalation exposure to alkyl oxide.

None of the other process alternatives use chemicals for which cancer slope factors were available, so no other cancer risks were estimated. Other identified chemicals in the MHC processes are suspected carcinogens, but do not have established slope factors. Dimethylformamide and carbon black have been determined by IARC to possibly be carcinogenic to humans (IARC Group 2B). Dimethylformamide is used in the electroless copper process. Carbon black is used in the carbon and conductive ink processes. Carbon black is not expected to be released to outside air in any significant amount from a facility using the carbon process. This is because carbon black is not a volatile compound, and aerosol releases are not expected because it is not used in an air-sparged bath. Conductive ink exposures and risks were not characterized. One proprietary chemical used in the electroless copper process, trisodium acetate amine B, was determined to possibly be carcinogenic to humans but does not have an established slope factor.

**Non-Cancer Risk.** Appendix E presents HQs for estimated chemical releases to ambient air, and subsequent inhalation by residents near a model facility. Chemicals below the emission rate cutoff of 23 kg/year are not included because below this emission rate exposures are

[18] It should be noted that alkyl oxide is present in the electroless copper and graphite baths at trace concentrations (less than one part per million) and it has a relatively high tendency to evaporate. Based on air modeling estimates, and assuming 100 liter baths, all of this chemical would be released to air within one hour. The assumption that chemical concentration in the baths remains constant over time would result, in this case, in large over-estimates of inhalation exposure. A correction factor was applied to the calculated cancer risks to reflect exposure from the chemical being present for one hour in the baths, at a yearly frequency equal to the bath replacement frequency.

expected to be negligible. All HQs are less than one for ambient exposure to the general population, indicating low concern.

These results suggest there is low risk to nearby residents, based on incomplete but best available data. Data limitations include the use of modeled air concentrations using average data rather than site-specific, measured concentrations. For estimating ambient (outdoor) air concentrations, one key assumption is that no air pollution control technologies are used to remove airborne chemicals from facility air prior to venting it to the outside. Other data limitations are the lack of waterborne and solid waste data to characterize exposure routes in addition to inhalation, and lack of toxicity data for many chemicals.

Appendix E presents MOEs from ambient air exposures. The chemicals included are those above the emission rate cutoff and for which NOAEL or LOAEL data were available. (Also if an HQ could be calculated an MOE was not.) All MOEs for ambient exposure are greater than 1,000 for all processes, indicating low concern from the estimated air concentrations.

### 3.4.5 Uncertainties

An important component of any risk characterization is the identification and discussion of uncertainties. There are uncertainties involved in the measurement and selection of hazard data, and in the data, models and scenarios used in the Exposure Assessment. Any use of the risk characterization should include consideration of these uncertainties.

Uncertainties in the Exposure Assessment include the following:

- Accuracy of the description of exposure setting: how well the model facility used in the assessment characterizes an actual facility; the likelihood of exposure pathways actually occurring (scenario uncertainty).
- Missing data and limitations of workplace practices data: this includes possible effects of any chemicals that may not have been included (e.g., minor ingredients in the formulations, proprietary chemical identities not disclosed by suppliers); possible effects of side reactions in the baths which were not considered; and questionnaire data with limited facility responses.
- Estimating exposure levels from averaged data and modeling in the absence of measured, site-specific data.
- Data limitations in the Source Release Assessment: releases to surface water and land could not be characterized quantitatively.
- Chemical fate and transport model applicability and assumptions: how well the models and assumptions represent the situation being assessed and the extent to which the models have been validated or verified (model uncertainty).
- Parameter value uncertainty, including measurement error, sampling (or survey) error, parameter variability, and professional judgement.

Key assumptions made in the Exposure Assessment are discussed in Section 3.4.1.

Uncertainties in the hazard data (typically encountered in a hazard assessment) include the following:

- Using dose-response data from high dose studies to predict effects that may occur at low levels.
- Using data from short-term studies to predict the effects of long-term exposures.
- Using dose-response data from laboratory animals to predict effects in humans.
- Using data from homogeneous populations of laboratory animals or healthy human populations to predict the effects on the general human population, with a wide range of sensitivities. (This uncertainty is due to natural variations in human populations.)
- Using LOAELs and NOAELs in the absence of peer-reviewed RfDs and RfCs.
- Possible increased or decreased toxicity resulting from chemical interactions.
- Assuming a linear dose-response relationship for cancer risk (in this case for formaldehyde).
- Effects of chemical mixtures not included in toxicity testing (effects may be independent, additive, synergistic, or antagonistic).
- Possible effects of substances not evaluated because of a lack of chronic/subchronic toxicity data.

Another source of uncertainty comes from use of structure-activity relationships (SARs) for estimating human health hazards in the absence of experimental toxicity data. Specifically, this was done for: dimethylaminoborane, EDTA (sodium salt), fluoroboric acid, graphite, magnesium carbonate, m-nitrobenzene sulfonic acid, monopotassium peroxymonosulfate, palladium chloride, phosphoric acid, potassium bisulfate, potassium carbonate, potassium persulfate, potassium sulfate, p-toluene sulfonic acid, sodium bisulfate, sodium hypophosphite, and sodium persulfate. SARs were also used for ten proprietary chemicals.

Uncertainties in assessing risk from dermal exposure come from the use of toxicological potency factors from studies with a different route of exposure than the one under evaluation (i.e., using oral toxicity measures to estimate dermal risk). This was done for nine chemicals with oral RfDs, 15 chemicals with oral NOAELs (as noted in Tables 3.25 and 3.26), and two proprietary chemicals with oral cancer slope factors. Uncertainties in dermal risk estimates also stem from the use of default values for missing gastrointestinal absorption data. Specifically, this was done for benzotriazole, diethylene glycol ethyl ether, diethylene glycol n-butyl ether, ethanolamine, 2-ethoxyethanol, hydrogen peroxide, hydroxyacetic acid, isopropyl alcohol, potassium cyanide, sodium chlorite, and sodium cyanide.

Finally, the risk characterization does not address the potential adverse health effects associated with acute exposure to peak levels of chemicals. This type of exposure is especially important when evaluating developmental risks associated with exposure.

### 3.4.6 Conclusions

This risk characterization uses a health-hazard based framework and a model facility approach to compare the health risks of one MHC process technology to the risks associated which switching to an alternative technology. As much as possible, reasonable and consistent assumptions are used across alternatives. Data to characterize the model facility and exposure patterns for each process alternative were aggregated from a number of sources, including PWB shops in the U.S. and abroad, supplier data, and input from PWB manufacturers at project

meetings. Thus, the model facility is not entirely representative of any one facility, and actual risk could vary substantially, depending on site-specific operating conditions and other factors.

When using the results of this risk characterization to compare health effects among alternatives, it is important to remember that this is a screening level rather than a comprehensive risk characterization, both because of the predefined scope of the assessment and because of exposure and hazard data limitations. It should also be noted that this approach does not result in any absolute estimates or measurements of risk, and even for comparative purposes, there are several important uncertainties associated with this assessment.

Primary among these uncertainties is the incomplete identification of all chemicals among the process alternatives because of trade secret considerations. This factor alone precludes any definitive recommendations among the processes because the health risks from all relevant chemicals could not be evaluated. It should be noted here also that chemical suppliers to the PWB industry are in the sole position to fill these data gaps for a more complete assessment.[19] Without that, conclusions can only be drawn based on the best available information. It should also be noted that chemical suppliers are required to report on an MSDS (under 29 CFR Part 1910.1200) that a product contains hazardous chemicals, if present at one percent or greater of a product composition, or 0.1 percent or greater for carcinogens. The chemical manufacturer may withhold the specific chemical identity from the MSDS, provided that the MSDS discloses the properties and effects of the hazardous chemical. A review of the available MSDSs indicates that there are hazardous chemicals listed as trade secret ingredients: three in electroless copper, one in graphite, three in organic-palladium, and one in tin-palladium. Section 2.1.4 presents these results and discusses the use of MSDS information further.

Another significant source of uncertainty is the limited data available for dermal toxicity and the use of oral to dermal extrapolation when dermal toxicity data were unavailable. There is high uncertainty in using oral data for dermal exposure and in estimating dermal absorption rates, which could result in either over- or under-estimates of exposure and risk.

A third significant source of uncertainty is from the use of structure-activity relationships to estimate toxicity in the absence of measured toxicity data, and the lack of peer-reviewed toxicity data for many MHC chemicals. Other uncertainties associated with the toxicity data include the possible effects of chemical interactions on health risks, and extrapolation of animal data to estimate human health risks from exposure to formaldehyde and other PWB chemicals.

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[19] Electrochemicals, LeaRonal, and Solution Technology Systems provided information on proprietary chemical ingredients to the project. Atotech provided information on one proprietary ingredient. W.R. Grace was preparing to transfer information on proprietary chemical ingredients in the conductive ink technology when it was determined that this information was no longer necessary because risk from the conductive ink technology could not be characterized. The other suppliers participating in the project (Enthone-OMI, MacDermid, and Shipley) declined to provide proprietary information on their MHC technologies. The absence of information on proprietary chemical ingredients is a significant source of uncertainty in the risk characterization. Risk information for proprietary ingredients, as available, is presented in this CTSA, but chemical identities, concentrations, and chemical properties are not listed.

Another major source of uncertainty in estimating exposure is the reliance on modeled data (i.e., modeled air concentrations) to estimate worker exposure. It should also be noted that there is no comparative evaluation of the severity of effects for which HQs and MOEs are reported.

The Exposure Assessment for this risk characterization used, whenever possible, a combination of central tendency and high-end assumptions, as would be used for an overall high-end exposure estimate. Some values used in the exposure calculations, however, are better characterized as "what-if," especially pertaining to bath concentrations, use of gloves, and process area ventilation rates for a model facility. Because some part of the exposure assessment for both inhalation and dermal exposures qualifies as a "what-if" descriptor, the entire assessment should be considered "what-if."

Among those health risks evaluated, it can be concluded that alternatives to the non-conveyorized electroless copper process appear to present a lower overall risk, due to reduced cancer risk to PWB workers when the use of formaldehyde is eliminated. Other adverse effects from chronic, low level exposures to chemicals in the alternative processes provide some basis for additional comparison. While alternatives to electroless copper appear to pose less overall risk, there is insufficient information to compare these alternatives among themselves to determine which of the alternatives pose the least risk.

**Occupational Exposures and Risks**

Health risk to workers are estimated for inhalation exposure to vapors and aerosols from MHC baths and for dermal exposure to MHC bath chemicals. Inhalation exposure estimates are based on the assumptions that emissions to indoor air from conveyorized lines are negligible, that the air in the process room is completely mixed and chemical concentrations are constant over time, and that no vapor control devices (e.g., bath covers) are used in non-conveyorized lines. Dermal exposure estimates are based on the assumption that workers do not wear gloves and that all non-conveyorized lines are operated by manual hoist. Dermal exposure to line operators on non-conveyorized lines is estimated for routine line operation and maintenance (e.g., bath replacement, filter replacement, etc.), and on conveyorized lines for bath maintenance activities alone.

Risk results indicate that alternatives to the non-conveyorized electroless copper process pose lower occupational risks. However, in addition to several chemicals in the non-conveyorized electroless copper process, there are occupational inhalation risk concerns for some chemicals in the non-formaldehyde electroless copper and tin-palladium non-conveyorized processes as well. There are also occupational risk concerns for dermal contact with some chemicals in the electroless copper, organic-palladium, and tin-palladium processes for either conveyorized or non-conveyorized equipment.

**Cancer Risk.** The non-conveyorized electroless copper process contains the only non-proprietary chemical for which an occupational cancer risk has been estimated (for formaldehyde). Formaldehyde has been classified by EPA as Group B1, a Probable Human Carcinogen. The upper bound excess individual cancer risk estimate for line operators in the non-conveyorized electroless copper process from formaldehyde inhalation may be as high as

one in a thousand, but may be 50 times less, or one in 50,000.[20] Risks to other workers were assumed to be proportional to the amount of time spent in the process area, which ranged from three to 61 percent of the risk for a line operator.

Inhalation cancer risk was also estimated for one proprietary chemical, alkyl oxide, in the non-conveyorized electroless copper process. The line operator inhalation exposure estimate for alkyl oxide results in an estimated upper bound excess individual life time cancer risk of $3 \times 10^{-7}$ (one in three million) based on high end exposure. Cancer risks less than $1 \times 10^{-6}$ (one in one million) are generally considered to be of low concern.

Additionally, dermal cancer risks were estimated for two proprietary chemicals, cyclic ether and alkyl oxide, in the graphite and electroless copper processes. For the conveyorized graphite process, the dermal cancer risks for a line operator may be as high as $8 \times 10^{-8}$ (about one in ten million) for the alkyl oxide and $1 \times 10^{-7}$ (one in ten million) for the cyclic ether. The upper bound cancer risks for a laboratory technician were much less than the risks for a line operator. The cancer risks for a laboratory technician were $6 \times 10^{-9}$ (one in 200 million) for alkyl oxide and $9 \times 10^{-9}$ (one in 100 million) for cyclic ether.

For non-conveyorized electroless copper, the dermal cancer risks for the line operator may be as high as $4 \times 10^{-7}$ (one in two million) for cyclic ether and $1 \times 10^{-8}$ (one in 100 million) for alkyl oxide. The estimated upper bound cancer risks for a laboratory technician were much less than the cancer risk for a line operator. The estimated cancer risks for a laboratory technician were $9 \times 10^{-9}$ (one in 100 million) for cyclic ether and $1 \times 10^{-10}$ (one in ten billion) for alkyl oxide.

For conveyorized electroless copper, the dermal cancer risk for a line operator may be as high as $8 \times 10^{-8}$ (about one in ten million) for cyclic ether and $4 \times 10^{-9}$ (one in 200 million) for alkyl oxide. The estimated upper bound cancer risks for a laboratory technician were much less than the cancer risks for a line operator. The estimated cancer risks for a laboratory technician were $9 \times 10^{-9}$ (one in 100 million) for cyclic ether and $1 \times 10^{-10}$ (one in ten billion) for alkyl oxide.

Other identified chemicals in the MHC processes are suspected carcinogens. Dimethylformamide and carbon black have been determined by IARC to possibly be carcinogenic to humans (IARC Group 2B). Also, a proprietary trisodium acetate amine has been classified as a possible human carcinogen. Dimethylformamide and the proprietary chemical are used in the electroless copper process and carbon black is used in the carbon and conductive ink processes. There are potential cancer risks to workers from these chemicals, but because there are no slope factors, the risks cannot be quantified.

[20] To provide further information on the possible variation of formaldehyde exposure and risk, an additional exposure estimate is provided using average and median values (rather than high-end) as would be done for a central tendency exposure estimate. This results in approximately a 100-fold reduction in occupational formaldehyde exposure and risk.

**Non-Cancer Risk.** For non-cancer risk, HQs greater than one were estimated for occupational exposures to chemicals in the non-conveyorized and conveyorized electroless copper processes, the non-conveyorized and conveyorized tin-palladium processes, and the non-conveyorized non-formaldehyde electroless process. Also, several chemicals had estimated MOEs lower than 100 or LOAEL-based MOEs lower than 1,000 for occupational exposures in the non-conveyorized and conveyorized electroless copper processes, non-conveyorized and conveyorized tin-palladium processes, non-conveyorized and conveyorized organic-palladium processes, and non-conveyorized non-formaldehyde electroless copper process.

Based on calculated occupational exposure levels, there may be adverse health effects to workers exposed to these chemicals with a HQ exceeding 1.0 or an MOE less than 100 or 1,000. However, it should be emphasized that these conclusions are based on screening level estimates.

These numbers are used here for relative risk comparisons between processes, and should not be used as absolute indicators for potential health risks to MHC line workers.

## Ambient (Outdoor) Exposures and Risks

Public health risk was estimated for inhalation exposure for the general populace living near a facility. Public exposure estimates are based on the assumption that emissions from both conveyorized and non-conveyorized process configurations are vented to the outside. The risk indicators for ambient exposures to humans, although limited to airborne releases, indicate low concern for nearby residents. The upper bound excess individual cancer risk for nearby residents from formaldehyde in the non-conveyorized electroless copper process was estimated to be from approaching zero to $1 \times 10^{-7}$ (one in ten million) and from approaching zero to $3 \times 10^{-7}$ (one in three million) for the conveyorized electroless copper process. Formaldehyde has been classified by EPA as Group B1, a Probable Human Carcinogen. The upper bound excess individual cancer risk for nearby residents from the proprietary alkyl oxide in the conveyorized graphite process was estimated to be from approaching zero to $9 \times 10^{-11}$ (one in 11 billion); in the non-conveyorized electroless copper process from approaching zero to $1 \times 10^{-11}$ (one in 100 billion), and in the conveyorized electroless copper process from approaching zero to $3 \times 10^{-11}$ (one in 33 billion). All hazard quotients are less than one for ambient exposure to the general population, and all MOEs for ambient exposure are greater than 1,000 for all processes, indicating low concern from the estimated air concentrations for chronic non-cancer effects.

## Ecological Hazards

The CTSA methodology typically evaluates ecological risk in terms of risks to aquatic organisms in streams that receive treated or untreated effluent from manufacturing processes. Stream concentrations were not available, however, and could not be estimated because of data limitations (i.e., insufficient characterization of constituents and their concentrations in facility wastewater). The upper limit of the aquatic release (and thus, its consequent exposure/risk) is controlled by regulation; the degree of control varies by site. Section 4.3, Regulatory Status, discusses the pertinent regulations. Because exposure (i.e., stream concentrations) could not be quantified, ecological (aquatic) risk is not characterized. Instead, an ecological hazard assessment was performed (Section 3.3.3), based only on chemical toxicity to aquatic organisms. The results of this evaluation are summarized briefly here.

Concern concentrations were estimated for MHC chemicals using an established EPA method. A CC is an acute or chronic toxicity value divided by an assessment factor (AsF). AsFs are dependent on the amount and type of toxicity data contained in a toxicity profile and reflect the amount of uncertainty about the potential effects associated with a toxicity value. CCs were determined for aquatic species (e.g., *Daphnia*, algae, and/or fish). The lowest CC is for copper sulfate, based on fish toxicity data.

Chemicals are also ranked for aquatic toxicity concern levels using established EPA criteria (high, moderate, and low concern) based on the available toxicity data. The number of chemicals with a high aquatic hazard concern level include nine in the electroless copper process, two in carbon, two in conductive ink, none in conductive polymer, three in graphite, three in non-formaldehyde electroless copper, two in organic-palladium, and nine in the tin-palladium process.

## 3.5 PROCESS SAFETY ASSESSMENT

Process safety is the concern of employers and employees alike. Each company has the obligation to provide its employees with a safe and healthy work environment, while each employee is responsible for his/her own safe personal work habits. An effective process safety program identifies potential workplace hazards and, if possible, seeks to eliminate or at least reduce their potential for harm. In the MHC process of PWB manufacturing, these hazards may be either chemical hazards or process hazards. Chemicals used in the MHC process can be hazardous to worker health and therefore must be handled and stored properly, using appropriate personal protective equipment and safe operating practices. Automated equipment can be hazardous to employees if safe procedures for cleaning, maintaining, and operating are not established and regularly performed. These hazards can result in serious injury and health problems to employees, and potential damage to equipment.

The U.S. Department of Labor and the Occupational Safety and Health Administration (OSHA) have established safety standards and regulations to assist employers in creating a safe working environment and protect workers from potential workplace hazards. In addition, individual states may also have safety standards regulating chemical and physical workplace hazards for many industries. Federal safety standards and regulations affecting the PWB industry can be found in the Code of Federal Regulation (CFR) Title 29, Part 1910 and are available by contacting your local OSHA field office. State and local regulations are available from the appropriate state office. This section of the CTSA presents chemical and process safety concerns associated with the MHC baseline and substitutes, as well as OSHA requirements to mitigate these concerns.

### 3.5.1 Chemical Safety Concerns

As part of its mission, OSHA's Hazard Communication Standard (29 CFR 1910.1200) requires that chemical containers be labeled properly with chemical name and warning information [.1200(f)], that employees be trained in chemical handling and safety procedures [.1200(h)], and that a MSDS be created and made available to employees for every chemical or formulation used in the workplace [.1200(g)]. Each MSDS must be in English and include information regarding the specific chemical identity of the hazardous chemical(s) involved and the common names. In addition, information must be provided on the physical and chemical characteristics of the hazardous chemical; known acute and chronic health effects and related health information; exposure limits; whether the chemical is a carcinogen; emergency and first-aid procedures; and the identification of the organization preparing the data sheet. Copies of MSDSs for all of the chemicals used must be kept and made available to workers who may come into contact with the process chemicals during their regular work shift.

In order to evaluate the chemical safety concerns of the various MHC processes, MSDSs for 172 chemical products comprising eight MHC technology categories were collected and reviewed for potential hazards to worker safety. The results of that review are summarized and discussed in the categories below. General information on OSHA storage and handling requirements for chemicals in these hazard categories are located in the process safety section of this chapter. For a more detailed description of OSHA storage and handling requirements for

MHC chemical products in these categories contact your area OSHA field office or state technical assistance program for assistance.

**Flammable, Combustible, and Explosive MHC Chemical Products**

A breakdown of MHC chemical products that when in concentrated form are flammable, combustible, explosive, or pose a fire hazard is presented in Table 3.40. The following lists OSHA definitions for chemicals in these categories, and discusses the data presented in the table.

**Table 3.40 Flammable, Combustible, Explosive, and Fire Hazard Possibilities for MHC Processes**

| MHC Process | Bath Type | Hazardous Property[a] | | | |
|---|---|---|---|---|---|
| | | Flammable | Combustible | Explosive | Fire Hazard |
| Carbon | Cleaner<br>Conditioner<br>Other (Anti-Tarnish) | 2 (2)<br>3 (3)<br>2 (2) | | | |
| Conductive Ink | Print Ink | | | 5 (5) | |
| Conductive Polymer[b] | Polymer | 1 (3) | | | |
| Electroless Copper | Accelerator<br>Anti-Tarnish<br>Cleaner/Conditioner<br>Electroless Copper<br>Microetch | 1 (5)<br>2 (4)<br>1 (8)<br>2 (25)<br>1 (9) | 1 (25) | 1 (8) | 1 (25) |
| Graphite | Microetch | | | | 1 (4) |
| Non-Formaldehyde Electroless Copper | Accelerator<br>Anti-Tarnish<br>Microetch | 1 (2)<br>1 (1)<br>1 (4) | | | |
| Palladium | Accelerator<br>Cleaner/Conditioner<br>Other (Anti-Tarnish) | <br>1 (6)<br>1 (3) | 1 (6) | 1 (10) | 1 (10) |

[a] Table entries are made in the following format - # of products meeting OSHA definition for the given hazardous property as reported in the products MSDSs (Total # of products in the process bath). A **blank** entry means that none of the products for the specific process bath meet the OSHA reporting criteria for the given property. Example: For the palladium process accelerator bath, 1 (10) means that one of the ten products in the bath were classified as explosive per OSHA criteria as reported on the products MSDSs.

[b] Hazardous properties based on German equivalent of MSDS, which may not have same reporting requirements of U.S. MSDS.

Flammable - A flammable chemical is defined by OSHA [29 CFR 1910.1200(c)] as one of the following:

- An aerosol that, when tested by the method described in 16 CFR 1500.45, yields a flame projection exceeding 18 inches at full valve opening, or a flashback at any degree of valve opening.

- A gas that has: 1) at ambient temperature and pressure, forms a flammable mixture with air at a concentration of 13 percent by volume or less; or 2) when it, at ambient temperature and pressure, forms a range of flammable mixtures with air wider than 12 percent by volume, regardless of the lower limit.
- A liquid that has a flashpoint below 100 °F (37.8 °C), except any mixture having components with flashpoints of 100 °F (37.8 °C) or higher, the total of which make up 99 percent or more of the total volume of the mixture.
- A solid, other than a blasting agent or explosive as defined in 29 CFR 1910.109(a), that is liable to cause fire through friction, absorption of moisture, spontaneous chemical change, or retained heat from manufacturing or processing, or which can be ignited readily and when ignited burns so vigorously and persistently as to create a serious hazard.

Twenty chemical products are reported as flammable according to MSDS data. While all of the products have flashpoints near or below 100 °F, several of the products reported as flammable have flashpoints greater than 200 °F with one as high as 400 °F. Although several chemical products are flammable in their concentrated form, most chemical baths in the MHC process line contain non-flammable aqueous solutions.

Combustible Liquid - As defined by OSHA [29 CFR 1910.1200(c)], a liquid that is considered combustible has a flashpoint at or above 100 °F (37.8 °C), but below 200 °F (93.3 °C), except any mixture having components with flashpoints of 200 °F (93.3 °C), or higher, the total volume of which make up 99 percent or more of the total volume of the mixture. Two chemical products have been reported as combustible by their MSDSs, both with flashpoints above 155 °F.

Explosive - As defined by OSHA [29 CFR 1910.1200(c)], a chemical is considered explosive if it causes a sudden, almost instantaneous release of pressure, gas, and heat when subjected to sudden shock, pressure, or high temperature. Seven chemical products are reported as explosive by their MSDSs.

Fire Hazard - A chemical product that is a potential fire hazard is required by OSHA to be reported on the product's MSDS. According to MSDS data, three chemical products are reported as potential fire hazards.

### 3.5.2 Corrosive, Oxidizer, and Reactive MHC Chemical Products

A breakdown of MHC chemical baths containing chemical products that are corrosive, oxidizers, or reactive in their concentrated form is presented in Table 3.41. The table also lists process baths that contain chemical products that may cause a sudden release of pressure when opened. The following lists OSHA definitions for chemicals in these categories and discusses the data presented in the table.

**Table 3.41 Corrosive, Oxidizer, Reactive, Unstable, and Sudden Release of Pressure Possibilities for MHC Processes**

| MHC Process | Bath Type | Hazardous Property[a] | | | | |
|---|---|---|---|---|---|---|
| | | Corrosive | Oxidizer | Reactive | Unstable | Sudden Release of Pressure |
| Carbon | Cleaner | 2 (2) | | | | |
| | Conditioner | 3 (3) | | | | |
| | Microetch | | 2 (2) | 2 (2) | | |
| Conductive Polymer[b] | Catalyst | 2 (3) | | | | |
| | Conductive Polymer | 2 (3) | | | | |
| | Microetch | 1 (1) | | | | |
| Electroless Copper | Accelerator | 1 (5) | 1 (5) | 3 (5) | | |
| | Catalyst | 5 (10) | | 2 (10) | | |
| | Cleaner/Conditioner | 5 (8) | | 2 (8) | | |
| | Electroless Copper | 11 (25) | | 5 (25) | | |
| | Microetch | 3 (9) | 5 (9) | 2 (9) | 1 (9) | 1 (9) |
| | Predip | 4 (6) | | 2 (6) | | |
| Graphite | Fixer | 1 (1) | | | | |
| | Graphite | 1 (3) | | | | |
| | Microetch | 2 (4) | 1 (4) | | 1 (4) | |
| Non-Formaldehyde Electroless Copper | Accelerator | | 1 (2) | 1 (2) | | |
| | Electroless Copper | 2 (6) | | 1 (6) | | |
| | Microetch | 2 (4) | 2 (4) | 2 (4) | | 1 (4) |
| Palladium | Accelerator | 4 (10) | | 1 (10) | | |
| | Catalyst | 4 (9) | | 1 (9) | | |
| | Cleaner/Conditioner | 1 (6) | | | | |
| | Microetch | | | 1 (5) | 1 (5) | |
| | Other | 2 (3) | | | | |
| | Predip | 1 (4) | | | | |

[a] Table entries are made in the following format - # of products meeting OSHA definition for the given hazardous property as reported in the product's MSDSs (Total # of products in the process bath). A **blank** entry means that none of the products for the specific process bath meet the OSHA reporting criteria for the given property. Example: For the graphite process microetch bath, 2 (4) means that two of the four products in the bath were classified as corrosive per OSHA criteria as reported by the products MSDSs.

[b] Hazardous properties based on German equivalent of MSDS, which may not have same reporting requirements of U.S. MSDS.

Corrosive - As defined by OSHA (29 CFR 1910.1200 [Appendix A]), a chemical is considered corrosive if it causes visible destruction of, or irreversible alterations in, living tissue by chemical action at the site of contact, as determined by the test method described by the U.S. Department of Transportation 49 CFR Part 173 Appendix A. This term does not apply to chemical action on inanimate surfaces. A review of MSDS data found that 59 MHC chemical products are reported as corrosive in their concentrated form. Some MHC baths may also be corrosive, but MSDSs do not provide data for the process chemical baths once they are prepared.

Oxidizer - As defined by OSHA (29 CFR 1910.1200[c]), an oxidizer is a chemical other than a blasting agent or explosive as defined by OSHA [29 CFR 1910.109(a)], that initiates or promotes combustion in other materials, thereby causing fire either of itself or through the release of oxygen or other gases. Twelve chemical products are reported as oxidizers according to MSDS data.

Reactive - A chemical is considered reactive if it is readily susceptible to change and the possible release of energy. EPA gives a more precise definition of reactivity for solid wastes. As defined by EPA (40 CFR 261.23), a solid waste is considered reactive if it exhibits any of the following properties: 1) is normally unstable and readily undergoes violent change without detonating; 2) reacts violently or forms potentially explosive mixtures with water; 3) when mixed with water, generates toxic gases, vapors, or fumes in a quantity that can present a danger to human health or the environment (for a cyanide or sulfide bearing waste, this includes exposure to a pH between 2 and 12.5); 4) is capable of detonation or explosive reaction if subjected to a strong initiated source or if heated under confinement; or 5) is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure. A review of MSDS data found that 25 chemical products from four different MHC processes are considered reactive.

Unstable - As defined by OSHA (29 CFR 1910.1200[c]), a chemical is unstable if in the pure state, or as produced or transported, will vigorously polymerize, decompose, condense, or will become self-reactive under conditions of shock, pressure, or temperature. Only three chemical products are reported as unstable according to MSDS data.

Sudden Release of Pressure - OSHA requires the reporting of chemical products that, while stored in a container subjected to sudden shock or high temperature, causes a pressure increase within the container that is released upon opening. MSDS data indicated only two chemical products that are potential sudden release of pressure hazards.

### 3.5.3 MHC Chemical Product Health Hazards

A breakdown of MHC process baths that contain chemical products that are sensitizers, acute or chronic health hazards, or irreversible eye damage hazards in their concentrated form is presented in Table 3.42. Also discussed in this section are MHC chemical products that are potential eye or dermal irritants and suspected carcinogens. The following presents OSHA definitions for chemicals in these categories and discusses the data in Table 3.42 where appropriate.

**Table 3.42 Sensitizer, Acute and Chronic Health Hazards, and Irreversible Eye Damage Possibilities for MHC Processes**

| MHC Process | Bath Type | Hazardous Property[a] | | | |
|---|---|---|---|---|---|
| | | Sensitizer | Acute Health Hazard | Chronic Health Hazard | Irreversible Eye Damage |
| Carbon | Carbon Black | | 3 (4) | 3 (4) | 4 (4) |
| | Cleaner | | 1 (2) | 1 (2) | 2 (2) |
| | Conditioner | | 3 (3) | 3 (3) | 2 (3) |
| | Microetch | | 2 (2) | | 2 (2) |
| | Other (Anti-Tarnish) | | 2 (2) | 2 (2) | 2 (2) |
| Conductive Ink | Print Ink | | | | 2 (5) |
| Conductive Polymer[b] | Catalyst | | | | 3 (3) |
| | Conductive Polymer | | | | 2 (3) |
| | Microetch | | | | 1 (1) |
| Electroless Copper | Accelerator | | 1 (5) | | 1 (5) |
| | Anti-Tarnish | | 2 (4) | 2 (4) | 2 (4) |
| | Catalyst | | 2 (10) | 2 (10) | 6 (10) |
| | Cleaner/Conditioner | | 1 (8) | 1 (8) | 3 (8) |
| | Electroless Copper | | 5 (25) | 4 (25) | 13 (25) |
| | Microetch | | 3 (9) | 1 (9) | 4 (9) |
| | Predip | | | | 5 (6) |
| Graphite | Cleaner/Conditioner | | 3 (4) | 2 (4) | |
| | Fixer | | | | 1 (1) |
| | Graphite | | 2 (3) | | 1 (3) |
| | Microetch | | 3 (4) | 2 (4) | 2 (4) |
| Non-Formaldehyde Electroless Copper | Accelerator | | 1 (2) | | |
| | Catalyst | | 2 (2) | 2 (2) | |
| | Electroless Copper | | 3 (6) | 2 (6) | 4 (6) |
| | Microetch | | 3 (4) | 1 (4) | 3 (4) |
| Organic-Palladium[b] | Conductor | | | | 2 (2) |
| | Microetch | | | | 1 (1) |
| | Postdip | | | | 1 (1) |
| Tin-Palladium | Accelerator | | 1 (10) | | 9 (10) |
| | Catalyst | | 3 (9) | 3 (9) | 4 (9) |
| | Cleaner/Conditioner | 2 (6) | 1 (6) | | 2 (6) |
| | Microetch | | 2 (5) | 2 (5) | 3 (5) |
| | Other | | 2 (3) | | 3 (3) |
| | Acid Dip | | | | 1 (1) |

[a] Table entries are made in the following format - # of products meeting OSHA definition for the given hazardous property as reported in the product's MSDSs (Total # of products in the process bath). A **blank** entry means that none of the products for the specific process bath meet the OSHA reporting criteria for the given property. Example: For the palladium process cleaner/conditioner bath, 2 (6) means that two of the six products in the bath were classified as sensitizers per OSHA criteria as reported by the products MSDSs.

[b] Hazardous properties based on German equivalent of MSDS, which may not have same reporting requirements of U.S. MSDS.

Sensitizer - A sensitizer is defined by OSHA [29 CFR 1910.1200 Appendix A (mandatory)] as a chemical that causes a substantial proportion of exposed people or animals to develop an allergic reaction in normal tissue after repeated exposure to the chemical. Only two chemical products were reported as sensitizers by MSDS data, both palladium MHC process chemicals.

Acute and Chronic Health Hazards - As defined by OSHA (29 CFR 1910.1200 Appendix A), a chemical is considered a health hazard if there is statistically significant evidence based on at least one study conducted in accordance with established scientific principles that acute or chronic health effects may occur in exposed employees. Health hazards are classified using the criteria below:

- Acute health hazards are those whose effects occur rapidly as a result of short-term exposures, and are usually of short duration.
- Chronic health hazards are those whose effects occur as a result of long-term exposure, and are of long duration.

Chemicals that are considered a health hazard include carcinogens, toxic or highly toxic agents, reproductive toxins, irritants, corrosives, sensitizers, hepatotoxins, nephrotoxins, nuerotoxins, agents which act on the hematopoietic system, and agents which damage the lungs, skin, eyes, or mucous membranes.

A review of MSDS data found 51 chemical products reported as potentially posing acute health hazards, and 33 chemical products potentially posing chronic health hazards. OSHA does not require reporting of environmental hazards such as aquatic toxicity data, nor are toxicity data on MSDSs as comprehensive as the toxicity data collected for the CTSA. OSHA health hazard data are presented here for reference purposes only, and are not used in the risk characterization component of the CTSA.

Carcinogen - As defined by OSHA (29 CFR 1910.1200 Appendix A), a chemical is considered to be a carcinogen if: 1) it has been evaluated by the International Agency for Research on Cancer (IARC), and found to be a carcinogen or potential carcinogen; 2) it is listed as a carcinogen or potential carcinogen in the Annual Report on Carcinogens published by the National Toxicology Program (NTP); or 3) it is regulated by OSHA as a carcinogen. Formaldehyde, which is used as a reducing agent in the electroless copper process, is a suspected human carcinogen. A review of MSDS data found that six chemical products were reported as potential carcinogens. All of the products contain formaldehyde and are utilized in the electroless copper bath of the traditional electroless copper process.

Dermal or Eye Irritant - An irritant is defined by OSHA [29 CFR 1910.1200 Appendix A (mandatory)] as a chemical, which is not corrosive, but which causes a reversible inflammatory effect on living tissue by chemical action at the site of contact. A chemical is considered a dermal or eye irritant if it is so determined under the testing procedures detailed in 16 CFR 1500.41- 42. A review of MSDS data found that all but six of the 181 MHC chemical products reviewed are reported as either dermal or eye irritants.

Irreversible Eye Damage - Chemical products that, upon coming in contact with eye tissue, can cause irreversible damage to the eye are required by OSHA to be identified as such on the product's MSDS. A review of MSDS data found that 91 chemical products are reported as having the potential to cause irreversible eye damage.

### 3.5.4 Other Chemical Hazards

MHC chemical products that have the potential to form hazardous decomposition products are presented below. In addition, chemical product incompatibilities with other chemicals or materials are described, and other chemical hazard categories presented. The following lists OSHA definitions for chemicals in these categories and summarizes the MSDS data where appropriate.

Hazardous Decomposition - A chemical product, under specific conditions, may decompose to form chemicals that are considered hazardous. With few exceptions, the MSDS data for the chemical products in the MHC process indicate the possibility of decomposition to form a potentially hazardous chemical. Each chemical product should be examined to determine its decomposition products so that potentially dangerous reactions and exposures can be avoided. The following are examples of hazardous decomposition of chemical products that are employed in the MHC alternatives:

- When heated, a chemical product used to create an electroless copper bath can generate toxic formaldehyde vapors.
- If allowed to heat to dryness, a graphite bath process chemical could result in gas releases of ammonia, carbon monoxide, and carbon dioxide.
- Thermal decomposition under fire conditions of certain chemical bath constituents of a palladium cleaner/conditioner bath can result in releases of toxic oxide gases of nitrogen and carbon.

Incompatibilities - Chemical products are often incompatible with other chemicals or materials with which they may come into contact. A review of MSDS data found that all of the MHC processes have chemical products with incompatibilities that can pose a threat to worker safety if the proper care is not taken to prevent such occurrences. Incompatibilities reported range from specific chemicals or chemical products, such as acids or cyanides, to other materials, such as rubber or textiles, like wood and leather. Chemical incompatibilities that are common to products from all the MHC processes include acids, alkalis, oxidizers, metals, and reducing agents. Incompatibilities were also found to exist between chemical products used on the same process line. Individual chemical products for each process bath should be closely examined to determine specific incompatibilities and care should be taken to avoid contact with incompatible chemicals and chemical products, textiles, and storage containers.

The following are examples of chemical incompatibilities that exist for chemical products that are employed in the MHC alternatives:

- An electroless copper bath contains chemical products that, when contacted with hydrochloric acid which is present in other electroless copper process baths, will result in reaction forming bis-chloromethyl ether, an OSHA-regulated carcinogen.

- Violent reactions can result when a chemical product of the conductive polymer catalyst bath comes into contact with concentrated acids or reducing agents, both of which are used in PWB manufacturing processes.
- A microetch bath of a graphite process contains chemicals that will react to form hazardous gases when contacted with other chemical products containing cyanides, sulfides, or carbides.
- Hazardous polymerization of a particular conductive ink product can occur when the product is mixed with chemicals products containing amines, anhydrides, mercaptans, or imidazoles.

Other Chemical Hazard Categories - OSHA requires the reporting of several other hazard categories on the MSDSs for chemicals or chemical products that have not already been discussed above. These additional categories include chemical products that are:

- Water-reactive (react with water to release a gas that presents a health hazard).
- Pyrophoric (will ignite spontaneously in air at temperatures below 130 °F).
- Stored as a compressed gas.
- Classified as an organic peroxide.
- Chemicals that have the potential for hazardous polymerization.

A review of MSDS data indicated that none of the chemical products are reported as being water-reactive, pyrophoric, a compressed gas, an organic peroxide, or as having the potential for hazardous polymerization.

### 3.5.5 Process Safety Concerns

Exposure to chemicals is just one of the safety issues that PWB manufacturers may have to deal with during their daily activities. Preventing worker injuries should be a primary concern for employers and employees alike. Work-related injuries may result from faulty equipment, improper use of equipment, bypassing equipment safety features, failure to use personal protective equipment, and physical stresses that may appear gradually as a result of repetitive motions (i.e., ergonomic stresses). Any or all of these types of injuries may occur if proper safeguards or practices are not in place and adhered to. An effective worker safety program includes:

- An employee training program.
- Employee use of personal protective equipment.
- Proper chemical storage and handling.
- Safe equipment operating procedures.

The implementation of an effective worker safety program can have a substantial impact on business, not only in terms of direct worker safety, but also in reduced operating costs as a result of fewer days of absenteeism, reduced accidents and injuries, and lower insurance costs. Maintaining a safe and efficient workplace requires that both employers and employees recognize and understand the importance of worker safety and dedicate themselves to making it happen.

## Employee Training

A critical element of workplace safety is a well-educated workforce. To help achieve this goal, the OSHA Hazard Communication Standard requires that all employees at PWB manufacturing facilities (regardless of the size of the facility) be trained in the use of hazardous chemicals to which they are exposed. A training program should be instituted for workers, especially those operating the MHC process, who may come into contact with, or be exposed to, potentially hazardous chemicals. Training may be conducted by either facility staff or outside parties who are familiar with the PWB manufacturing process and the pertinent safety concerns. The training should be held for each new employee, as well as periodic retraining sessions when necessary (e.g., when a new MHC process is instituted), or on a regular schedule. The training program should explain to the workers the types of chemicals with which they work and the precautions to be used when handling or storing them; when and how personal protection equipment should be worn; and how to operate and maintain equipment properly.

## Storing and Using Chemicals Properly

Because the MHC process requires handling of a variety of chemicals, it is important that workers know and follow the correct procedures for the use and storage of the chemicals. Much of the use, disposal, and storage information about MHC process chemicals may be obtained from the MSDSs provided by the manufacturer or supplier of each chemical or formulation. Safe chemical storage and handling involves keeping chemicals in their proper place, protected from adverse environmental conditions, as well as from other chemicals with which they may react. Examples of supplier recommended storage procedures found on the MSDSs for MHC chemicals are listed below:

- Store chemical containers in a cool, dry place away from direct sunlight and other sources of heat.
- Chemical products should only be stored in their properly sealed original containers and labeled with the generic name of the chemical contents.
- Incompatible chemical products should never be stored together.
- Store flammable liquids separately in a segregated area away from potential ignition sources or in a flammable liquid storage cabinet.

Some products have special storage requirements and precautions listed on their MSDSs (e.g., relieving the internal pressure of the container periodically). Each chemical product should be stored in a manner consistent with the recommendation on the MSDS. In addition, chemical storage facilities must be designed to meet any local, state, and federal requirements that may apply.

Not only must chemicals be stored correctly, but they must also be handled and transported in a manner which protects worker safety. Examples of chemical handling recommendations from suppliers include:

- Wear appropriate protective equipment when handling chemicals.
- While transporting chemicals, do not use open containers.
- Use only spark-proof tools when handling flammable chemicals.

- Transfer chemicals using only approved manual or electrical pumps to prevent spills created from lifting and pouring.

Proper chemical handling procedures should be a part of the training program given to every worker. Workers should also be trained in chemical spill containment procedures and emergency medical treatment procedures in case of chemical exposure to a worker.

**Use of Personal Protective Equipment**

OSHA has developed several personal protective equipment standards that are applicable to the PWB manufacturing industry. These standards address general safety and certification requirements (29 CFR Part 1910.132), the use of eye and face protection (Part 1910.133), head protection (Part 1910.135), foot protection (Part 1910.136), and hand protection (Part 1910.138). The standards for eye, face, and hand protection are particularly important for the workers operating the MHC process where there is close contact with a variety of chemicals, of which nearly all irritate or otherwise harm the skin and eyes. In order to prevent or minimize exposure to such chemicals, workers should be trained in the proper use of personal safety equipment.

The recommended personal protective equipment for a worker handling chemicals is also indicated on the MSDS. For the majority of MHC chemicals, the appropriate protective equipment indicated by the MSDS includes:

- Goggles to prevent the splashing of chemical into the eyes.
- Chemical aprons or other impervious clothing to prevent splashing of chemicals on clothing.
- Gloves to prevent dermal exposure while operating the process.
- Boots to protect against chemical spills.

Other items less widely suggested include chemically resistant coveralls and hats. In addition to the personal protective equipment listed above, some MSDSs recommended that other safety equipment be readily available. This equipment includes first aid kits, oxygen supplies (SCBA), and fire extinguishers.

Other personal safety considerations are the responsibility of the worker. Workers should be discouraged from eating or keeping food near the MHC process. Because automated processes contain moving parts, workers should also be prohibited from wearing jewelry or loose clothing, such as ties, that may become caught in the machinery and cause injury to the worker or the machinery itself. In particular, the wearing of rings or necklaces may lead to injury. Workers with long hair that may also be caught in the machinery should be required to securely pull their hair back or wear a hair net.

**Use of Equipment Safeguards**

In addition to the use of proper personal protection equipment for all workers, OSHA has developed safety standards (29 CFR Part 1910.212) that apply to the actual equipment used in a PWB MHC process. Among the safeguards recommended by OSHA that may be used for conveyorized equipment are barrier guards, two-hand trip devices, and electrical safety devices.

Safeguards for the normal operation of conveyor equipment are included in the standards for mechanical power-transmission apparatus (29 CFR Part 1910.219) and include belts, gears, chains, sprockets, and shafts. PWB manufacturers should be familiar with the safety requirements included in these standards and should contact their local OSHA office or state technical assistance program for assistance in determining how to comply with them.

In addition to normal equipment operation standards, OSHA also has a lockout/tagout standard (29 CFR Part 1910.147). This standard is designed to prevent the accidental start-up of electric machinery during cleaning or maintenance operations that apply to the cleaning of conveyorized equipment as well as other operations. OSHA has granted an exemption for minor servicing of machinery provided the equipment has other appropriate safeguards, such as a stop/safe/ready button which overrides all other controls and is under the exclusive control of the worker performing the servicing. Such minor servicing of conveyorized equipment can include clearing fluid heads, removing jammed panels, lubricating, removing rollers, minor cleaning, adjusting operations, and adding chemicals. Rigid finger guards should also extend across the rolls, above and below the area to be cleaned. Proper training of workers is required under the standard whether lockout/tagout is employed or not. For further information on the applicability of the OSHA lockout/tagout standard to MHC process operations, contact the local OSHA field office.

**Occupational Noise Exposure**

OSHA has also developed standards (29 CFR Part 1910.95) that apply to occupational noise exposure. These standards require protection against the effects of noise exposure when the sound levels exceed certain levels specified in the standard. No data was collected on actual noise levels from MHC process lines, but one PWB manufacturer suggested protective measures may be needed to reduce noise levels from air knife ovens on carbon and graphite lines. This manufacturer installed baffles on his system to reduce noise levels (Kerr, 1997).

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# Chapter 4
# Competitiveness

This chapter of the Cleaner Technologies Substitutes Assessment (CTSA) presents information on basic issues traditionally important to the competitiveness of a printed wiring board (PWB) manufacturer: the performance characteristics of the making holes conductive (MHC) technologies relative to industry standards; the direct and indirect production costs associated with the MHC technologies; the federal environmental regulations affecting chemicals used in or waste streams generated by a technology; and the implications of an MHC technology choice on global competitiveness. A CTSA weighs these traditional competitiveness issues against issues business leaders now know are equally important: the health and environmental impacts of alternatives products, processes, and technologies. Section 4.1 presents the results of the Performance Demonstration Project. Section 4.2 presents a comparative cost analysis of the MHC technologies. Section 4.3 lists the federal environmental regulations affecting chemicals in the various technologies. Section 4.4 summarizes information pertaining to the international use of the technologies, including reasons for adopting alternatives to electroless copper worldwide.

## 4.1 PERFORMANCE DEMONSTRATION RESULTS

### 4.1.1 Background

This section of the CTSA summarizes performance information collected during performance demonstrations of MHC technologies. These demonstrations were conducted at 25 volunteer PWB facilities in the U.S. and Europe, between September and November, 1995. Information from the performance demonstrations, taken in conjunction with risk, cost, and other information in this document, provides a more complete assessment of alternative technologies than has previously been available from one source.

In a joint and collaborative effort, Design for the Environment (DfE) project partners organized and conducted the performance demonstrations. The demonstrations were open to all suppliers of MHC technologies. Prior to the start of the demonstrations, DfE project partners advertised the project and requested participation from all interested suppliers through trade shows, conferences, trade journals, and direct telephone calls.

### 4.1.2 Performance Demonstration Methodology

The detailed performance demonstration methodology is attached in Appendix F. The general plan for the demonstrations was to collect information about MHC technologies at facilities where the technologies were already in use. The information collected through the demonstrations was intended to provide a "snapshot" of the way the technology was performing at that particular facility at that particular time. It is important to note that the methodology was developed by consensus by a technical workgroup, which included suppliers, trade association representatives, the U.S. Environmental Protection Agency (EPA), and many PWB manufacturers.

Each supplier was asked to submit the names of up to two facilities where they wanted to see the demonstrations of their technology conducted. This selection process encouraged the suppliers to nominate the facilities where their technology was performing at its best. This, in turn, provided for more consistent comparisons across technologies. The sites included 23 production facilities and two supplier testing facilities. While there were no pre-screening requirements for the technologies, the demonstration facilities did have to meet the requirements of the performance demonstration methodology.

For the purposes of the Performance Demonstration Project, the MHC process was defined as everything from the desmear step through 0.1 mil of copper flash plating. In order to minimize differences in performance due to processes outside this defined MHC function, the panels used for testing were all manufactured and drilled at one facility. One hundred panels, described below, were produced. After drilling, three panels were sealed in plastic bags with desiccant and shipped to each test site to be processed through the site's MHC line. All bags containing panels remained sealed until the day of processing.

An on-site observer from the DfE project team was present at each site from the point the bags were opened until processing of the test panels was completed. Observers were present to confirm that all processing was completed according to the methodology and to record data. Each test site's process was completed within one day; MHC processing at all sites was completed over a two month period.

When the MHC processing was completed, the panels were put into sealed bags with desiccant and shipped to a single facility, where they remained until all the panels were collected. At this facility, the panels were electroplated with 1.0 mil of copper followed by a tin-lead etch resist, etched, stripped of tin-lead, solder mask coated, and finished with hot air solder leveling (HASL). A detailed account of the steps taken in this process is included in Appendix F.

After HASL, the microsection coupons were routed out of the panels and sent to Robisan Laboratory Inc. for mechanical testing. The Interconnect Stress Test (IST) coupons were left in panel format. The panels containing the coupons were passed twice through an IR reflow to simulate assembly stress. A detailed protocol describing the IR reflow process is also included in Appendix F. The panels with the IST coupons were then sent to Digital Equipment Corporation of Canada (DEC Canada) for electrical prescreening and electrical testing.

**Limitations of Performance Demonstration Methodology**

This performance demonstration was designed to provide a snapshot of the performance of different MHC technologies. Because the test sites were not chosen randomly, the sample may not be representative of all PWB manufacturing facilities in the U.S. (although there is no specific reason to believe that they are not representative). In addition, the number of test sites for each type of technology ranged from one to ten. Due to the smaller number of test sites for some technologies, results for these technologies could more easily be due to chance than the results from technologies with more test sites. Statistical relevance cannot be determined.

### 4.1.3 Test Vehicle Design

All of the test panels were manufactured by H-R Industries, Inc. The test panel measured 24" x 18", laminated to 0.062", with eight layers. Test panels were produced from B and C stage FR4 materials. Artwork, lamination specifications, and a list of the steps taken to manufacture the panels are included in Appendix F.

Each test panel contained 54 test coupons: 27 IST coupons (used for electrical testing) and 27 microsection coupons. IST coupons measured 6.5" x 3/4" and contained 700 interconnecting vias on a seven row by 100 via 0.050" grid. This coupon contained two independent circuits: the post circuit and the plated through-hole (PTH) circuit. The post circuit contained 200 interconnects, and was used to measure post interconnect resistance degradation. The PTH circuit contained 500 interconnects, and was used to measure PTH (barrel) interconnect resistance degradation. IST coupons had either 0.013" or 0.018" holes (finished).

The microsection coupon measured 2" x 2" and contained 100 interconnected vias on a 10 row by 10 via 0.100" grid. It had internal pads at the second and seventh layer and a daisy chain interconnect between the two surfaces of the coupon through the via. Microsection coupons had either 0.013", 0.018", or 0.036" holes (finished).

This study was a snapshot based on products built with B and C stage FR4 materials and this specific board construction. The data cannot necessarily be extrapolated to other board materials or constructions.

### 4.1.4 Electrical and Microsection Testing Methodology

**Electrical Testing Methodology**

The IST coupons in panel format were electrically prescreened to determine defects on arrival. The panels were then shipped to another facility for routing of the IST coupons, and were shipped back to DEC Canada for completion of electrical testing.

Electrical testing was completed using the IST technology. IST is an accelerated stress test method used for evaluating the failure modes of PWB interconnect. This method uses DC current to create the required temperatures within the interconnect. There are three principal types of information generated from the IST:

- Initial resistance variability.
- Cycles to failure (barrel integrity).
- Post separation/degradation (post interconnect).

The resistance value for the first internal circuit (PTH circuit) for each coupon was determined. This gives an indication of the resistance variability (plating thickness) between coupons and between panels. The initial resistance testing was also used to determine which coupons had defects on arrival, or were unsuitable for further testing.

The cycles to failure indicate how much stress the individual coupons can withstand before failing to function (measuring barrel integrity). IST coupons contained a second internal circuit (post circuit) used to monitor the resistance degradation of the post interconnect.

The level of electrical degradation in conjunction with the number of cycles completed is used to determine the presence and level of post separation. The relative performance of the internal circuits indicates which of the two internal circuits, the post circuit or the PTH circuit, has the dominant failure mechanism. The draft Institute for Interconnecting and Packaging Electronic Circuits (IPC) IST test method is included in Appendix F.

**Mechanical Testing Methodology**

The coupons for mechanical testing were sent to Robisan Laboratory Inc. for testing. Mechanical testing consisted of evaluations of metallurgical microsections of plated through-holes in the "as produced" condition and after thermal stress. One test coupon of each hole size from each panel was sectioned. The direction the coupons were microsectioned was determined by visually examining the coupons to determine the direction of best registration to produce the most inner layer circuitry connections in the microsections.

Microsections were stressed per IPC-TM-650, method 2.6.8, included in Appendix F. The plated through-holes were evaluated for compliance to the requirements found in IPC-RB-276. Microsections were examined after final polish, prior to metallurgical microetch, and after microetch.

The original test plan called for selection of IST and microsectioning coupons from similar locations on each panel. Following prescreening, the coupon selection criteria was amended to be based on coupons with the best registration. This resulted in some coupons being selected from areas with known thicker copper (see Results of Electrical Prescreening below).

Four 0.013" IST coupons were selected from each of the three test panels from each test site. Test Site #3 and Test Site #4 had only two available test panels, therefore six coupons were selected from each panel. Three coupons from within six inches of the IST coupons selected were microsectioned from the same panels. In some cases, the desired microsection coupons exhibited misregistration, so next-best locations were used. In all cases, coupons selected were located as close to the center of the panel as possible.

**Limitations of Testing Methodology**

Fine line evaluations in microsections have always been a point of contention within the industry. Current microsection specifications state that any indication of separation between the hole wall plating and the inner layer is sufficient grounds to reject the product. An indication of post separation would be a line on the microsection thicker than what normally appears with electroless copper technology (normal average: 0.02 - 0.04 mils). Separation may also be determined by a variation in the thickness of the line across the inner layer connection, especially on electroless deposits that are very thin. The rationale for these rejection criteria is that product with post separation degrades with time and temperature cycling.

With traditional electroless copper products where post separation is present, it can usually be determined where the separation occurs: between the electroless and foil, within the electroless, or between the electroless and the electrolytic plating. This determination often helps in troubleshooting the plating process. In this study, some of the alternative technologies resulted in no line at all after microetch on the microsections. This posed a problem in interpretation of results. If traditional criteria are used to determine inner layer separation (i.e., the line of demarcation is thicker on some inner connects than others, and the electroless can be seen as continuous between the inner layer and plated copper), then accurate evaluations of product with no lines would not be possible. In this study, the criteria used on "no line" products was that if the sections exhibited any line of demarcation after microetch, the product is considered to have inner layer separation.

This issue is significant to the PWB industry because there remains a question about the relationship between the appearance of a line on the microsection to the performance of a board. Traditionally (with electroless copper products), the appearance of a line thicker than normal electroless line is considered to be post separation, and the board is scrapped. However, there are no criteria for how to evaluate "no line" products. In addition, there are no official means of determining when "a little separation" is significant to the performance of the board.

IST is not a subjective test and is not dependent upon the presence or absence of a line in a microsection after microetch. The test provides a relative number of IST cycles necessary to cause a significant rise in resistance in the post interconnect. This number of cycles may be used to predict interconnect performance. Tests such as this, when correlated with microsections, can be useful in determining how to interpret "no line" product characteristics. In addition, IST may be able to determine levels of post separation.

The figures included in Appendix F in the IPC IST test method show various failure mechanisms exhibited by different test sites and panels. Future industry studies must determine the relevance of these curves to performance, based on number of cycles needed to raise the resistance as well as the amount of change in resistance. Definitions for "marginal" and "gross" separations may be tied to life-cycle testing and subsequently related to class of boards produced.

### 4.1.5 Results

Product performance for this study was divided into two functions: PTH cycles to failure and the integrity of the bond between the internal lands (post) and the PTH. The PTH cycles to failure observed in this study is a function of both electrolytic plating and the MHC process. The results indicate that each MHC technology has the capability to achieve comparable (or superior) levels of performance to electroless copper.

Results are presented in this section for all three stages of testing conducted:

1. Electrical prescreening, which included tests for:

- Defects on arrival based on resistance measurements.
- Print and etch variability based on resistance distribution of the post circuit.
- Plating variability based on resistance distribution of the PTH circuit.

2. Microsection evaluation, which examined:

- Plating voids.
- Drill smear.
- Resin recession.
- Post separation.
- Average copper plating thickness.

3. Interconnect stress testing, which measured:

- Mean cycles to failure of the PTH interconnect.
- Post degradation/separation within the post interconnect.

**Results of Electrical Prescreening**

Seventy-four of 75 test panels from 25 test facilities were returned. One of the 74 proved to be untestable due to missing inner layers. The results of the prescreening will be reported in the following categories: defects on arrival (unacceptable for testing), print and etch variability, and plating (thickness) variability.

**Defects on Arrival.** A total of 1,971 coupons from the 73 panels each received two resistance measurements using a four wire resistance meter. The total number of holes tested was 1.4 million. As shown in Table 4.1, one percent (19) of coupons were found to be defective, and were considered unacceptable for IST testing because of opens and shorts.

**Table 4.1 Defective Coupons Found at Prescreening**

| Test Site # | MHC Technology | Opens | Shorts |
|---|---|---|---|
| 1 | Electroless | | 4 |
| 3 | Electroless | 1 | 2 |
| 11 | Graphite | 2 | |
| 12 | Graphite | | 5 |
| 14 | Palladium | 1 | |
| 16 | Palladium | 2 | |
| 20 | Palladium | 2 | |

Following an inspection of the defective coupons, the opens were found to be caused by voiding, usually within a single via. Shorts were caused by misregistration. The type of MHC technology did not contribute to the shorts.

**Print and Etch Variability.** The resistance distribution for the post circuit was determined. Throughout manufacturing, the layers/panels were processed in the same orientation, which provided an opportunity to measure resistance distributions for each coupon/panel. The distribution proved very consistent. This result confirms that inner layer printing and etching did not contribute to overall resistance variability. Table 4.2 depicts the mean post circuit resistance for five 0.013" coupon locations (in milliohms) for all 73 panels.

**Table 4.2 Mean Post Circuit Resistance Measurements, in Milliohms**
**(coupon locations on panel)**

| | | |
|---|---|---|
| 409 | | 405 |
| | | |
| | 399 | |
| | | |
| 415 | | 411 |

**Plating Variability.** The resistance distribution for the PTH circuit was determined as an indicator of variability. The results indicated that overall resistance variability was due to plating thickness variability rather than print and etch variability. Table 4.3 depicts the mean PTH circuit resistance for five 0.013" coupon locations (in milliohms) for all 73 panels.

**Table 4.3 Mean PTH Circuit Resistance Measurements, in Milliohms**
**(coupon locations on panel)**

| | | |
|---|---|---|
| 254 | | 239 |
| | | |
| | 244 | |
| | | |
| 241 | | 225 |

The PTH interconnect resistance distribution showed the electrolytic copper plating increased in thickness from the top to the bottom of each panel. Copper thickness variability was calculated to be 0.0003" thicker at the bottom compared to the top of each panel. Resistance variability, based on 54 measurements per panel, was also found from right to left on the panels. Inconsistent drill registration or outer layer etching was thought to be the most probable cause of this variability. When a number of holes break out of their pads, it increases the internal copper area, causing the resistance to decrease. This reduction in resistance creates the impression the coupons have thicker copper.

Table 4.4 lists the means and standard deviation of all PTH resistance measurements and the levels of correlation among panels observed at each site. As seen in Table 4.4, copper plating distribution at each site was good. Plating cells and rack/panel locations did not create large variability that could affect the results of each test site. Because resistance (plating thickness) distribution was also consistent among test sites, relative comparisons among the different MHC technology sites can be made. Only one site, Test Site #12, was calculated to have poor correlation between all three panels.

It was determined during correlation that the variations in hole wall plating thickness indicated by electrical prescreening were due to variations in the flash plate provided by each test site and not due to variations in electrolytic plating.

**Table 4.4 Prescreening Results - 0.013" Vias for All Test Sites[a]**

| Site # | Mean Res. | Std Dev. | Pnl #1 | Pnl #2 | Pnl #3 | Corr. |
|---|---|---|---|---|---|---|
| 1 | 239 | 14.5 | 234 | 245 | 237 | All |
| 2 | 252 | 17.6 | 269 | 251 | 234 | 2 |
| 3 | 238 | 12.5 | 227 | 248 | N/A | All |
| 4 | 232 | 11.2 | 224 | 239 | N/A | All |
| 5 | 236 | 12.1 | 239 | 241 | 229 | 2 |
| 6 | 266 | 15.7 | 255 | 275 | 266 | 2 |
| 7 | 253 | 14.2 | 240 | 259 | 259 | All |
| 8 | 230 | 11.6 | 221 | 228 | 241 | 2 |
| 9 | 243 | 10.6 | 247 | 247 | 235 | 2 |
| 10 | 248 | 13.0 | 256 | 242 | 247 | All |
| 11 | 226 | 19.0 | 216 | 221 | 241 | 2 |
| 12 | 240 | 23.0 | 254 | 235 | 231 | None |
| 13 | 231 | 16.0 | 243 | 235 | 215 | 2 |
| 14 | 247 | 26.8 | 256 | 227 | 258 | All |
| 15 | 243 | 11.1 | 236 | 244 | 248 | 2 |
| 16 | 239 | 15.9 | 232 | 243 | 241 | All |
| 17 | 240 | 12.8 | 247 | 243 | 231 | All |
| 18 | 245 | 9.7 | 245 | 249 | 240 | All |
| 19 | 226 | 10.2 | 223 | 232 | 223 | 2 |
| 20 | 229 | 10.2 | 219 | 238 | 229 | 2 |
| 21 | 250 | 13.3 | 258 | 243 | 249 | 2 |
| 22 | 256 | 8.8 | 256 | 261 | 250 | All |
| 23 | 253 | 12.5 | 257 | 257 | 244 | All |
| 24 | 239 | 12.0 | 241 | 232 | 246 | All |
| 25 | 224 | 13.9 | 210 | 232 | 231 | All |

[a] Site #6, an electroless copper site, may not have performed to its true capability on the day of the test. Due to a malfunction in the line, the electroless copper bath was controlled by manual lab analysis instead of by the usual single-channel controller.

Mean Res. - Mean resistance of all coupons on the three panels.

Std Dev. - Standard deviation for all coupons per test site.

Pnl # - Mean resistance for listed panel.

Corr. - Correlation Coefficient >.7 between each panel.

Sample size for each test site: 12.

Remaining test results will be reported for each type of MHC technology, represented by the following test sites shown in Table 4.5.

**Table 4.5 Correlation of MHC Technologies with Test Site Numbers**

| Test Site # | MHC Technology | # of Test Sites |
|---|---|---|
| 1 - 7 | Electroless Copper | 7 |
| 8 - 9 | Carbon | 2 |
| 10 - 12 | Graphite | 3 |
| 13 - 22 | Palladium | 10 |
| 23 - 24 | Non-Formaldehyde Electroless Copper | 2 |
| 25 | Conductive Polymer | 1 |

## Results of Microsection Evaluation

The only defects reported in this study were voids in hole wall copper, drill smear, resin recession, and inner layer separation. Average hole wall thickness was also reported for each panel. Defects present but not included as part of this report are registration, inner layer foil cracks, and cracks in flash plating at the knees of the holes. These defects were not included because they were not believed to be a function of the MHC technology. The inner layer foil cracks appear to be the result of the drilling operation and not a result of z-axis expansion or defective foil. None of the cracks in the flash plating extended into the electrolytic plate in the coupons as received or after thermal stress. Therefore, the integrity of the hole wall was not affected by these small cracks.

**Plating Voids.** There were no plating voids noted on any of the coupons evaluated. The electrolytic copper plating was continuous and very even with no indication of any voids.

**Drill Smear.** The panels exhibited significant amounts of nailheading. Since nailheading was present on all panels, it was determined that all test sites had received similar panels to process and therefore, comparisons were possible. The main concern with the presence of nailheading was that the amount of drill smear might be excessive compared to each test site's "normal" product. Drill smear negatively impacts inner layer connections to the plated hole wall if not removed.

**Resin Recession.** No samples failed current specification requirements for resin recession. There was, however, a significant difference in the amount of resin recession among test sites.

**Inner Layer Separation.** Different chemistries had different appearances after metallurgical microetch. Electroless copper microsections traditionally have a definite line of demarcation between foil copper and electrolytic copper after metallurgical microetch. This line also appeared in electroless copper samples in this study. The line is the width of the electroless deposit, and is very important in making a determination as to whether inner layers are separated from the plated hole wall. Many of the products tested in this study had no line of demarcation or lines which had little, if any, measurable width. For those MHC technologies that should not have a line after microetch, the determination as to whether inner layer separation was present on the samples was based on the presence of a line.

Over half of the test sites supplied product which did not exhibit inner layer separations on as received or thermal stressed microsections. Some of the product exhibited inner layer separation in the as received samples which further degraded after thermal stress. Other test sites had product that showed very good interconnect as received and became separated as a result of thermal stress.

The separations ranged from complete, very wide separations to very fine lines which did not extend across the complete inner layer connection. No attempt was made to track these degrees of separation because current specification requirements dictate that any separation is grounds for rejection of the product.

Table 4.6 gives the percentage of panels from a test site that did or did not exhibit a defect. The data are not presented by hole size because only Test Site #11 had defects on only one size of hole. In all other test sites exhibiting defects, the defects were noted on all sizes of holes.

**Table 4.6 Proportion of Panels Exhibiting Defects**

| Test Site # | Percentage of Panels Exhibiting Defect | | | Percentage of Panels Exhibiting Defect per Technology (average of all test sites) | | | MHC Technology |
|---|---|---|---|---|---|---|---|
| | Drill Smr | Res Rec | Post Sep | Drill Smr | Res Rec | Post Sep | |
| 1 | 0 | 33 | 0 | 21 | 31.6 | 31.6 | Electroless Copper |
| 2 | 66 | 66 | 100 | | | | |
| 3 | 0 | 0 | 0 | | | | |
| 4 | 100 | 0 | 0 | | | | |
| 5 | 0 | 0 | 0 | | | | |
| 6 | 0 | 0 | 100 | | | | |
| 7 | 0 | 100 | 0 | | | | |
| 8 | 0 | 0 | 0 | 0 | 0 | 0 | Carbon |
| 9 | 0 | 0 | 0 | | | | |
| 10 | 0 | 0 | 0 | 0 | 11 | 55.6 | Graphite |
| 11 | 0 | 33 | 66 | | | | |
| 12 | 0 | 0 | 100 | | | | |
| 13 | 0 | 33 | 0 | 3.3 | 26.5 | 43.3 | Palladium |
| 14 | 0 | 0 | 0 | | | | |
| 15 | 0 | 0 | 33 | | | | |
| 16 | 0 | 0 | 100 | | | | |
| 17 | 33 | 33 | 33 | | | | |
| 18 | 0 | 33 | 66 | | | | |
| 19 | 0 | 100 | 0 | | | | |
| 20 | 0 | 0 | 100 | | | | |
| 21 | 0 | 0 | 100 | | | | |
| 22 | 0 | 66 | 0 | | | | |
| 23 | 0 | 0 | 100 | 0 | 0 | 50 | Non-Formaldehyde Electroless Copper |
| 24 | 0 | 0 | 0 | | | | |
| 25 | 0 | 0 | 0 | 0 | 0 | 0 | Conductive Polymer |

Table 4.7 depicts the average measured copper plating thickness for all panels.

**Table 4.7 Microsection Copper Plating Thickness (in mils)**

| Test Site | Panel # 1 | Panel # 2 | Panel # 3 | Average Cu |
|---|---|---|---|---|
| 1 | 1.4 | 1.1 | 1.2 | 1.24 |
| 2 | 0.95 | 1.1 | 1.3 | 1.11 |
| 3 | 1.3 | 1.1 | N/A | 1.2 |
| 4 | 1.3 | 1.2 | N/A | 1.25 |
| 5 | 1.2 | 1.3 | 1.3 | 1.24 |
| 6 | 1.1 | 1.1 | 1.1 | 1.1 |
| 7 | 1.5 | 1.1 | 1.1 | 1.2 |
| 8 | 1.3 | 1.3 | 1.2 | 1.3 |
| 9 | 1.2 | 1.4 | 1.3 | 1.3 |
| 10 | 1.0 | 1.1 | 1.3 | 1.14 |
| 11 | 1.5 | 1.5 | 1.1 | 1.4 |
| 12 | 1.3 | 1.3 | 1.3 | 1.3 |
| 13 | 1.2 | 1.3 | 1.3 | 1.3 |
| 14 | 1.2 | 1.1 | 1.2 | 1.2 |
| 15 | 1.1 | 1.1 | 1.2 | 1.13 |
| 16 | 1.1 | 1.2 | 1.3 | 1.2 |
| 17 | 1.2 | 1.3 | 1.4 | 1.3 |
| 18 | 1.1 | N/A | 1.5 | 1.3 |
| 19 | 1.5 | 1.3 | 1.3 | 1.4 |
| 20 | 1.6 | 1.4 | 1.3 | 1.4 |
| 21 | 1.1 | 1.2 | 1.2 | 1.14 |
| 22 | 1.2 | 1.1 | 1.1 | 1.13 |
| 23 | 1.4 | 1.1 | 1.2 | 1.24 |
| 24 | 1.3 | 1.2 | 1.2 | 1.23 |
| 25 | 1.4 | 1.7 | 1.4 | 1.5 |

## Results of Interconnect Stress Testing

Test results will be reported in various formats. Both tables and graphs will be used to describe IST cycles to failure for the PTH interconnect and post degradation/separation within the post interconnect. IST was completed on a total of 12 coupons from each test site.

**Mean Cycles to Failure Testing Results.** The mean cycles to failure for the PTH interconnect are established at the point when the coupon exceeds a ten percent increase in the initial elevated resistance. Mean IST cycles to failure and standard deviation by test site are shown in Table 4.8. Table 4.9 shows the mean IST cycles to failure and standard deviations by MHC technology.

**Table 4.8 Mean IST Cycles to Failure, by Test Site**

| Test Site # & MHC Technology Type | IST Cycles to Fail | Standard Deviation |
|---|---|---|
| 1 Electroless Copper | 346 | 91.5 |
| 2 Electroless Copper | 338 | 77.8 |
| 3 Electroless Copper | 323 | 104.8 |
| 4 Electroless Copper | 384 | 70 |
| 5 Electroless Copper | 314 | 50 |
| 6 Electroless Copper | 246 | 107 |
| 7 Electroless Copper | 334 | 93.4 |
| 8 Carbon | 344 | 62.5 |
| 9 Carbon | 362 | 80.3 |
| 10 Graphite | 317 | 80 |
| 11 Graphite | 416 | 73.4 |
| 12 Graphite | 313 | 63 |
| 13 Palladium | 439 | 55.2 |
| 14 Palladium | 284 | 62.8 |
| 15 Palladium | 337 | 75.3 |
| 16 Palladium | 171 | 145.7 |
| 17 Palladium | 370 | 122.9 |
| 18 Palladium | 224 | 59.7 |
| 19 Palladium | 467 | 38.4 |
| 20 Palladium | 443 | 52.5 |
| 21 Palladium | 267 | 40.5 |
| 22 Palladium | 232 | 86.6 |
| 23 Non-Formaldehyde Electroless Copper | 214 | 133.3 |
| 24 Non-Formaldehyde Electroless Copper | 261 | 41.6 |
| 25 Conductive Polymer | 289 | 63.1 |

Sample size = 12 coupons from each site.

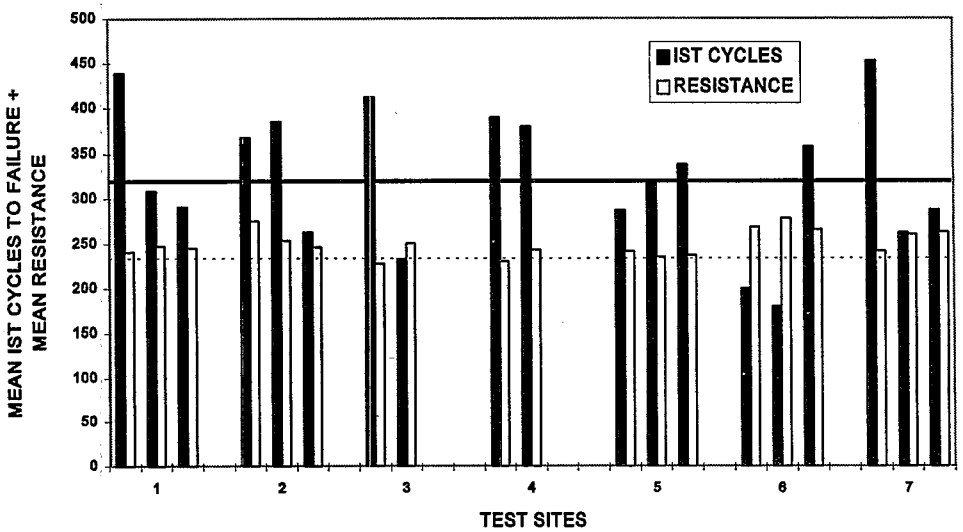
**Table 4.9 Mean IST Cycles to Failure, by MHC Technology**

| MHC Technology | IST Cycles to Fail | Standard Deviation |
|---|---|---|
| Electroless Copper | 327 | 92.5 |
| Carbon | 354 | 71 |
| Conductive Polymer | 289 | 63.1 |
| Graphite | 349 | 85.3 |
| Non-Formaldehyde Electroless Copper | 238 | 99.5 |
| Palladium | 332 | 126 |

High standard deviations indicate that high levels of performance variability exist within and among test sites.

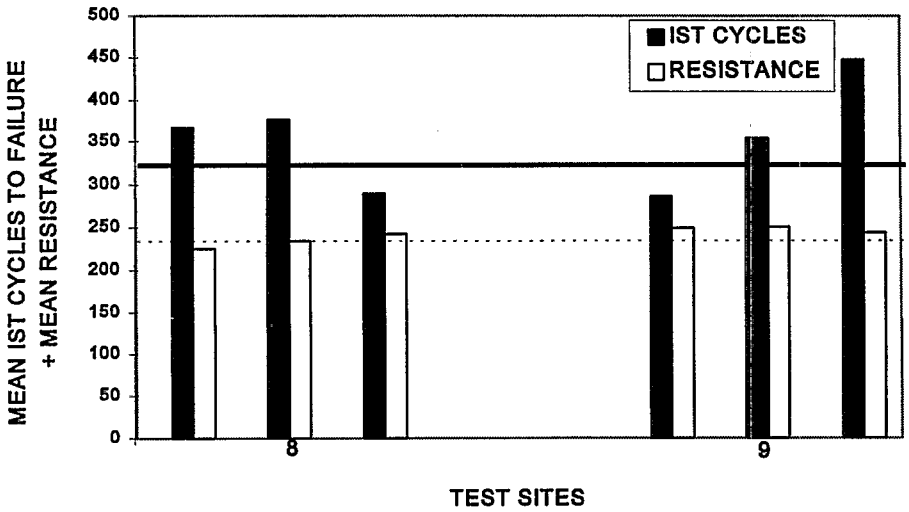
Figures 4.1 through 4.6 identify the IST cycles to failure for each panel and test site for each MHC technology. The two reference lines on each graph identify the mean cycles to failure (solid line) for all 300 coupons tested (324 cycles) and the mean resistance (dotted line) for all coupons measured (241 milliohms). When considering the overall performance of each panel, it is useful to compare the mean resistance of the coupons to the dotted reference line. As mentioned before, each test site was instructed to flash plate 0.0001" of electrolytic copper into the holes. If the sites exceeded this thickness, the total copper thickness would be thicker, lowering the resistance and increasing the performance of the panels. Therefore, panels with lower resistance should be expected to perform better, and vice versa. Although each site was requested to plate 0.0001" of electrolytic copper, the actual range was between 0.00005" and 0.0005".

**Figure 4.1 Electroless Copper - IST Cycles to Fail vs. Resistance**



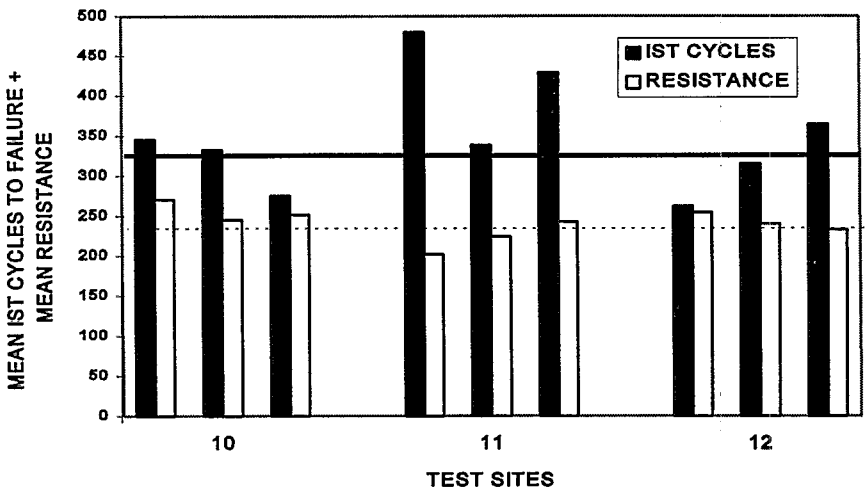

All electroless copper test sites had at least one panel that met or exceeded the mean performance. As shown in Figure 4.1, for the panels that did not achieve the mean performance, it can be seen that the mean resistance column was above the reference line (thinner copper). The exception was Test Site #6, which exhibited a high degree of post separation (see post separation results section below for an explanation of results). As noted previously, Test Site #6 may not have performed to its true capability on the day of the test. Due to a malfunction in the line, the electroless copper bath was controlled by manual lab analysis instead of by the usual single-channel controller.

**Figure 4.2 Carbon - IST Cycles to Fail vs. Resistance**



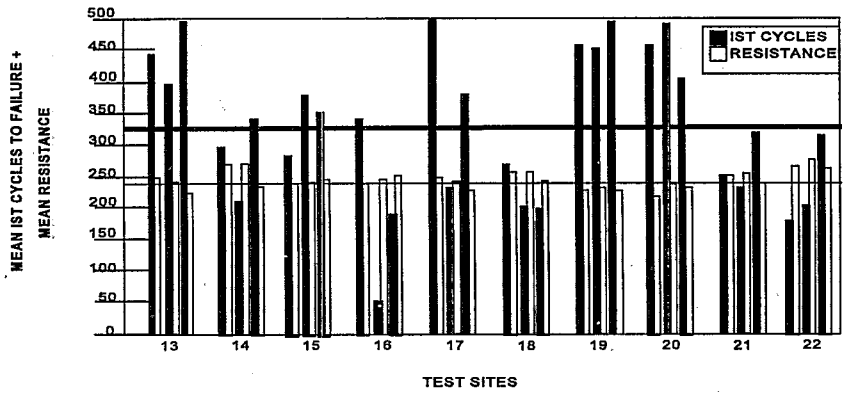

As shown in Figure 4.2, both carbon test sites had at least two panels that met or exceeded the mean performance.

**Figure 4.3 Graphite - IST Cycles to Fail vs. Resistance**



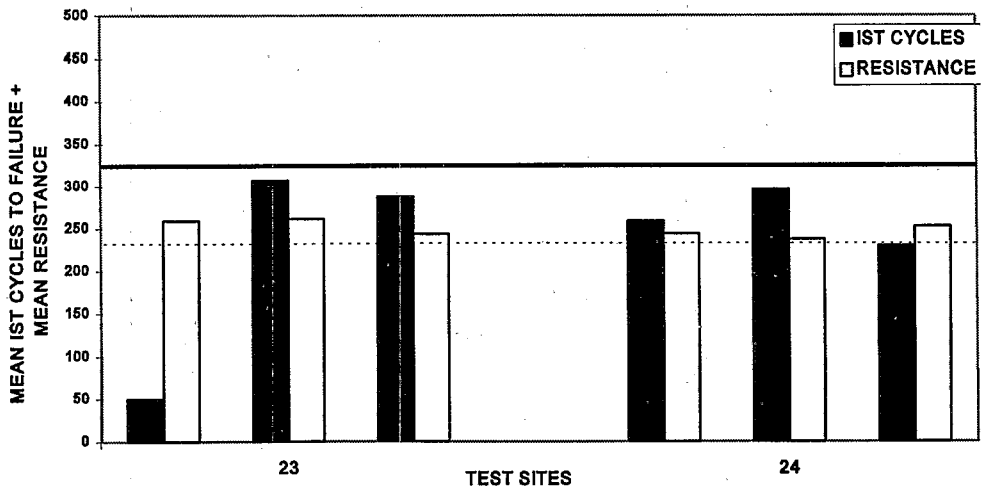

All three graphite test sites had at least one panel that met or exceeded mean performance, as shown in Figure 4.3.

**Figure 4.4 Palladium - IST Cycles to Fail vs. Resistance**



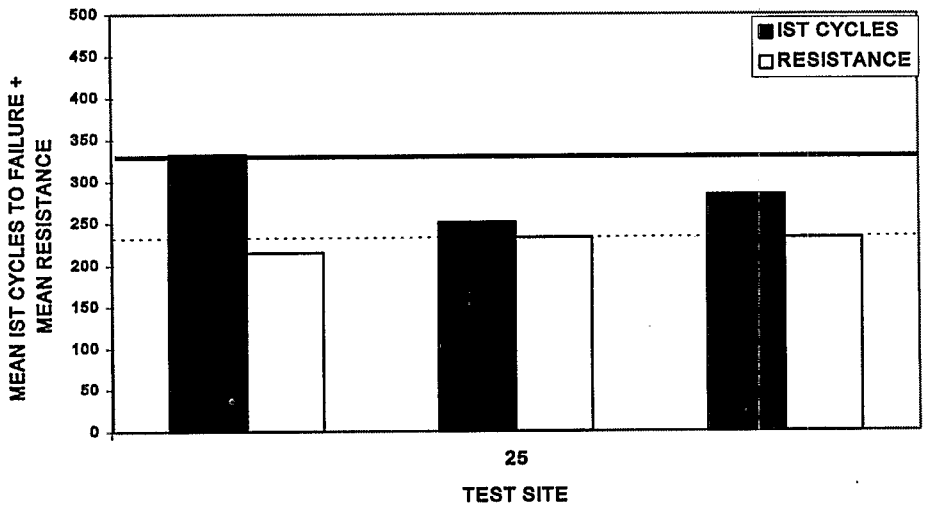

As shown in Figure 4.4, most palladium test sites had at least one panel that met or exceeded the mean performance. Three test sites did not. Those test sites that did not achieve the mean performance exhibited either high resistance or post separation.

**Figure 4.5 Non-Formaldehyde Electroless Copper - IST Cycles to Fail vs. Resistance**




Neither non-formaldehyde electroless copper test site met or exceeded mean performance, as shown in Figure 4.5. Test Site #23 exhibited a high degree of post separation (see post separation results section below for an explanation of results).

**Figure 4.6 Conductive Polymer - IST Cycles to Fail vs. Resistance**




As shown in Figure 4.6, the single conductive polymer test site had one panel that met or exceeded the mean performance.

## Post Separation Testing Results

IST determines post interconnect performance (post separation) simultaneously with the PTH cycles to failure performance. The failure criteria for post separation has not been established. Further work is in progress with the IPC to create an accept/reject criteria. For this study, the IST rejection criteria is based on a 15 milliohm resistance increase derived from the mean resistance degradation measurement for all 300 coupons tested.

A reliable post interconnect should measure minimal resistance degradation throughout the entire IST. Low degrees of degradation (<15 milliohms) are common and relate to the fatigue of the internal copper foils. Resistance increases greater than 50 milliohms were reported as 50 milliohms. This was done in order to avoid skewing results.

The mean resistance degradation of the post interconnect is determined at the time the PTH failed. The readings (in milliohms) for the post interconnect and the standard deviations for each test site (sample size = 12 coupons from each site) and for each MHC technology are shown in Tables 4.10 and 4.11, respectively.

**Table 4.10 Mean Resistance Degradation of Post Interconnect, by Test Site (in milliohms)**

| Test Site # and MHC Technology Type | Post Degradation | Standard Deviation |
|---|---|---|
| 1 Electroless Copper | 13.1 | 3.5 |
| 2 Electroless Copper | 17.2 | 12.9 |
| 3 Electroless Copper | 6.6 | 3.7 |
| 4 Electroless Copper | 6.7 | 2.7 |
| 5 Electroless Copper | 3.8 | 2.4 |
| 6 Electroless Copper | 34.8 | 13.1 |
| 7 Electroless Copper | 4.1 | 4.6 |
| 8 Carbon | 2.8 | 2.9 |
| 9 Carbon | 2 | 2.5 |
| 10 Graphite | 5.2 | 3.9 |
| 11 Graphite | 8 | 8.1 |
| 12 Graphite | 16 | 15 |
| 13 Palladium | 9.5 | 4.7 |
| 14 Palladium | 2.8 | 2.6 |
| 15 Palladium | 7.9 | 7.4 |
| 16 Palladium | 32.2 | 18.1 |
| 17 Palladium | 0.8 | 1.8 |
| 18 Palladium | 7.6 | 6.4 |
| 19 Palladium | 4.7 | 3.3 |
| 20 Palladium | 13.7 | 5.6 |
| 21 Palladium | 40.5 | 11.3 |
| 22 Palladium | 4.5 | 2.6 |
| 23 Non-Formaldehyde Electroless Copper | 47.9 | 7.2 |
| 24 Non-Formaldehyde Electroless Copper | 4.2 | 1.9 |
| 25 Conductive Polymer | 2.8 | 1.8 |

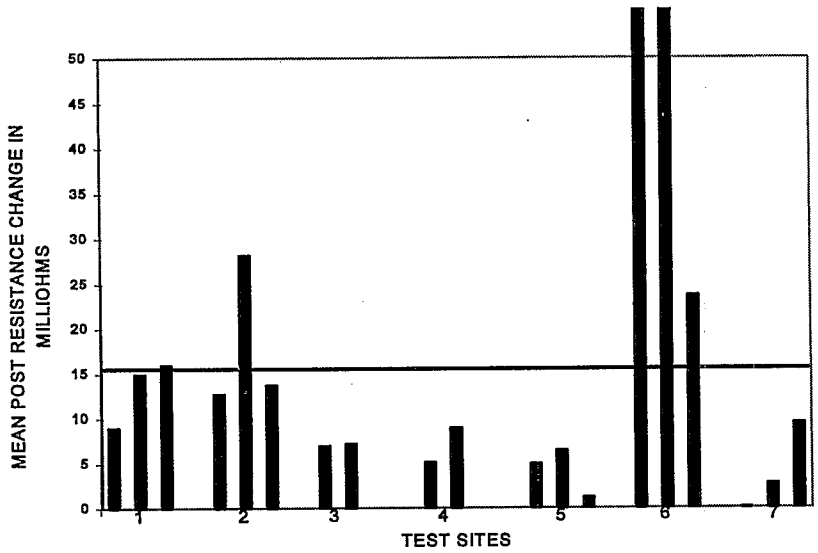
**Table 4.11 Mean Resistance Degradation of Post Interconnect, by MHC Technology**

| MHC Technology Type | Post Degradation | Standard Deviation |
|---|---|---|
| Electroless Copper | 12.3 | 12.6 |
| Carbon | 2.4 | 2.7 |
| Conductive Polymer | 2.75 | 1.8 |
| Graphite | 9.7 | 10.8 |
| Non-Formaldehyde Electroless Copper | 26 | 22.9 |
| Palladium | 12.4 | 14.3 |

High standard deviations indicate that high levels of variability exist within and among test sites and within an MHC technology.

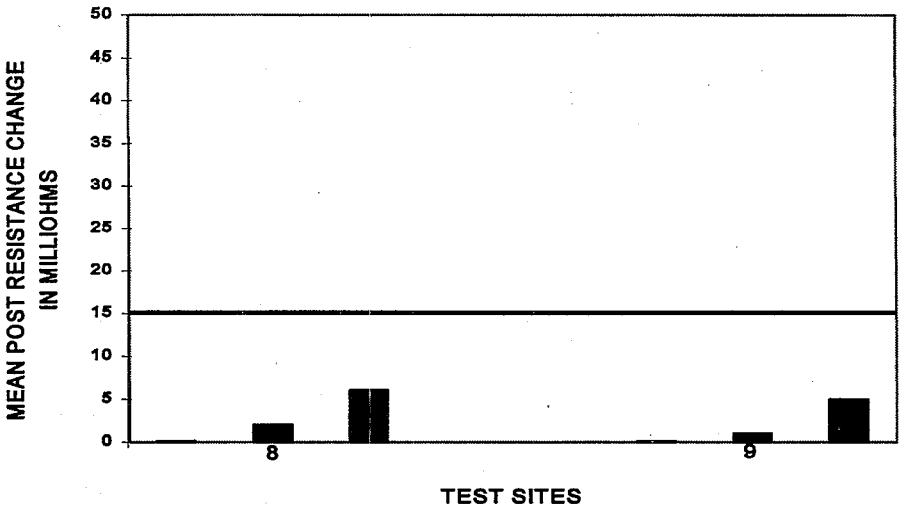
Figures 4.7 through 4.12 identify the mean (average of four coupons per panel) IST post resistance degradation results. The reference line on each graph identifies the mean resistance degradation measurement for all 300 coupons tested (15 milliohms). If the mean resistance degradation column is above the reference line, the panel had coupons that exhibited post separation. The post resistance change was the value recorded at the point where the PTH (barrel) failed.

**Figure 4.7 Electroless Copper - Post Resistance Degradation**



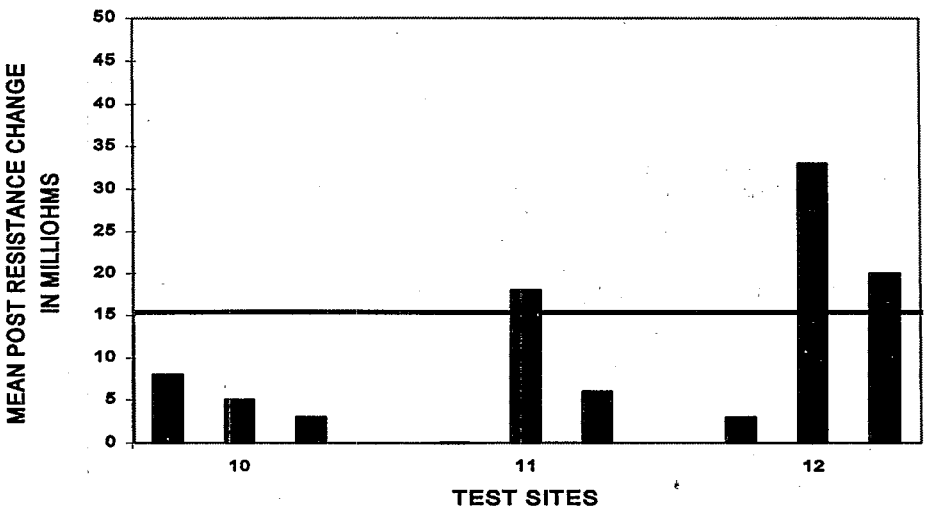

As shown in Figure 4.7, two of the seven electroless copper test sites had at least one panel that exhibited post separation. All three panels from Test Site #6 clearly exhibited gross post separation. Both test methods for post separation failed all panels from Test Site #6. As noted previously, Test Site #6 may not have performed to its true capability on the day of the test. Due to a malfunction in the line, the electroless copper bath was controlled by manual lab analysis instead of by the usual single-channel controller.

**Figure 4.8 Carbon - Post Resistance Degradation**



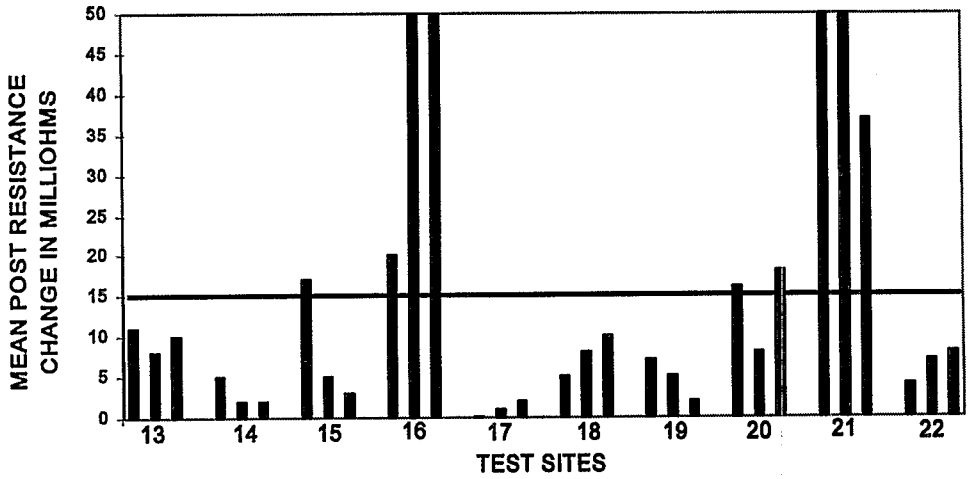

No post separation was detected on any carbon panels, as shown in Figure 4.8.

**Figure 4.9 Graphite - Post Resistance Degradation**



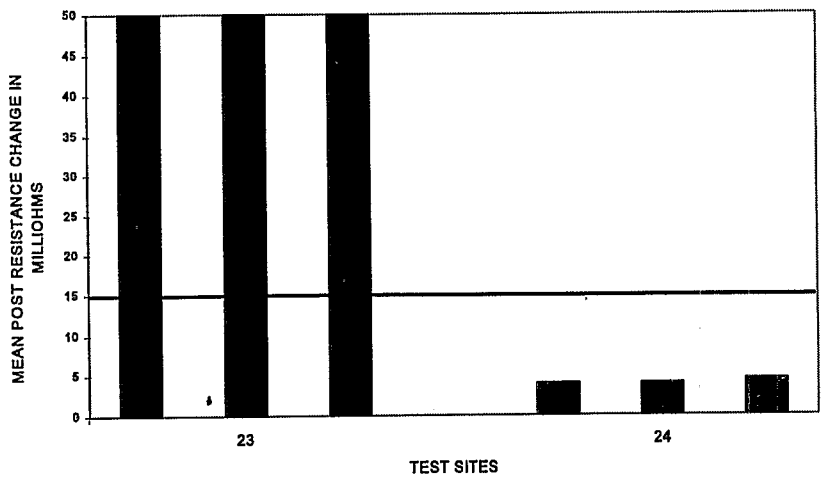

As shown in Figure 4.9, two of the three graphite test sites had at least one panel that exhibited post separation.

**Figure 4.10 Palladium - Post Resistance Degradation**



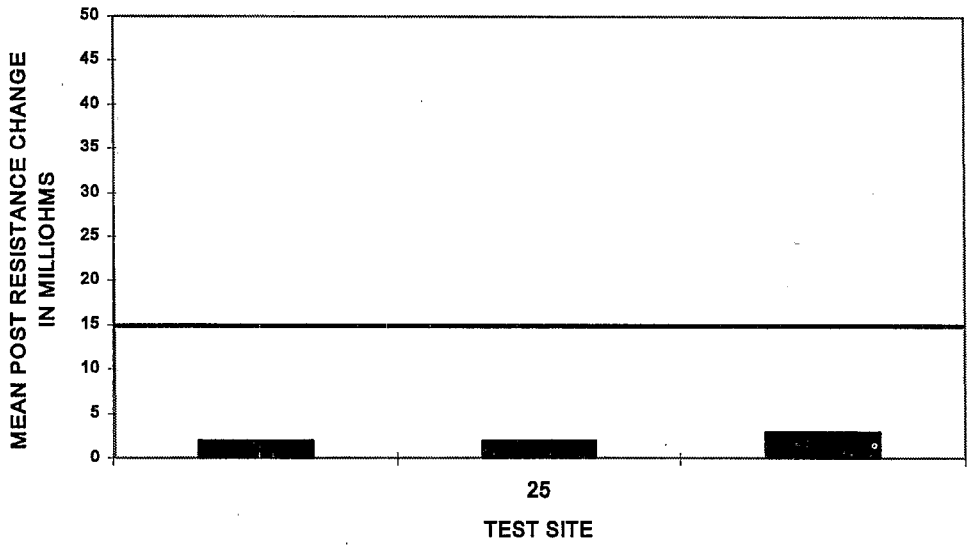

As shown in Figure 4.10, four of the ten palladium test sites had at least one panel that exhibited post separation. Test Site #16 and Test Site #21 clearly exhibited gross post separation.

**Figure 4.11 Non-Formaldehyde Electroless Copper - Post Resistance Degradation**




As shown in Figure 4.11, all three panels for non-formaldehyde electroless copper Test Site #23 clearly exhibited gross post separation.

**Figure 4.12 Conductive Polymer - Post Resistance Degradation**




No post separation was detected on any conductive polymer panels, as shown in Figure 4.12.

### 4.1.6 Comparison of Microsection and IST Test Results

Microsection and IST were run independently, and test results were not shared until both sets of data were completed and delivered to EPA. To illustrate the consistency of the test results, Table 4.12 identifies both test methods and their results for post separation detection.

"Y" or "N" (yes or no) denote whether post separation was detected on any coupon or panel from each test site. The "panels affected" column refers to how many of the panels within each test site exhibited post separation. Test Site #17 was the only site with post separation found in the microsection but not on IST.

Post separation results indicated percentages of post separation that were unexpected by many members of the industry. It was apparent that all MHC technologies, including electroless copper, are susceptible to this type of failure. The results of this study further suggest that post separation may occur in different degrees. The level of post separation may play a role in determining product performance; however, the determination of levels of post separation remains to be discussed and confirmed by the PWB industry.

**Table 4.12 IST/Microsection Data Correlation**

| Test Site # | Microsection | Panels Affected | IST | Panels Affected |
|---|---|---|---|---|
| 1 | N | 0 | N | 0 |
| 2 | Y | 3 | Y | 3 |
| 3 | N | 0 | N | 0 |
| 4 | N | 0 | N | 0 |
| 5 | N | 0 | N | 0 |
| 6 | Y | 3 | Y | 3 |
| 7 | N | 0 | N | 0 |
| 8 | N | 0 | N | 0 |
| 9 | N | 0 | N | 0 |
| 10 | N | 0 | N | 0 |
| 11 | Y | 2 | Y | 1 |
| 12 | Y | 3 | Y | 2 |
| 13 | N | 0 | N | 0 |
| 14 | N | 0 | N | 0 |
| 15 | Y | 1 | Y | 1 |
| 16 | Y | 3 | Y | 3 |
| 17 | Y | 1 | N | 0 |
| 18 | Y | 2 | Y | 2 |
| 19 | N | 0 | N | 0 |
| 20 | Y | 3 | Y | 2 |
| 21 | Y | 3 | Y | 3 |
| 22 | N | 0 | N | 0 |
| 23 | Y | 3 | Y | 3 |
| 24 | N | 0 | N | 0 |
| 25 | N | 0 | N | 0 |

## 4.2 COST ANALYSIS

Operating an efficient and cost-effective manufacturing process with strict control of material and production costs is the goal of every successful company. Fueled by consumer demand for smaller and lighter electronics, rapid and continuous advances in circuit technology make this goal a necessity for PWB manufacturers attempting to compete in today's global marketplace. The higher aspect-ratio holes and tighter circuit patterns on current PWBs are forcing manufacturers to continually evaluate and eventually replace aging manufacturing processes that are unable to keep up with the ever-increasing technology threshold. When coupled with the typically slim profit margins of PWB manufacturers, these process changes represent a major capital investment to a company and emphasize the importance of selecting an efficient, cost-effective process that will allow the company to remain competitive. As a result, manufacturers are seeking comprehensive and more detailed cost data before investing in alternative processes.

This section presents a comparative cost analysis of the MHC technologies. Costs were developed for each technology and equipment configuration (vertical, immersion-type equipment, or horizontal, conveyorized equipment) for which data were available from the IPC Workplace Practices Questionnaire and Performance Demonstration. Table 4.13 presents the processes (alternatives and equipment configurations) evaluated.

**Table 4.13 MHC Processes Evaluated in the Cost Analysis**

| MHC Alternative | Non-Conveyorized | Conveyorized |
|---|---|---|
| Electroless Copper | ✔ | ✔ |
| Carbon | | ✔ |
| Conductive Polymer | | ✔ |
| Graphite | | ✔ |
| Non-Formaldehyde Electroless Copper | ✔ | |
| Organic-Palladium | ✔ | ✔ |
| Tin-Palladium | ✔ | ✔ |

Costs were analyzed using a cost model developed by the University of Tennessee Department of Industrial Engineering. The model employs generic process steps and functional groups (see Section 2.1, Chemistry and Process Description of MHC Technologies) and typical bath sequences (see Section 3.1, Source Release Assessment) for each process alternative. Figure 4.13 presents the generic process steps and typical bath sequences. To develop comparative costs on a $/surface square foot (ssf) basis, the cost model was formulated to calculate the cost of performing the MHC function on a job consisting of 350,000 ssf. This is the average annual throughput for facilities in the IPC Workplace Practices Questionnaire database. The cost for each process is compared to a generic non-conveyorized electroless copper process, defined here as the baseline process.

Figure 4.13 Generic Process Steps and Typical Bath Sequences of MHC Technologies

The overall objective of this analysis was to determine the comparative costs of the MHC technologies using a cost model that adheres to fundamental principles of cost analysis. Other objectives were to make the analysis flexible and to consider environmental costs. The cost model was designed to estimate the comparative costs of fully operational MHC process lines. It does not estimate start-up costs for a facility switching to an alternative MHC technology or the cost of other process changes that may be required to implement a new MHC technology. Section 4.2.1 gives an overview of the cost methodology. Section 4.2.2 presents simulation model results. Section 4.2.3 describes details of the cost methodology and presents sample cost calculations. Section 4.2.4 contains analysis results, while Section 4.2.5 presents a sensitivity analysis of the results. Section 4.2.6 presents conclusions.

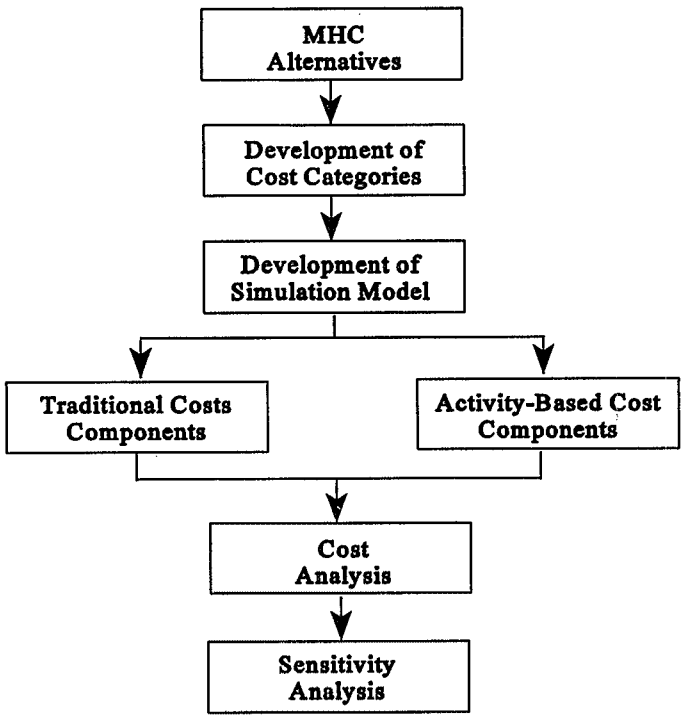
### 4.2.1 Overview of the Cost Methodology

The costs of the MHC technologies were developed by identifying the steps in each process, breaking each step down into its cost components, and determining the cost of each component. Component costs were determined utilizing traditional costing mechanisms, computer simulation, and ABC. Computer simulation was used to replicate each of the MHC processes to determine the time required to complete the specified job and other job-specific metrics. ABC is a cost accounting method that allocates indirect or overhead costs to the products or processes that actually incur those costs. Activity-based costs are determined by developing bills of activities (BOAs) for tasks essential to the process. A BOA is a listing of the component activities involved in the performance of a certain task, together with the number of times each component activity is performed. The BOA determines the cost of a task by considering the sequence of actions and the resources utilized while performing that task.

**Framework for the Cost Formulation**

Figure 4.14 presents the hybrid cost formulation framework used in this analysis. The first step in the framework was to develop or define the alternatives to be evaluated. The generic process descriptions, chemical baths, typical bath sequences, and equipment configurations were defined in Table 4.13 and Figure 4.13. This information was used to identify critical variables and cost categories that needed to be accounted for in the cost analysis. Cost categories were analyzed to identify the data required to calculate the costs (i.e., unit costs, utilization or consumption rates, criteria for performing an activity, such as chemical bath replacement, the number of times an activity is performed, etc.). For each process, a computer simulation was then developed using ARENA® computer simulation software and information derived from the cost components. The simulations were designed to model a MHC manufacturing job consisting of 350,000 ssf.

**Figure 4.14 Hybrid Cost Formulation Framework**




Simulation modeling provides a number of advantages to the cost analysis, including the following:

- Simulation modeling can replicate a production run on the computer screen, allowing an analyst to observe a process when the actual process does not exist. In this case, the generic MHC technologies, as they are defined in Figure 4.13, may not exist within any one facility.
- Simulation allows for process-based modifications and variations, resulting in inherent flexibility within the system. Simulation models can be designed to vary the sequence of operations, add or delete operations, or change process times associated with operations, materials flows, and other variables.
- Data gathered from PWB manufacturers, chemical suppliers, and the Performance Demonstration have some data gaps and inconsistencies. However, these data must be aggregated to develop comparative costs of the generic MHC alternatives. Thus, data collected from one or more facilities may not fully represent a generic MHC alternative or group of alternatives. Process simulation based on fundamental assumptions and data helps clear up data inconsistencies and fill data gaps.
- Simulation enables one to study the sensitivity of critical performance measures to changes in underlying input variables. Constant input variables may be modified in the sensitivity analysis to determine the uncertainty (in terms of probability distributions) associated with these input variables.

Direct results of the simulation model and results derived from simulation outputs include the following:

- The amount of time the MHC line operates to produce the job.
- The number of times an activity is performed during the course of the job.
- Consumption rates (e.g., water, energy, and chemical consumption).
- Production rates (e.g., wastewater generation).

Simulation results were combined with traditional cost components to adjust these costs for the specified job. An example of this is the determination of equipment cost. Simulation results were used to calculate a utilization ratio (UR), defined as the amount of time in days required to produce 350,000 ssf divided by one operating year (defined as 250 days). Annualized equipment costs were determined utilizing industry sources for equipment price and depreciation guidelines from the Internal Revenue Service. These costs were multiplied by the UR to determine the equipment costs for the job being evaluated.

Activity-based costs were determined by combining simulation results for the frequency of activities with the cost of an activity developed on a BOA. For example, the activity costs of replacing a particular bath were determined by developing a BOA, developing costs for each activity on the BOA, and multiplying these costs by the number of bath replacements required to complete a job of 350,000 ssf. In this manner, the overall analysis combines traditional costs with simulation outputs and activity-based costs. The effects of critical variables on the overall costs were then evaluated using sensitivity analysis.

**Cost Categories**

Table 4.14 summarizes the cost components considered in this analysis, gives a brief description of each cost component and key assumptions, and lists the primary sources of data for determining the costs. Section 4.2.3 gives a more detailed accounting of the cost components, including sample cost calculations for each component.

In addition to traditional costs, such as capital, production, and maintenance costs, the cost formulation identifies and captures some environmental costs associated with the alternatives. In this regard, both simulation and ABC assist in analyzing the impact of the MHC alternatives on the environment. Specifically, the amounts of energy and water consumed as well as the amount of wastewater generated are determined for each MHC alternative. Environmental costs that could not be quantified include wastewater treatment and solid waste disposal costs. Also, the costs of defective boards and the consequent waste of resources were not quantified. These costs are discussed in more detail, below.

**Table 4.14 Cost Components**

| Cost Category | Component | Description of Cost Component | Sources of Cost Data |
|---|---|---|---|
| Capital Cost | Primary Equipment | Annualized cost of equipment with throughput capacity of 100 panels/hr times UR[a]; assumes 10 year equipment life and straight-line depreciation. | Vendor quote for equipment cost; time to complete job from simulation. |
| | Installation | Annualized cost of delivering and installing equipment times UR[a]; assumes 10 year equipment life and straight-line depreciation. | Vendor quote for installation costs; time to complete job from simulation. |
| | Facility | Annualized cost of floor space required to operate MHC equipment times UR[a]; assumes 25 year facility life and straight-line depreciation. | Floor space requirements from Workplace Practices Survey; unit cost for industrial floor space from published sources. |
| Material Cost | Process Chemicals | Costs of chemicals used in initial bath setup and to replace spent process baths. | Vendor quotes for chemical product cost; bath sizes from Workplace Practices Survey; bath replacement criteria from supplier data; number of bath replacements required for job from simulation. |
| Utility Cost | Water | Water consumption costs based on number of rinse tanks per process line; daily water usage per tank, and days to complete job. | Number of rinse tanks and daily water usage per tank from Section 5.1, Resource Conservation; days to complete job from simulation. |
| | Electricity | Electricity costs based on daily electricity consumption by MHC equipment and days to complete job. | Daily electricity consumption from Section 5.2, Energy Impacts; days to complete job from simulation. |
| | Natural Gas | Natural gas consumption based on daily natural gas consumption from drying ovens (carbon and graphite processes only) and days to complete job. | Daily natural gas consumption from Section 5.2, Energy Impacts; days to complete job from simulation. |
| Wastewater Cost | POTW Permit | Cost for permit to discharge wastewater to publicly-owned treatment works (POTW). | Not quantified; assumed to be the same for all alternatives. |
| | Wastewater Pretreatment Cost | Cost to pretreat wastewater prior to discharge to POTW. | Not quantified; pretreatment costs are expected to differ significantly among the alternatives, but insufficient data were available to reliably estimate these costs. |
| | Wastewater Discharge Costs | Fees for wastewater discharge assessed by local utility. | Quantity of wastewater discharged assumed equal to water usage; discharge fees based on fees charged by Knoxville, Tennessee Utility Board (KUB). |

| Cost Category | Component | Description of Cost Component | Sources of Cost Data |
|---|---|---|---|
| Production Cost | Labor | Labor costs for line operator, excluding labor costs for maintenance activities (included under maintenance costs). Assumes one line operator per day per conveyorized process, 1.1 line operators per day per non-conveyorized process. | Number of line operators based on Workplace Practices Survey data and site visits; days to produce job from simulation; labor rate = $10.22/hr based on published data. |
| | Transportation of Materials | Cost to transport chemicals required for bath replacement from storage to process line. | Cost of transporting materials from BOA; number of bath replacements required from simulation. |
| Maintenance Cost | Bath Clean-up | Labor and materials (excluding replacement chemicals) costs to clean up a chemical tank during bath replacement. | Cost to clean up tank from BOA; number of bath cleanups (replacements) required from simulation. |
| | Bath Setup | Labor and equipment costs to set up a chemical tank after bath replacement. | Cost to set up bath from BOA; number of bath setups required from simulation. |
| | Sampling and Analysis | Labor and materials costs for sampling and analysis of chemical baths. | Assumes analytical work done in-house. Cost for one activity from BOA; annual number of samples from Workplace Practices Survey adjusted using UR[a]. |
| | Filter Replacement | Labor costs for replacing bath filters. | Labor cost for one activity from BOA; annual number of filters replaced from Workplace Practices Survey adjusted using UR[a]. |
| Waste Disposal Cost | Sludge Disposal | Disposal cost to recycle or dispose of sludge from wastewater treatment. | Not quantified; sludge disposal costs are expected to differ significantly among the alternatives, but insufficient data were available to reliably estimate these costs. Factors affecting sludge disposal cost include the characteristics of the sludge (i.e., metal content, percent solids, waste classification, etc.) and the amount of sludge generated. |
| | Filter Disposal | Disposal cost to recycle or dispose of bath filters. | Not quantified; filter disposal costs are expected to differ significantly among the alternatives, but insufficient data were available to reliably estimate these costs. Factors affecting filter disposal cost include the waste classification of the filter, the size (weight and volume) of the filter, and the number of waste filters generated. |
| Quality Cost | Defective Boards | Costs of defective boards due to failure of MHC process lines to adequately make holes conductive. | Not quantified; assumed equal among the alternatives. Performance Demonstration showed that all alternatives can work at least as well as the baseline process as long as they are operated according to supplier specifications. |

[a] UR = utilization ratio = the time in days required to process 350,000 ssf ÷ one operating year (250 days).

**Wastewater Treatment and Sludge Disposal Costs.** PWB manufacturing consists of a number of process steps (see Section 1.2.3 for an overview of rigid multi-layer PWB manufacturing). In addition to the MHC process line, these steps include electroplating operations and other steps which consume large quantities of rinse water and, consequently, generate large quantities of wastewater. Most PWB manufacturers combine the effluents from various process lines into one wastewater stream which is treated on-site in a continuous process prior to discharge. As part of the *Pollution Prevention and Control Survey* (EPA, 1995a), PWB manufacturers were asked to provide the following about their on-site wastewater treatment facility:

- A process flow diagram for wastewater treatment.
- The quantity of sludge generated from wastewater treatment.
- The percent solids of the sludge.
- The costs of on-site wastewater treatment.
- The method and costs of sludge recycle and disposal.

Capital costs for wastewater treatment ranged from $1.2 million for a system purchased in 1980 with a capacity of 135 gallons per minute (gpm) to $4,000 for a system purchased in 1987 with a capacity of nine gpm. Costs for operating an on-site wastewater treatment system were as high as 3.1 percent of total annual sales. The median cost for wastewater treatment operation was 0.83 percent and the average was 1.02 percent of annual sales.

Wastewater treatment sludges from PWB electroplating operations are classified as an F006 hazardous waste under the Resources Conservation and Recovery Act (RCRA); most facilities combine effluents from the electroplating line with other process wastewaters. Eighty-eight percent of respondents to the Survey reported that wastewater treatment sludges are sent to an off-site recycling facility to recover the metals. The average and median costs for off-site recovery of sludge were $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. In some cases, respondents whose sludge had a higher solids content also reported lower costs; dewatered sludge has a higher recovery value.

Eighty-six percent of Survey respondents used an electroless copper MHC process, 14 percent used a palladium-based process (the Survey did not distinguish between tin- and organic-palladium processes), and one respondent used a graphite process. None of the other MHC alternatives were represented in the Survey.

The IPC Workplace Practices Questionnaire attempted to characterize costs by collecting information about the percent the MHC line contributes to overall wastewater and sludge generation rates. However, most manufacturers were unable to provide this information and the data that were reported were of variable to poor quality.

Since the MHC line is only one of several process lines that discharge effluent to wastewater treatment and because little or no information is available on the contribution of the MHC line to overall wastewater effluents, on-site wastewater treatment and sludge disposal costs could not be reliably estimated. However, costs of wastewater treatment and sludge disposal are expected to differ significantly among the alternatives. For example, the presence of the chelator

EDTA in electroless copper wastewater discharges makes these effluents more difficult to treat. However, complexing agents, such as the ammonia found in other PWB manufacturing steps, also adversely affect the treatability of wastewater.

**Other Solid Waste Disposal Costs.** Two other types of solid wastes were identified that could have significantly different waste disposal costs among the alternatives: filter disposal cost and defective boards disposal costs. Table 4.15 presents the number of filters that would be replaced in each process during a job of 350,000 ssf. These data are based on data from the IPC Workplace Practices Questionnaire and a UR calculated for each process from simulation results. (Simulation results are discussed further in Section 4.2.2.) While these results illustrate that the number of waste filters generated by the alternatives differ significantly, no information is available on the characteristics of the filters used in alternative processes. For example, the volume or mass of the filters and waste classification of the filters (hazardous or non-hazardous) would significantly affect the unit cost for disposal. Therefore, filter disposal costs were not estimated.

**Table 4.15 Number of Filter Replacements by MHC Process**

| MHC Process | Filter Replacements per Year[a] | Filter Replacements per Job[b] |
|---|---|---|
| Electroless Copper, non-conveyorized (BASELINE) | 100 | 160 |
| Electroless Copper, conveyorized | 100 | 35 |
| Carbon, conveyorized | 20 | 7 |
| Graphite, conveyorized | 103 | 52 |
| Conductive Polymer, conveyorized | 74 | 21 |
| Non-Formaldehyde Electroless Copper, non-conveyorized | 17 | 12 |
| Organic-Palladium, non-conveyorized | 50 | 22 |
| Organic-Palladium, conveyorized | 50 | 16 |
| Tin-Palladium, non-conveyorized | 74 | 35 |
| Tin-Palladium, conveyorized | 74 | 19 |

[a] 90th percentile data based on Workplace Practices Survey data. Data not adjusted for throughput or to account for differing maintenance policies at individual PWB manufacturing facilities.
[b] Based on simulation results for a job of 350,000 ssf.

The number of defective boards produced by an alternative has significance not only from the standpoint of quality costs, but also from the standpoint of waste disposal costs. Clearly, a higher defect rate leads to higher scrap and, therefore, waste of resources. However, the Performance Demonstration showed that each of the alternatives can perform as well as the electroless copper process if operated according to specifications. Thus, for the purposes of this analysis, no differences would be expected in the defect rate or associated costs of the alternatives.

## Simulation Model Assumptions and Input Values

Appendix G presents a graphic representation of the simulation models developed for each of the MHC alternatives. The assumptions used to develop the simulation models and model input values are discussed below.

**Assumptions.** Several assumptions used in the simulation model are based on the characteristics of a model facility presented in the Source Release Assessment and Exposure Assessment (Sections 3.1 and 3.2, respectively). Assumptions include the following:

- The facility operates an MHC line 250 days/year, one shift/day. Many facilities operate two shifts, but the Exposure Assessment and this analysis use first shift data as representative. This assumption could tend to underestimate labor costs for companies that pay higher rates to second shift workers. Or it could tend to overestimate equipment costs for a company running two shifts and using equipment more efficiently. However, since this assumption is used consistently across alternatives, the effects on the comparative cost results are expected to be minor.
- The MHC process line operates an average of 6.8 hrs/shift.
- The MHC line is down at least 1.2 hours per day for start-up time and for maintenance, including lubricating of equipment, sampling of baths, and filter replacement.
- Additional down time occurs when the MHC line is shut down to replace a spent or contaminated bath.
- PWB panels that have been processed up to the MHC step are available whenever the MHC process line is ready for panels.
- If a chemical bath is replaced at the end of the day, such that the amount of time required to replace the bath exceeds the time remaining in the shift hours, employees will stay after hours and have the bath ready by the beginning of the next shift.
- The entire MHC process line is shut down whenever a bath requires replacing, but partially processed racks or panels are finished before the line is shut down.
- The MHC process only shuts down at the end of a shift and for bath replacement.
- The process is empty of all panels or racks at the end of each shift and starts the process empty at the beginning of a shift.

Further simulation assumptions have to be defined separately for conveyorized and non-conveyorized systems. Conveyorized MHC process assumptions are as follows:

- The size of a panel is 17.7" x 22.9" (from IPC Workplace Practices Questionnaire data for conveyorized processes).
- Panels are placed on the conveyor whenever space on the conveyor is available, and each panel requires 18" (including space between panels).
- Conveyor speed is constant, thus, the volume (gallons) of chemicals in a bath varies by bath type (i.e., microetch, conditioner, etc.) and with the length of the process step (e.g., bath or rinse tank) to provide the necessary contact time (see Table 4.16 for bath volumes).
- The conveyor speed, cycle time, and process down time are critical factors that determine the time to complete a job.

**Table 4.16 Bath Volumes Used for Conveyorized Processes**

| Chemical Bath | Bath Volume by MHC Alternative (gallons) | | | | | |
|---|---|---|---|---|---|---|
| | Electroless Copper | Carbon | Conductive Polymer | Graphite | Organic-Palladium | Tin-Palladium |
| Cleaner/Conditioner | **65** | NA | **65** | **65** | NA | **65** |
| Cleaner | NA | **44** | NA | NA | **44** | NA |
| Carbon | NA | **128** | NA | NA | NA | NA |
| Graphite | NA | NA | NA | **37** | NA | NA |
| Conditioner | NA | **56** | NA | NA | **56** | NA |
| Polymer | NA | NA | **26** | NA | NA | NA |
| Microetch | **64** | **64** | **64** | **64** | **64** | **64** |
| Predip | **50** | NA | NA | NA | **50** | **59** |
| Catalyst | **139** | NA | **139** | NA | NA | **139** |
| Accelerator | **80** | NA | NA | NA | NA | **80** |
| Conductor | NA | NA | NA | NA | **108** | NA |
| Electroless Copper | **185** | NA | NA | NA | NA | NA |
| Post Dip | NA | NA | NA | NA | **45** | NA |
| Acid Dip | **79** | NA | NA | NA | **79** | **79** |
| Anti-Tarnish | **39** | NA | NA | NA | NA | NA |

NA: Not Applicable.

Non-conveyorized MHC process assumptions are as follows:

- The average volume of a chemical bath is 75 gallons (from IPC Workplace Practices Questionnaire data for non-conveyorized processes).
- Only one rack of panels can be placed in a bath at any one time.
- A rack contains 20 panels (based on IPC Workplace Practices Questionnaire data, including the dimensions of a bath, the size of a panel, and the average distance between panels in a rack).
- The size of a panel is 16.2" x 21.5" to give 96.8 ssf per rack.
- The frequency at which racks are entered into the process is dependent upon the bottleneck or rate limiting step.
- The duration of the rate limiting step, cycle time, and process down time are critical factors that determine the time to complete a job.

**Inputs Values.** Input values for the critical factors identified above (cycle time, down time, and conveyor speed for conveyorized processes, and cycle time, down time, and duration of rate limiting step for non-conveyorized processes) were developed from IPC Workplace Practices Questionnaire data and Product Data Sheets prepared by suppliers which describe how to mix and maintain chemical baths. Tables 4.17 and 4.18 present time-related inputs to the simulation models for non-conveyorized and conveyorized processes, respectively.

**Table 4.17 Time-Related Input Values for Non-Conveyorized Processes[a]**

| Non-Conveyorized MHC Alternative | Time Required to Replace a Bath[b] (minutes) | Rate Limiting Bath | Time in Rate Limiting Bath[c] (minutes) | Process Cycle Time[c] (minutes) |
|---|---|---|---|---|
| Electroless Copper | 180 | Electroless Copper | 34 | 48 |
| Non-Formaldehyde Electroless Copper | 30 | Electroless Copper | 16 | 51 |
| Organic-Palladium | 180 | Accelerator | 9.2 | 30 |
| Tin-Palladium | 108 | Conductor | 5.3 | 52 |

[a] Values are averages or 90th percentile data from the IPC Workplace Practices Questionnaire and may represent chemical products from more than one supplier. For example, five suppliers of electroless copper chemical products participated in the project. Input values may underestimate or overestimate those of any one facility, depending on factors such as individual operating procedures, the chemical or equipment supplier, and the chemical product used.
[b] 90th percentile value used in the Exposure Assessment from IPC Workplace Practices Questionnaire data (see Section 3.2). Used to calculate down time.
[c] Average values from the IPC Workplace Practices Questionnaire.

**Table 4.18 Time-Related Input Values for Conveyorized Processes[a]**

| Conveyorized MHC Alternative | Time Required to Replace a Bath[b] (minutes) | Length of Conveyor[c] (feet) | Process Cycle Time[c] (minutes) | Conveyor Speed[d] (ft/min) |
|---|---|---|---|---|
| Electroless Copper | 180 | 71 | 15 | 4.7 |
| Carbon | 180 | 31 | 13 | 2.4 |
| Conductive Polymer | 180 | 34 | 8.0 | 4.3 |
| Graphite | 219 | 27 | 7.8 | 3.5 |
| Organic-Palladium | 108 | 50 | 15 | 3.3 |
| Tin-Palladium | 180 | 47 | 8.6 | 5.5 |

[a] Values are averages or 90th percentile data from the IPC Workplace Practices Questionnaire and may represent chemical products from more than one supplier. For example, five suppliers of electroless copper chemical products participated in the project. Input values may underestimate or overestimate those of any one facility, depending on factors such as individual operating procedures, the chemical or equipment supplier, and the chemical product used.
[b] 90th percentile value used in the Exposure Assessment from IPC Workplace Practices Questionnaire data (see Section 3.2). Used to calculate down time.
[c] Average values from IPC Workplace Practices Questionnaire.
[d] Conveyor speed = length of conveyor ÷ process cycle time.

The input values for the time required to replace a bath time (in Tables 4.17 and 4.18) are used together with bath replacement criteria in the calculation of down time. Suppliers provide instructions with their products (called Product Data Sheets for the purposes of this project) that describe when a bath should be replaced because it is expected to be spent or too contaminated to be used. These replacement criteria are usually given in one of three forms:

- As a bath capacity in units of ssf per gallon of bath.
- As a concentration-based criterion that specifies an upper concentration limit for contaminants in the bath, such as grams of copper per liter in the microetch bath.
- As elapsed time since bath creation.

Bath replacement criteria submitted by suppliers were supplemented with IPC Workplace Practices Questionnaire data and reviewed to determine average criteria for use in the simulation models. Criteria in units of ssf/gallon were preferred because these can be correlated directly to the volume of a bath. Once criteria in ssf/gallon were determined, these were converted to units of racks per bath replacement for non-conveyorized processes and panels per bath replacement for conveyorized processes. The converted values were used as inputs to the simulation models. As an example, Table 4.19 presents bath replacement criteria used to calculate input values for electroless copper processes. Appendix G presents the different bath replacement criteria recommended by chemical suppliers, and the input values used in this analysis.

**Table 4.19 Bath Replacement Criteria for Electroless Copper Processes**

| Chemical Bath | Bath Replacement Criteria[a] (ssf/gal) |
|---|---|
| Cleaner/Conditioner | 510 |
| Microetch | 250 |
| Predip | 540 |
| Catalyst | Replace once per year |
| Accelerator | 280 |
| Electroless Copper | 430 |
| Acid Dip | 675 |
| Anti-Tarnish | 325 |

[a] Values were selected from data provided by more than one electroless copper chemical supplier. To convert to units of racks per bath replacement for non-conveyorized processes, multiply by 75 gallons (the average bath size) and divide by 96.8 ssf (ssf per rack). To convert to units of panels per bath replacement for conveyorized processes, multiply by the bath size in gallons and divide by 5.6 ssf/panel.

## Activity-Based Costing (ABC)

As discussed previously, ABC is a method of allocating indirect or overhead costs to the products or processes that actually incur those costs. Activity-based costs are determined by developing BOAs for critical tasks. A BOA is a listing of the component activities involved in the performance of a certain task, together with the number of times each component activity is performed. The BOA determines the cost of a task by considering the sequence of actions and the resources utilized while performing that task. In this analysis, the costs of critical tasks determined by a BOA are combined with the number of times a critical task is performed, derived from simulation results to determine the total costs of that activity.

BOAs were developed for the following critical tasks performed within MHC alternatives:

- Chemical transport from storage to the MHC process.
- Tank cleanup.
- Bath setup.
- Bath sampling and analysis.
- Filter replacement.

These BOAs were developed based on information developed for earlier projects involving similar tasks and on information gathered through site visits and general process knowledge. The following discussion uses the BOA for chemical transport, presented in Table 4.20, as an example of how BOAs were developed and used. Appendix G presents the BOAs for other activities.

Key assumptions were developed to set the limits and to designate the critical activity's characteristics. For chemical transport, the assumptions were:

- Chemical costs are not included in the BOA, but are considered within material costs.
- The portion of labor costs considered are not included within production costs.
- Labor rate used is $10.22 per hour, consistent with the labor rate for an operator level job.
- Multiple chemicals are required for each bath replacement.
- All chemicals for a bath replacement are transported on one forklift trip.
- Chemicals are purchased in containers larger than the line containers used to move chemicals to the MHC process.
- All chemicals are stored in a central storage location.
- Chemicals are maintained in central storage via inventory tracking and physical monitoring.
- A forklift costs $580/month or $0.06/minute, including leasing, maintenance, and fuel.
- Forklifts are utilized to move all chemicals.
- Forklifts are parked in an assigned area when not in use.

Each critical task was broken down into primary and secondary activities. For chemical transport, the six primary activities are: paperwork associated with chemical transfer, moving forklift to chemical storage area, locating chemicals in storage area, preparation of chemicals for transfer, transporting chemicals to MHC process, and transporting chemicals from MHC process to actual bath. The secondary activities for the primary activity of "transport chemicals to MHC process" are: move forklift with chemicals, unload line containers, and park forklift in assigned parking area. For each secondary activity the labor, material, and forklift costs are calculated. The sum of the costs of a set of secondary activities equals the cost of the primary activity. The forklift costs are a function of the time that labor and the forklift are used.

For example, for a chemical transport activity that requires two minutes, the labor cost is $0.34 (based on a labor rate of $10.22 per hour) and the forklift cost is $0.12 (based on $0.06 per minute). Materials costs are determined for materials other than chemicals and tools required for an activity. The total of $9.11 in Table 4.20 represents the cost of a single act of transporting chemicals to the MHC line. The same BOAs are used for all MHC technologies because either the activities are similar over all MHC technologies or information is unavailable to distinguish among the technologies. However, individual facilities could modify a BOA to best represent their unique situations. Table 4.21 presents costs to perform each of the critical tasks one time.

**Table 4.20 BOAs for Transportation of Chemicals to MHC Line**

| Activities | Time (min) | Resources | | | Cost ($/transport) |
|---|---|---|---|---|---|
| | | Labor[a] | Materials[b] | Forklift[c] | |
| A. Paperwork and Maintenance | | | | | |
| 1. Request for chemicals | 2 | $0.34 | $0.10 | $0.00 | $0.44 |
| 2. Updating inventory logs | 1 | $0.17 | $0.05 | $0.00 | $0.22 |
| 3. Safety and environmental record keeping | 2 | $0.34 | $0.10 | $0.00 | $0.44 |
| B. Move Forklift to Chemical Storage Area | | | | | |
| 1. Move to forklift parking area | 2 | $0.34 | $0.00 | $0.12 | $0.46 |
| 2. Prepare forklift to move chemicals | 5 | $0.85 | $0.00 | $0.30 | $1.15 |
| 3. Move to line container storage area | 2 | $0.34 | $0.00 | $0.12 | $0.46 |
| 4. Prepare forklift to move line container | 3 | $0.51 | $0.00 | $0.18 | $0.69 |
| 5. Move forklift to chemical storage area | 2 | $0.34 | $0.00 | $0.12 | $0.46 |
| C. Locate Chemicals in Storage Area | | | | | |
| 1. Move forklift to appropriate areas | 1 | $0.17 | $0.00 | $0.06 | $0.23 |
| 2. Move chemical containers from storage to staging | 2 | $0.34 | $0.00 | $0.12 | $0.46 |
| 3. Move containers from staging to storage | 2 | $0.34 | $0.00 | $0.12 | $0.46 |
| D. Preparation of Chemicals for Transfer | | | | | |
| 1. Open chemical container(s) | 1 | $0.17 | $0.05 | $0.00 | $0.22 |
| 2. Utilize correct tools to obtain chemicals | 3 | $0.51 | $0.05 | $0.00 | $0.56 |
| 3. Place obtained chemicals in line container(s) | 3 | $0.51 | $0.00 | $0.00 | $0.51 |
| 4. Close chemical container(s) | 1.5 | $0.09 | $0.00 | $0.00 | $0.09 |
| 5. Place line container(s) on forklift | 1 | $0.17 | $0.00 | $0.06 | $0.23 |
| E. Transport Chemicals to Line | | | | | |
| 1. Move forklift to line | 2 | $0.34 | $0.00 | $0.12 | $0.46 |
| 2. Unload line container(s) at line | 1 | $0.17 | $0.00 | $0.06 | $0.23 |
| 3. Move forklift to parking area | 2 | $0.34 | $0.00 | $0.12 | $0.46 |
| F. Transport Chemicals from Line to Bath | | | | | |
| 1. Move line container(s) to bath | 1 | $0.17 | $0.00 | $0.00 | $0.17 |
| 2. Clean line container(s) | 2 | $0.34 | $0.20 | $0.00 | $0.54 |
| 3. Store line container(s) in appropriate area | 1 | $0.17 | $0.00 | $0.00 | $0.17 |
| **Total Cost per Transport** | | | | | **$9.11** |

[a] Labor rate = $10.22 per hour.
[b] Materials do not include chemicals or tools.
[c] Forklift operating cost = $0.06 per minute.

**Table 4.21 Costs of Critical Tasks**

| Task | Cost |
|---|---|
| Transportation of Chemicals | $9.11 |
| Tank Cleanup | $67.00 |
| Bath Setup | $15.10 |
| Sampling and Analysis | $3.70 |
| Filter Replacement | $17.50 |

## Fundamental Principles of Cost Analysis

Previous studies have defined seven principles of a fundamentally sound cost analysis (DeGamo et al., 1996), listed below. This analysis was designed to strictly adhere to these fundamental principles to increase the validity and credibility of the cost formulation.

**Principle 1. Develop the alternatives to be considered:** Table 4.13 identified the MHC technologies and equipment configurations considered in the cost analysis. Figure 4.13 listed the generic process steps and typical bath sequences for each of these technologies. These process steps and bath sequences are used consistently throughout the CTSA.

**Principle 2. Focus on the difference between expected future outcomes among alternatives:** Costs that are the same among all technologies do not need to be considered as there is no difference among alternatives for these costs. However, all costs that differ should be considered, provided the costs can be reliably estimated. Costs quantified in this analysis are capital costs, material costs, utility costs, wastewater costs, production costs, and maintenance costs. These cost categories were summarized earlier in this section and are discussed in more detail in Section 4.2.3.

Other cost categories are expected to differ in the future outcomes, but cannot be reliably estimated. These include waste treatment and disposal costs and quality costs. These costs were considered qualitatively earlier in this section.

**Principle 3. Use a consistent viewpoint:** The costs to produce a job consisting of 350,000 ssf are estimated for each technology and equipment configuration. Efficient MHC technologies with the ability to produce the 350,000 ssf quicker are rewarded by having the cost rates (i.e., $/hr, etc.) of certain costs held constant, but the overall cost is calculated over a proportionally shorter time period. For example, if labor rates and the number of workers per day are the same, a process that takes 50 percent less time than the baseline to complete a job will have 50 percent lower labor costs than the baseline.

**Principle 4. Use a common unit of measurement:** Costs are normalized to a common unit of measurement, $/ssf, to compare the relative costs of technologies.

**Principle 5. Consider all relevant criteria:** A thorough cost analysis requires the consideration of all criteria relevant to the overall costs of the technologies. The costs considered in this analysis were defined earlier in this section and are discussed in more detail in Section 4.2.3.

**Principle 6. Make uncertainty explicit:** Uncertainty is inherent in projecting the future outcomes of the alternatives and should be recognized in the cost analysis. Sensitivity analysis techniques are utilized to evaluate the effects of critical variables on cost.

**Principle 7. Examine the analysis for accuracy:** The cost analysis has been peer reviewed by industry, EPA, and other stakeholders to assess its accuracy and validity.

### 4.2.2 Simulation Results

Simulation models were run for each of the MHC processes. Three types of simulation outputs were obtained for use in the cost analysis:

- The duration and frequency of bath replacements.
- The production time required for each process.
- Down time incurred in producing 350,000 ssf.

The baseline process is used below as an example to explain the results of the simulation.

Table 4.22 presents the bath replacement simulation outputs. The values in the table represent the actual average time for bath replacement for the baseline process. Reviewing the table reveals that the cleaner/conditioner bath requires replacement nine times. Each replacement takes an average of 133 minutes. The total replacement time represents the total time the process is down due to bath replacements. Summing over all baths, bath replacement consumes 179 hours (10,760 minutes) when using the non-conveyorized electroless copper process to produce 350,000 ssf. Bath replacement simulation outputs for the other MHC processes are presented in Appendix G.

**Table 4.22 Example Simulation Output for Non-Conveyorized Electroless Copper Process: Frequency and Duration of Bath Replacements**

| Chemical Bath | Frequency | Avg. Time/Replacement (minutes) | Total Time (minutes) |
|---|---|---|---|
| Cleaner/Conditioner | 9 | 138 | 1,240 |
| Microetch | 18 | 146 | 2,630 |
| Predip | 8 | 125 | 1,000 |
| Catalyst | 1 | 230 | 230 |
| Accelerator | 16 | 130 | 2,080 |
| Electroless Copper | 10 | 114 | 1,140 |
| Acid Dip | 6 | 146 | 876 |
| Anti-Tarnish | 13 | 120 | 1,560 |
| **Total** | **81** | **133** | **10,760** |

As shown in the example, the bath replacement output value may be more than or less than the bath replacement input values reported in Tables 4.17 and 4.18. In this case, the input value for non-conveyorized electroless copper processes is 180 minutes, but the output values range from 114 to 230 minutes. Bath maintenance output values are less than input values when, on average, the bath is shut down with less than 180 minutes remaining in the shift. Under this

scenario, the simulation model assumes that the employee will stay on past the end of the shift to complete the bath replacement. Thus, only the time remaining in a normal 8-hour shift is charged to down time.

Alternately, bath maintenance output values may be greater than input values if more than 180 minutes remain in the shift when the bath is shut down. In this case, the simulation model assumes that all racks or panels will clear the system prior to shutting down the line for a bath replacement. Thus, bath replacement times greater than 180 minutes account for the cycle time required for racks and/or panels to clear the system.

Table 4.23 presents the second and third types of simulation output, the total production time required for each process, and the down time incurred by each process in producing 350,000 ssf. Total production time is the sum of actual operating time and down time. Down time includes the 1.2 hours per day the line is assumed inactive plus the time the process is down for bath replacements. Again, actual simulation outputs are presented in Appendix G.

**Table 4.23 Production Time and Down Time for MHC Processes to Produce 350,000 ssf**

| MHC Process | Total Production Time[a] | | Total Down Time[a] | |
|---|---|---|---|---|
| | minutes | days | minutes | days |
| Electroless Copper, non-conveyorized (BASELINE) | 163,500 | 401 | 33,900 | 83.2 |
| Electroless Copper, conveyorized | 36,100 | 88.4 | 16,300 | 40.0 |
| Carbon, conveyorized | 50,800 | 125 | 11,800 | 28.9 |
| Conductive Polymer, conveyorized | 29,100 | 71.3 | 7,110 | 17.4 |
| Graphite, conveyorized | 33,400 | 82.0 | 6,490 | 15.9 |
| Non-Formaldehyde Electroless Copper, non-conveyorized | 74,600 | 183 | 16,400 | 40.1 |
| Organic-Palladium, non-conveyorized | 31,800 | 77.9 | 10,800 | 26.4 |
| Organic-Palladium, conveyorized | 45,300 | 111 | 18,000 | 44.1 |
| Tin-Palladium, non-conveyorized | 48,500 | 119 | 13,600 | 33.4 |
| Tin Palladium, conveyorized | 26,100 | 63.9 | 9,010 | 22.1 |

[a] To convert from minutes to days, divide by 6.8 hrs per day (408 minutes).

### 4.2.3 Cost Formulation Details and Sample Calculations

This section develops and describes in detail the cost formulation used for evaluating the MHC processes. The overall cost was calculated from individual cost categories that are common to, but expected to vary with, the MHC process alternatives. The cost model was validated by cross-referencing the cost categories with Tellus Institute (White et al., 1992), and Pacific Northwest Pollution Prevention Research Center (Badgett et al., 1995).

The cost model for an MHC alternative is as follows:

$$TC = C + M + U + WW + P + MA$$

where:

TC = total cost to produce 350,000 ssf
C = capital cost
M = material cost
U = utility cost
WW = wastewater cost
P = production cost
MA = maintenance cost

The unit cost of producing 350,000 ssf is then represented as follows:

Unit Cost ($/ssf) = TC ($) / 350,000 ssf

The following sections presents a detailed description of cost calculation methods together with sample calculations for the baseline non-conveyorized electroless copper process. Finally, the results of the sample calculations are summarized and then combined to calculate the total cost and unit cost for the non-conveyorized electroless copper process.

## Capital Costs

This section presents methods and sample calculations for calculating capital costs. Capital costs are one-time or periodic costs incurred in the purchase of equipment or facilities. In this analysis, capital costs include the costs of primary equipment, equipment installation, and facility space utilized by the process. Primary equipment is the equipment vital to the operation of the MHC process without which the process would not be able to operate (i.e., bath tanks, heaters, rinse water system, etc.). Installation costs include costs to install the process equipment and prepare it for production. Facility space is the floor space required to operate the MHC process.

Total capital costs for the MHC technologies were calculated as follows:

$$C = (E + I + F) \times UR$$

where:

E = annualized capital cost of equipment ($/yr)
I = annualized capital cost of installation ($/yr)
F = annualized capital cost of facility ($/yr)
UR = utilization ratio, defined as the time in days required to manufacture 350,000 ssf divided by one operating year (250 days)

The UR adjusts annualized costs for the amount of time required to process 350,000 ssf, determined from the simulation models of each process alternative. The components of capital costs are discussed further below followed by sample calculations of capital costs.

**Equipment and Installation Costs.** Primary equipment and installation costs estimates were provided by equipment suppliers and include delivery of equipment and sales tax. Equipment estimates were based on basic, no frills equipment capable of processing 100

panels/hr. Equipment estimates did not include auxiliary equipment such as statistical process control or automated sampling equipment sometimes found on MHC process lines.

Annual costs for both the equipment and installation costs were calculated assuming 10-year, straight-line depreciation of equipment and no salvage value. These annual costs were calculated using the following equations:

E = equipment cost ($) ÷ 10 years
I = installation cost ($) ÷ 10 years

**Facility Costs.** Facility costs are capital costs for the floor space required to operate the MHC line. Facility costs were calculated assuming industrial floor space costs $65/ft$^2$ and the facility is depreciated over 25 years using straight-line depreciation. The cost per square foot of floor space applies to Class A light manufacturing buildings with basements. This value was obtained from the Marshall Valuation Service (Vishanoff, 1995) and mean square foot costs (Ferguson, 1996). Facility costs were calculated using the following equation:

F = [unit cost of facility utilized ($/ft$^2$) x footprint area/process step (ft$^2$/step) x number of steps] ÷ 25 years

The "footprint area" is the area of floor space required by MHC equipment, plus a buffer zone to maneuver equipment or have room to work on the MHC process line.[1] The footprint area per process step was calculated by determining the footprint dimensions of each process alternative, adjusting the dimensions for working space, and then determining the area per process step. Because the footprint area depends on the type of process automation, the average dimensions of both conveyorized (5 ft x 38 ft) and non-conveyorized (6 ft x 45 ft) processes were determined from IPC Workplace Practices Questionnaire data. Since these dimensions account for the equipment footprint only, an additional 8 ft was added to every dimension to allow space for line operation, maintenance, and chemical handling. The floor space required by either equipment type was calculated (1,134 ft$^2$ for conveyorized processes and 1,342 ft$^2$ for non-conveyorized processes) and used to determine the area required per process step. This was done by first identifying the process alternative with the fewest process steps for each automation type, and then dividing the required floor space by that number of steps. This method conservatively estimated the amount of floor space required per process step for conveyorized processes at 160 ft$^2$/step and for non-conveyorized processes at 110 ft$^2$/step. The overall area required for each MHC alternative was then calculated using the following equations:

Conveyorized:

$F_C$ = [$65/ft$^2$ x 160 ft$^2$/step x number of steps per process] ÷ 25 years

Non-conveyorized:

$F_N$ = [$65/ft$^2$ x 110 ft$^2$/step x number of steps per process] ÷ 25 years

[1] PWB manufacturers and their suppliers use the term "footprint" to refer to the dimensions of process equipment, such as the dimensions of the MHC process line.

**Sample Capital Costs Calculations.** This section presents sample capital costs calculations for the baseline process. From Figure 4.13, the non-conveyorized electroless copper process consists of 19 chemical bath and rinse steps. Simulation outputs in Table 4.23 indicate this process takes 401 days to manufacture 350,000 ssf of PWB. Equipment vendors estimated equipment and installation costs at $400,000 and $70,000, respectively (Microplate, 1996; Coates ASI, 1996; PAL Inc., 1996; Circuit Chemistry, 1996; Western Technology Associates, 1996). The components of capital costs are calculated as follows:

$E = \$400{,}000 \div 10 \text{ yrs} = \$40{,}000/\text{yr}$
$I = \$70{,}000 \div 10 \text{ yrs} = \$7{,}000/\text{yr}$
$F_N = (\$65/\text{ft}^2 \times 110 \text{ ft}^2/\text{step} \times 19 \text{ steps}) \div 25 \text{ yrs} = \$5{,}430/\text{yr}$
$UR = 401 \text{ days} \div 250 \text{ days/yr} = 1.60 \text{ yrs}$

Thus, the capital costs for the non-conveyorized electroless copper process to produce 350,000 ssf of PWB are as follows:

$C = (\$40{,}000/\text{yr} + \$7{,}000/\text{yr} + \$5{,}430/\text{yr}) \times 1.60 \text{ yrs} = \$83{,}900$

## Materials Costs

Materials costs were calculated for the chemical products consumed in MHC process lines through the initial setup and subsequent replacement of process chemical baths. The following presents equations for calculating materials costs and sample materials cost calculations for the baseline process.

**Materials Cost Calculation Methods.** Chemical suppliers were asked to provide estimates of chemical costs ($/ssf) early in the project. While some suppliers furnished estimates for one or more of their process alternatives, several suppliers did not provide chemical cost estimates for all of their MHC process lines being evaluated. Still others provided incomplete cost estimates or did not provide any supporting documentation of assumptions used to estimate chemical costs. Therefore, these data could not be used in the comparative cost estimates. Instead, chemical costs were estimated using the methods detailed below.

Chemical baths are typically made-up of one or more separate chemical products mixed together at specific concentrations to form a chemical solution. As PWBs are processed by the MHC line, the chemical baths become contaminated or depleted and require chemical additions on replacement. Baths are typically replaced according to analytical results or by supplier recommended replacement criteria specific to each bath. When the criteria are met or exceeded, the spent bath is removed and a new bath is created. The chemical cost to replace a specific bath one time is the sum of the costs of each chemical product in the bath and is given by the following equation:

$$\text{Chemical cost/bath replacement} = \Sigma_i \text{ [chemical product cost/bath (\$/gal) x \% chemical product in bath x total volume of bath (gal)]}$$

where:

$i$ = number of chemical products in a bath

The University of Tennessee Department of Industrial Engineering contacted suppliers to obtain price quotes in $/gallon or $/lb for MHC chemical products. The compositions of the individual process baths were determined from Product Data Sheets for each bath. The average volume of a chemical bath for non-conveyorized processes was calculated to be 75 gallons from IPC Workplace Practices Questionnaire data. For conveyorized processes, however, conveyor speed is constant, thus, the volume of chemicals in a bath varies by bath type to provide the necessary contact time (see Table 4.16 for conveyorized process bath volumes). These data were used in the above equation to calculate the chemical cost per bath replacement for each product line. The bath replacement costs were then averaged across like product lines (i.e., chemical costs from various suppliers of electroless copper processes were averaged by bath type, etc.) to determine an average chemical cost per replacement for each process bath.

To obtain the total materials cost, the chemical cost per bath replacement for each bath was multiplied by the number of bath replacements required (determined by simulation) and then summed over all the baths in an alternative. The cost of chemical additions was not included since no data were available to determine the amount and frequency of chemical additions. Materials costs are given by the following equation:

$$M = \Sigma_j [\text{chemical cost/bath replacement (\$)} \times \text{number of replacements/bath}]$$

where:

$j$ = number of baths in a process

The frequency of replacement for individual process baths was determined using supplier recommended criteria provided on Product Data Sheets and from IPC Workplace Practices Questionnaire data. Simulation models were used to determine the number of times a bath would be replaced while an MHC line processes 350,000 ssf of PWB. Appendix G presents bath replacement criteria used in this analysis and summaries of chemical product cost by supplier and by MHC technology.

**Sample Materials Cost Calculations.** Table 4.24 presents an example of chemical costs per bath replacement for one supplier's electroless copper line. Similar costs are presented in Appendix G for the six electroless copper chemical product lines evaluated. The chemical costs per process bath for all six processes were averaged to determine the average chemical cost per bath for the non-conveyorized electroless copper process.

The chemical cost per bath was then calculated by multiplying the average chemical cost for a bath by the number of bath replacements required to process 350,000 ssf. The costs for each bath were then summed to give the total materials cost for the overall non-conveyorized electroless copper process. Table 4.25 presents the chemical cost per bath replacement, the number of bath replacements required as determined by simulation, the total chemical cost per bath, and the total material cost for the non-conveyorized electroless copper process. Similar material cost calculations for each of the MHC process alternatives are presented in Appendix G.

**Table 4.24 Chemical Cost per Bath Replacement for One Supplier of the Non-Conveyorized Electroless Copper Process**

| Bath | Chemical Product | Product Cost[a] ($) | Percentage of Chemical Product[b] | Chemical Cost/Bath Replacement[c] ($) |
|---|---|---|---|---|
| Cleaner/Conditioner | A | $25.45/gal | 6 | $115 |
| Microetch | B | $2.57/lb | 13.8 g/l | $59 |
| | C | $7.62/gal | 2.5 | |
| | D | $1.60/gal | 18.5 | |
| Predip | E | $1.31/lb | 31.7 g/l | $22 |
| | F | $2.00/gal | 1.5 | |
| Catalyst | G | $391.80/gal | 4 | $1,186 |
| | H | $1.31/lb | 0.17 g/l | |
| | I | $2.00/gal | 3.5 | |
| Accelerator | J | $18.10/gal | 20 | $273 |
| Electroless Copper | K | $27.60/lb | 7 | $252 |
| | L | $16.45/gal | 8.5 | |
| | M | $4.50/gal | 0.22 | |
| Neutralizer | N | $1.60/gal | 100 | $120 |
| Anti-Tarnish | O | $39.00/gal | 0.25 | $7 |

[a] Product cost from supplier of the chemical product.

[b] The percentage of a chemical product in each process bath was determined from Product Data Sheets provided by the supplier of the chemical product.

[c] Cost per bath calculated assuming bath volumes of 75 gallons.

**Table 4.25 Materials Cost for the Non-Conveyorized Electroless Copper Process**

| Bath | Chemical Cost/Bath Replacement[a] | Number of Bath Replacements[b] | Total Chemical Cost |
|---|---|---|---|
| Cleaner/Conditioner | $188 | 9 | $1,690 |
| Microetch | $66 | 18 | $1,190 |
| Predip | $340 | 8 | $2,720 |
| Catalyst | $1,320 | 1 | $1,320 |
| Accelerator | $718 | 16 | $11,500 |
| Electroless Copper | $317 | 10 | $3,170 |
| Neutralizer | $120 | 6 | $720 |
| Anti-Tarnish | $16 | 13 | $208 |
| **Total Materials Cost** | | | **$22,500[c]** |

[a] Reported data represents the chemical cost per bath replacement averaged over six electroless copper product lines.

[b] Number of bath replacements required to process 350,000 ssf determined by simulation.

[c] Does not include cost of chemical additions.

## Utility Costs

Utility costs for the MHC process include water consumed by rinse tanks,[2] electricity used to power the panel transportation system, heaters and other process equipment, and natural gas consumed by drying ovens employed by some MHC alternatives. The utility cost for the MHC process was determined as follows:

$$U = W + E + G$$

where:

W = cost of water consumed ($/ssf) to produce 350,000 ssf
E = cost of electricity consumed ($/ssf) to produce 350,000 ssf
G = cost of natural gas consumed ($/ssf) to produce 350,000 ssf

The following presents utility costs calculation methods and sample utility costs for the baseline process.

**Utility Cost Calculation Methods.** The rate of water consumption depends on both the number of distinct water rinse steps and the flow rate of the water in those steps. The typical number of water rinse steps for each MHC alternative was determined using supplier provided data together with data from the IPC Workplace Practices Questionnaire. Cascaded rinse steps were considered as one rinse step when calculating water consumption since the cascaded rinse steps all utilize the same water. Based on IPC Workplace Practices Questionnaire data, the average water flow rate for individual rinse steps was estimated at 1,185 gals/tank for conveyorized processes and 1,840 gals/tank for non-conveyorized processes. However, it was assumed that the rinse steps are shut off during periods of process down time. Therefore, daily water consumption rates were adjusted for the percentage of time the process was in operation.

The cost of water was calculated by multiplying the water consumption rate of the MHC process by the production time required to produce 350,000 ssf of PWB, and then applying a unit cost factor to the total. Water consumption rates for MHC alternatives are presented in Section 5.1, Resource Conservation, while production times were determined from the simulation models. A unit cost of $1.60/1,000 gallons of water was obtained from the *Pollution Prevention and Control Survey* (EPA, 1995a). Following is the equation for calculating water cost:

W = quantity of rinse water consumed (gal) x $1.60/1,000 gal

The rate of electricity consumption for each MHC alternative depends upon the equipment required to operate each alternative. Differences in required process equipment such as the number of heaters, pumps, and type and extent of panel agitation directly affect electricity consumption. The cost of electricity is calculated by multiplying the electricity consumption rate of the MHC process by the production time required to produce 350,000 ssf of PWB, and then applying a unit cost factor to the total. Electricity consumption rates for MHC alternatives are

[2] Water is also used in MHC chemical baths to dilute chemical products to the appropriate concentration, but this use of water was assumed negligible compared to the water consumed in rinse tanks.

presented in Section 5.2, Energy Impacts, while the required production time was determined by simulation. A unit cost of $0.0473/kW-hr was obtained from the International Energy Agency. Therefore, the energy cost was calculated using the following equation:

E = hourly consumption rate (kW) x required production time (hrs) x $0.0473/kW-hr

Natural gas is utilized to fire the drying ovens required by both the graphite and carbon MHC alternatives. The amount of gas consumed was determined by multiplying the natural gas consumption rate for the MHC process by the amount of operating time required by the process to produce 350,000 ssf of PWB and then applying a unit cost to the result. Knoxville Utilities Board (KUB) charges $0.3683 per therm of natural gas consumed (KUB, 1996a). Thus, the cost of natural gas consumption was calculated by the following equation:

G = natural gas consumption rate (therm/hr) x required production time (hrs) x $0.3683/therm

The graphite process typically requires a single drying stage while the carbon process requires two drying oven stages. Natural gas consumption rates in cubic feet per hour for both carbon (180 cu.ft./hr) and graphite (90 cu.ft./hr) processes were obtained from Section 5.2, Energy Impacts. The production time required to produce 350,000 ssf of PWB came from simulation results.

**Sample Utility Cost Calculations.** The above methodology was used to calculate the utility costs for each of the MHC alternatives. This section presents sample utility cost calculations for the non-conveyorized electroless copper process.

Simulation results indicate the non-conveyorized electroless copper process is down 83.2 days and takes 401 days overall (at 6.8 hrs/day) to produce 350,000 ssf. It is comprised of seven rinse steps which consume approximately 4.1 million gallons of water during the course of the job (see Section 5.1, Resource Conservation). Electricity is consumed at a rate of 27.2 kW/hr (see Section 5.2, Energy Impacts). The non-conveyorized electroless copper process has no drying ovens and, therefore, does not use natural gas. Based on this information, water, electricity, and gas costs were calculated as follows:

W = 4,089,000 gallons x $1.60/1,000 gals = $6,540
E = 27.2 kW x (401 days-83.2 days) x 6.8 hrs/day x $.0473/kW-hr = $2,780
G = $0

Thus, the utility cost for the non-conveyorized electroless copper process was determined by the calculation:

U = $6,540 + $2,780 + $0 = $9,320

## Wastewater Costs

**Wastewater Cost Calculation Methods.** Wastewater costs for the MHC processes were only determined for the cost of discharging wastewater to a POTW. The analysis assumes that discharges are made in compliance with local allowable limits for chemical concentrations and other parameters so that no fines are incurred.

Wastewater quantities were assumed equal to the quantity of rinse water used. Rinse water usage was calculated in Section 5.1, Resource Conservation, and used to calculate water costs in the Utility Costs section. The unit costs for fees charged by a POTW for both city and non-city discharges of wastewater were obtained from KUB and averaged for use in calculating wastewater cost (KUB, 1996b). These average unit costs are not flat rates applied to the total wastewater discharge, but rather combine to form a tiered cost scale that applies an incremental unit cost to each level of discharge. The tiered cost scale for wastewater discharges to a POTW is presented in Table 4.26.

**Table 4.26 Tiered Cost Scale for Monthly Wastewater Discharges to a POTW**

| Wastewater Discharge Quantity (ccf/month) | City Discharge Cost ($/ccf/month) | Non-City Discharge Cost ($/ccf/month) | Average Discharge Cost ($/ccf/month) |
|---|---|---|---|
| 0 - 2 | $6.30 | $7.40 | $6.85 |
| 3 - 10 | $2.92 | $3.21 | $3.06 |
| 11 - 100 | $2.59 | $2.85 | $2.72 |
| 101 - 400 | $2.22 | $2.44 | $2.33 |
| 401 - 5,000 | $1.85 | $2.05 | $1.95 |

Source: KUB, 1996b.
ccf: 100 cubic ft.

The unit costs displayed for each level of discharge are applied incrementally to the quantity of monthly discharge. For example, the first two cubic feet of wastewater discharged in a month are assessed a charge of $6.85, while the next eight cubic feet cost $3.06, and so on. The production time required to produce 350,000 ssf of PWB comes from the simulation models. Thus, wastewater costs were calculated as follows:

$$WW = \sum_i [\text{quantity of discharge in tier (ccf/mo)} \times \text{tier cost factor (\$/ccf)}] \times \text{required production time (months)}$$

where:

i = number of cost tiers
ccf = 100 cubic ft

**Sample Wastewater Cost Calculations.** This section presents sample wastewater calculations for the non-conveyorized electroless copper process. Based on rinse water usage, the total wastewater release was approximately 4.1 million gallons. The required production time in months was calculated using the required production time from Table 4.23 and a 250 day operating year (401 days ÷ 250 days/year x 12 months/yr = 19.2 months). Thus, the monthly

wastewater release was 285 ccf (4,089,000 gallons ÷19.2 months ÷ 748 gal/hundred cu ft). To calculate the wastewater cost for the non-conveyorized electroless copper process, the tiered cost scale was applied to the quantity of discharge and the resulting costs per tier were summed, as follows:

$6.85 x 2 ccf/month = $13.70 ccf/month
$3.06 x 8 ccf/month = $24.48 ccf/month
$2.72 x 90 ccf/month = $245 ccf/month
$2.33 x 185 ccf/month = $431 ccf/month

Monthly discharge cost = $13.70 + $24.48 + $245 + $431 = $714/month

The monthly cost was then multiplied by the number of months required to produce 350,000 ssf of PWB to calculate the overall wastewater treatment cost:

WW = $714/month x 19.2 month = $13,700

**Production Costs**

**Production Cost Calculation Methods.** Production costs for the MHC process include both the cost of labor required to operate the process and the cost of transporting chemicals to the production line from storage. Production costs were calculated by the following equation:

P = LA + TR

where:

LA = production labor cost ($/ssf) to produce 350,000 ssf
TR = chemical transportation cost ($/ssf) to produce 350,000 ssf

Production labor cost is a function of the number and type of employees and the length of time required to complete a job. The calculation of production labor cost assumes that line operators perform all of the daily activities, excluding bath maintenance, vital to the operation of the MHC process. Labor costs associated with bath maintenance activities, such as sampling and analysis, are presented in the discussion of maintenance costs, below. An average number of line operators was determined for both conveyorized (one line operator) and non-conveyorized (1.1 line operators) processes from IPC Workplace Practices Questionnaire data and supported by site visit observations. Although no significant difference in the number of line operators by automation type was reported in the data, the number of line operators for non-conveyorized processes was adjusted upward to 1.1 to reflect the greater level of labor content for these processes as compared to conveyorized processes.

The labor time required to complete the specified job (350,000 ssf) was calculated assuming an average shift time of eight hours per day and using the number of days required to produce 350,000 ssf of PWB from simulation results. A labor wage of $10.22/hr was obtained from the American Wages and Salary Survey (Fisher, 1995) and utilized for MHC line operators. Therefore, labor costs for MHC alternatives were calculated as follows:

LA = number of operators x $10.22/hr x 8 hrs/day x required production time (days)

The production cost category of chemical transportation cost includes the cost of transporting chemicals from storage to the MHC process line. A BOA, presented in Appendix G, was developed and used to calculate the unit cost per chemical transport. Since chemicals are consumed whenever a bath is replaced, the number of trips required to supply the process line with chemicals equals the number of bath replacements required to produce 350,000 ssf of PWB. Chemical transportation cost was calculated as follows:

TR = number of bath replacements x unit cost per chemical transport ($)

**Sample Production Cost Calculations.** For the example of the non-conveyorized electroless copper process, production labor cost was calculated assuming 1.1 operators working for 401 days (see Table 4.23). Chemical transportation cost was calculated based on a cost per chemical transport of $9.11 (see Table 4.20 and Appendix G) and 81 bath replacements (see Table 4.22). Thus, the production cost was calculated as follows:

LA = 1.1 x $10.22 x 8 hrs/day x 401 days = $36,100
TR = 81 x $9.11 = $737

thus:

P = $36,100 + $737 = $36,800

## Maintenance Costs

**Maintenance Costs Calculation Methods.** The maintenance costs for the MHC process include the costs associated with tank cleaning, bath setup, sampling and analysis of bath chemistries, and bath filter replacement. Maintenance costs were calculated as follows:

MA = TC + BS + FR + ST

where:

TC = tank cleanup cost ($/ssf) to produce 350,000 ssf
BS = bath setup cost ($/ssf) to produce 350,000 ssf
FR = filter replacement cost ($/ssf) to produce 350,000 ssf
ST = sampling cost ($/ssf) to produce 350,000 ssf

The maintenance costs listed above depend on the unit cost per repetition of the activity and the number of times the activity was performed. For each maintenance cost category, a BOA was developed to characterize the cost of labor, materials, and tools associated with a single repetition of that activity. The BOA and unit cost per repetition for each cost category are presented in Appendix G. It was assumed that the activities and costs characterized on the BOAs are the same regardless of the MHC process or process baths. Unit costs per repetition for both tank cleanup and bath setup were determined to be $67.00 and $15.10, respectively.

The number of tank cleanups and bath setups equals the number of bath replacements obtained from process simulation results (see Appendix G). Each time a bath is replaced, the tank is cleaned before a replacement bath is created. The costs of tank cleanup and bath setup are thus given by the following:

TC = number of tank cleanups x $67.00
BS = number of bath setups x $15.10

IPC Workplace Practices Questionnaire data for both filter replacement and bath sampling and analysis were reported in occurrences per year instead of as a function of throughput. Ninetieth percentile values were calculated from these data and used in dermal exposure estimates in Section 3.2, Exposure Assessment. These frequencies were adjusted for this analysis using the URs for the production time required to manufacture 350,000 ssf of PWB. Using the unit costs determined by the BOAs developed for filter replacement ($17.50 per replacement) and bath sampling and testing ($3.70 per test), the costs for these maintenance activities were calculated as follows:

FR = annual number of filter replacement x UR x $17.50
ST = annual number of sampling & testing x UR x $3.70

The total maintenance cost for each MHC process alternative was determined by first calculating the individual maintenance costs using the above equations and then summing the results.

**Maintenance Costs Sample Calculations.** This section presents sample maintenance costs calculations for the non-conveyorized electroless copper process. From Table 4.23, this process has a production time of 401 days, which gives a UR of 1.60 (UR = 401 ÷ 250). The number of tank cleanups and bath setups equals the number of bath replacements reported in Table 4.22 (81 bath replacements). As reported in Section 3.2, Exposure Assessment, chemical baths are sampled and tested 720 per year and filters are replaced 100 times per year. Thus, the maintenance costs for the non-conveyorized electroless copper process are:

TC = 81 x $67.00 = $5,430
BS = 81 x $15.10 = $1,220
ST = 720 x 1.60 x $3.70 = $4,260
FR = 100 x 1.60 x $17.50 = $2,800

therefore:

MA = $5,430 + $1,220 + $4,260 + $2,800 = $13,700

**Determination Total Cost and Unit Cost**

The total cost for MHC process alternatives was calculated by summing the totals of the individual costs categories. The unit cost (UC), or cost per ssf of PWB produced, can then be calculated by dividing the total cost by the amount of PWBs produced. Table 4.27 summarizes

the total cost of manufacturing 350,000 ssf of PWB using the non-conveyorized electroless copper process.

The UC for the non-conveyorized electroless copper process was then calculated as follows:

UC = total cost (TC) ÷ 350,000 ssf
= $180,000 ÷ 350,000 ssf
= $0.51/ssf

**Table 4.27 Summary of Costs for the Non-Conveyorized Electroless Copper Process**

| Cost Category | Component | Component Cost | Totals |
|---|---|---|---|
| Capital Cost | Primary Equipment | $64,000 | |
| | Installation | $11,200 | |
| | Facility | $8,690 | **$83,900** |
| Material Cost | Chemical(s) | $22,500 | **$22,500** |
| Utility Cost | Water | $6,540 | |
| | Electricity | $2,780 | |
| | Natural Gas | $0 | **$9,320** |
| Wastewater Cost | Wastewater Discharge | $13,700 | **$13,700** |
| Production Cost | Transportation of Material | $737 | |
| | Labor for Line Operation | $36,100 | **$36,800** |
| Maintenance Cost | Tank Cleanup | $5,430 | |
| | Bath Setup | $1,220 | |
| | Sampling and Analysis | $4,260 | |
| | Filter Replacement | $2,800 | **$13,700** |
| **Total Cost** | | | **$180,000** |

### 4.2.4 Results

Table 4.28 presents the costs for each of the MHC technologies. Table 4.29 presents unit costs ($/ssf). The total cost of producing 350,000 ssf ranged from a high of $180,000 for the non-conveyorized electroless copper process to a low of $33,500 for the conveyorized conductive polymer process. Corresponding unit costs ranged from $0.51/ssf for the baseline process to $0.09/ssf for the conveyorized conductive polymer process. With the exception of the non-conveyorized, non-formaldehyde electroless copper process, all of the alternatives cost at least 50 percent less than the baseline. Both conveyorized and non-conveyorized equipment configurations were costed for the electroless copper, tin-palladium, and organic-palladium MHC alternatives. For the electroless copper technology, the conveyorized process was much more economical than the non-conveyorized process. Less difference in unit cost was seen between the tin-palladium technologies ($0.12/ssf for conveyorized processes and $0.14/ssf for non-conveyorized processes) and the organic-palladium technologies ($0.17/ssf for conveyorized processes and $0.15/ssf for non-conveyorized processes). Non-conveyorized processes are, on average, more expensive ($0.30) than conveyorized systems ($0.16).

Total cost data in Table 4.28 illustrate that chemical cost is typically the largest cost (in nine out of ten MHC processes) followed by equipment cost (in one out of ten MHC processes). The high costs of the baseline process appear to be primarily due to the length of time it took this process to produce 350,000 ssf (4,015 days). This is over twice as long as that required by the next process (183 days for non-conveyorized, non-formaldehyde electroless copper).

**Table 4.28 Total Cost of MHC Alternatives**

| Cost Category | Cost Components | Electroless Copper, non-conveyorized | Carbon, conveyorized | Conductive Polymer, conveyorized |
|---|---|---|---|---|
| Capital Cost | Primary Equipment | $64,000 | $7,470 | $5,560 |
| | Installation | $11,200 | $299 | $0 |
| | Facility | $8,690 | $2,690 | $2,250 |
| Material Cost | Chemical(s) | $22,500 | $32,900 | $10,400 |
| Utility Cost | Water | $6,540 | $725 | $410 |
| | Electricity | $2,780 | $836 | $460 |
| | Natural Gas | $0 | $418 | $0 |
| Wastewater Cost | Wastewater Discharge | $13,700 | $1,710 | $965 |
| Production Cost | Transportation of Material | $737 | $446 | $673 |
| | Labor for Normal Production | $36,100 | $10,200 | $5,830 |
| Maintenance Cost | Tank Cleanup | $5,430 | $3,280 | $4,960 |
| | Bath Setup | $1,220 | $740 | $1,120 |
| | Sampling and Testing | $4,260 | $405 | $436 |
| | Filter Replacement | $2,800 | $116 | $376 |
| **Total Cost** | | **$180,000** | **$62,200** | **$33,400** |

| Cost Category | Cost Components | Electroless Copper, conveyorized | Graphite, conveyorized | Non-Formaldehyde Electroless Copper, non-conveyorized |
|---|---|---|---|---|
| Capital Cost | Primary Equipment | $6,190 | $3,580 | $29,300 |
| | Installation | $212 | $131 | $5,120 |
| | Facility | $2,800 | $1,090 | $3,350 |
| Material Cost | Chemical(s) | $22,600 | $59,800 | $69,600 |
| Utility Cost | Water | $642 | $251 | $2,100 |
| | Electricity | $669 | $462 | $1,310 |
| | Natural Gas | $0 | $145 | $0 |
| Wastewater Cost | Wastewater Discharge | $1,450 | $612 | $4,520 |
| Production Cost | Transportation of Material | $883 | $319 | $682 |
| | Labor for Normal Production | $7,230 | $6,700 | $16,200 |
| Maintenance Cost | Tank Cleanup | $6,500 | $2,350 | $5,030 |
| | Bath Setup | $1,460 | $529 | $1,130 |
| | Sampling and Testing | $942 | $316 | $691 |
| | Filter Replacement | $612 | $901 | $214 |
| **Total Cost** | | **$52,200** | **$77,200** | **$139,200** |

**Table 4.28 Total Cost of MHC Alternatives (cont.)**

| Cost Category | Cost Components | Organic-Palladium, conveyorized | Organic-Palladium, non-conveyorized |
|---|---|---|---|
| Capital Cost | Primary Equipment | $5,780 | $4,160 |
| | Installation | $356 | $256 |
| | Facility | $2,220 | $1,100 |
| Material Cost | Chemical(s) | $28,900 | $27,000 |
| Utility Cost | Water | $635 | $758 |
| | Electricity | $720 | $325 |
| | Natural Gas | $0 | $0 |
| Wastewater Cost | Wastewater Discharge | $1,510 | $1,670 |
| Production Cost | Transportation of Material | $1,260 | $1,050 |
| | Labor for Normal Production | $6,530 | $7,190 |
| Maintenance Cost | Tank Cleanup | $9,250 | $7,710 |
| | Bath Setup | $2,080 | $1,740 |
| | Sampling and Testing | $411 | $288 |
| | Filter Replacement | $271 | $385 |
| **Total Cost** | | **$59,900** | **$53,700** |

| Cost Category | Cost Components | Tin-Palladium, conveyorized | Tin-Palladium, non-conveyorized |
|---|---|---|---|
| Capital Cost | Primary Equipment | $1,280 | $4,760 |
| | Installation | $205 | $381 |
| | Facility | $1,490 | $1,910 |
| Material Cost | Chemical(s) | $25,500 | $22,300 |
| Utility Cost | Water | $317 | $1,010 |
| | Electricity | $468 | $635 |
| | Natural Gas | $0 | $0 |
| Wastewater Cost | Wastewater Discharge | $754 | $2,340 |
| Production Cost | Transportation of Material | $537 | $455 |
| | Labor for Normal Production | $5,230 | $10,700 |
| Maintenance Cost | Tank Cleanup | $3,950 | $3,350 |
| | Bath Setup | $891 | $755 |
| | Sampling and Testing | $493 | $916 |
| | Filter Replacement | $332 | $616 |
| **Total Cost** | | **$41,400** | **$50,100** |

**Table 4.29 MHC Alternative Unit Costs**

| MHC Alternative | Production (ssf/yr) | Total Cost ($) | Unit Cost ($/ssf) |
|---|---|---|---|
| Electroless Copper, non-conveyorized (BASELINE) | 350,000 | $180,000 | $0.51 |
| Carbon, conveyorized | 350,000 | $62,200 | $0.18 |
| Conductive Polymer, conveyorized | 350,000 | $33,400 | $0.09 |
| Electroless Copper, conveyorized | 350,000 | $52,200 | $0.15 |
| Graphite, conveyorized | 350,000 | $77,200 | $0.22 |
| Non-Formaldehyde Electroless Copper, non-conveyorized | 350,000 | $139,200 | $0.40 |
| Organic-Palladium, conveyorized | 350,000 | $59,900 | $0.17 |
| Organic-Palladium, non-conveyorized | 350,000 | $53,700 | $0.15 |
| Tin-Palladium, conveyorized | 350,000 | $41,400 | $0.12 |
| Tin-Palladium, non-conveyorized | 350,000 | $50,100 | $0.14 |

### 4.2.5 Sensitivity Analysis

This section presents the results of sensitivity analyses to determine the effects of critical variables on overall costs. Three separate sensitivity analyses were performed, including sensitivity analyses to determine the following:

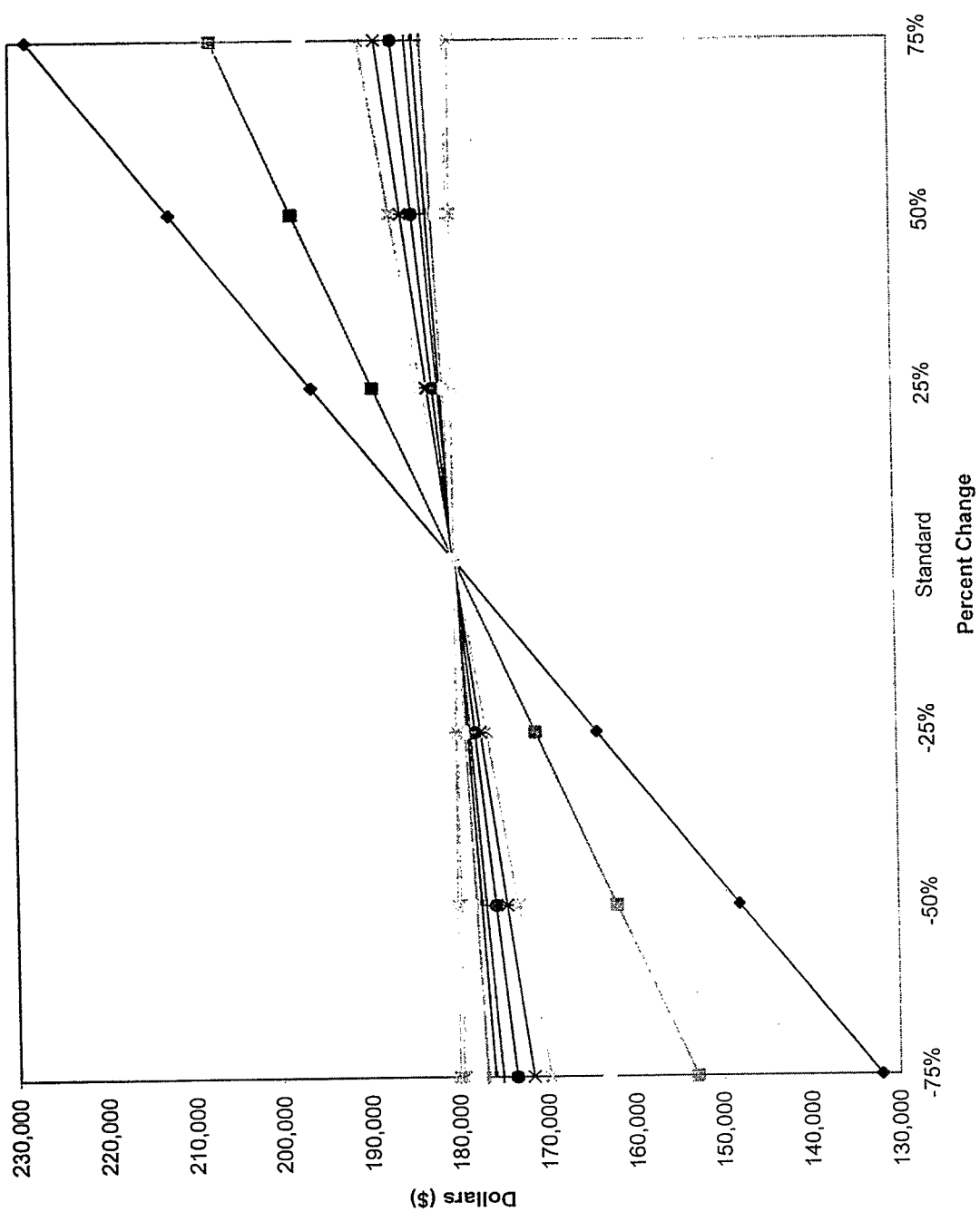
- The effects of the various cost components on the overall cost of the alternatives.
- The effects of down time on the cost of the baseline process.
- The effects of water consumption on the cost of the baseline process.

To determine the effects of the various cost components on overall cost, each cost component was increased and decreased by 25 percent, 50 percent and 75 percent, and an overall cost was calculated. Figure 4.15 presents the results of this sensitivity analysis for the baseline process. Appendix G presents the results of this type of sensitivity analysis for the alternatives. The results indicate two groupings of cost components: 1) those that have little impact on the overall cost; and 2) those which have significant impact on the overall cost of an MHC alternative. The first category includes tank cleanup, electricity, filter replacement, sampling and analysis, bath setup, transportation, and natural gas costs. The second category includes equipment, labor, and chemical costs.

To determine the effects of down time on the overall cost of the baseline process, the duration of bath replacements was reduced by 33 percent and 67 percent. Both the 33 and 67 percent reductions led to a less than one percent reduction in overall cost. These results indicate the effects of down time on overall costs are small.

Water consumption was also reduced by 33 percent and 67 percent to determine its effects on the overall cost of the baseline process. Reducing water consumption affects both water costs and wastewater discharge costs. Reducing water consumption by 33 percent resulted in an overall cost reduction of 2.8 percent, while reducing water consumption by 67 percent reduced the overall cost by 5.9 percent.

**Figure 4.15 Sensitivity Analysis for the Non-Conveyorized Electroless Copper Process**



### 4.2.6 Conclusions

This analysis developed comparative costs for seven MHC technologies, including electroless copper, conductive polymer, carbon, graphite, non-formaldehyde electroless copper, organic-palladium, and tin-palladium processes. Costs were developed for each technology and equipment configuration for which data were available from the IPC Workplace Practices Questionnaire and Performance Demonstration, for a total of ten processes (four non-conveyorized processes and six conveyorized processes). Costs were estimated using a hybrid cost model which combines traditional costs with simulation modeling and activity-based costs. The cost model was designed to determine the total cost of processing a specific amount of PWBs through a fully operational MHC line, in this case 350,000 ssf. The cost model does not estimate start-up costs for a facility switching to an MHC alternative. Total costs were divided by the throughput (350,000 ssf) to determine a unit cost in $/ssf.

The cost components considered include capital costs (primary equipment, installation, and facility costs), materials costs (limited to chemical costs), utility costs (water, electricity, and natural gas costs), wastewater costs (limited to wastewater discharge cost), production costs (production labor and chemical transport costs), and maintenance costs (tank cleanup, bath setup, sampling and analysis, and filter replacement costs). Other cost components may contribute significantly to overall costs, but were not quantified because they could not be reliably estimated. These include wastewater treatment cost, sludge recycling and disposal cost, other solid waste disposal costs, and quality costs.

Based on the results of this analysis, all of the alternatives are more economical than the non-conveyorized electroless copper process. In general, conveyorized processes cost less than non-conveyorized processes. Costs ranged from $0.51/ssf for the baseline process to $0.09/ssf for the conveyorized conductive polymer process. Seven process alternatives cost less than $0.20/ssf (conveyorized carbon at $0.18/ssf, conveyorized conductive polymer at $0.09/ssf, conveyorized electroless copper at $0.15/ssf, non-conveyorized organic palladium at $0.15/ssf, conveyorized organic-palladium at $0.17/ssf, and conveyorized and non-conveyorized tin-palladium at $0.12/ssf and $0.14/ssf, respectively). Three processes cost more than $0.20/ssf (non-conveyorized electroless copper at $0.51/ssf, non-conveyorized non-formaldehyde electroless copper at $0.40/ssf, and conveyorized graphite at $0.22/ssf).

Chemical cost was the single largest component cost for nine of the ten processes. Equipment cost was the largest cost for one process. Three separate sensitivity analyses of the results indicated that chemical cost, production labor cost, and equipment cost have the greatest effect on the overall cost results.

## 4.3 REGULATORY STATUS

This section of the CTSA describes the federal environmental regulations that may affect the chemicals in the MHC technologies. Discharges of these chemicals may be restricted by air, water or solid waste regulations, and releases may be reportable under the federal Toxic Release Inventory (TRI) program. This section discusses pertinent portions of the Clean Water Act (Section 4.3.1), the Safe Drinking Water Act (Section 4.3.2), the Clean Air Act (Section 4.3.3), the Resources Conservation and Recovery Act (Section 4.3.4), the Comprehensive Environmental Response, Compensation and Liability Act (Section 4.3.5), the Superfund Amendments and Reauthorization Act and Emergency Planning and Community Right-to-Know Act (Section 4.3.6), and the Toxic Substances Control Act (Section 4.3.7). In addition, it summarizes pertinent portions of the Occupational Safety and Health Act (Section 4.3.8). Section 4.3.9 summarizes the federal environmental regulations by MHC technology. This information is intended to provide an overview of environmental regulations potentially triggered by MHC chemicals. It is not intended to be used as regulatory guidance.

The primary sources of information for this section were the EPA Register of Lists (EPA, 1996) and the EPA document, *Federal Environmental Regulations Affecting the Electronics Industry* (EPA, 1995b). This is a database of federal regulations applicable to specific chemicals that can be searched by chemical. The latter was prepared by the DfE PWB Project. Of the 62 chemicals used in one or more of the MHC technologies, no regulatory listings were found for 21 chemicals.

### 4.3.1 Clean Water Act

The Clean Water Act (CWA) is the basic federal law governing water pollution control in the U.S. today. The various MHC processes used by the PWB industry contain a number of chemicals that are regulated under the CWA. Applicable provisions, as related to specific chemicals found in MHC technologies, are presented in Table 4.30; these particular provisions and process-based regulations are discussed in greater detail below.

**CWA Hazardous Substances and Reportable Quantities**

The CWA designates hazardous substances under Section 311(b)(2)(a) which, when discharged to navigable waters or adjoining shorelines, present an imminent and substantial danger to the public health or welfare, including fish, shellfish, wildlife, shorelines, and beaches. 40 Code of Federal Regulations (CFR) Part 117 establishes the *Reportable Quantity* (RQ) for each substance listed in 40 CFR Part 116. When an amount equal to or in excess of the RQ is discharged, the facility must provide notice to the federal government of the discharge, following Department of Transportation requirements set forth in 33 CFR Section 153.203. Liability for cleanup can result from such discharges. This requirement does not apply to facilities that discharge the substance under a National Pollutant Discharge Elimination System (NPDES) Permit or a CWA Section 404 dredge and fill permit, or to a Publicly-Owned Treatment Works (POTW), as long as any applicable effluent limitations or pretreatment standards have been met. Table 4.30 lists RQs of hazardous substances under the CWA that may apply to chemicals used in the MHC process.

**Table 4.30 CWA Regulations That May Apply to Chemicals in MHC Technologies**

| Chemical | CWA 311 RQ (lbs.) | CWA Priority Pollutant | CWA 307a | CWA 304b |
|---|---|---|---|---|
| Ammonia | 100 | | | ✓ |
| Ammonium Chloride | 5,000 | | | |
| Copper (I) Chloride; Copper | 10 | ✓ | ✓ | ✓ |
| Copper Sulfate | 10 | ✓ | ✓ | ✓ |
| Ethylenediaminetetraacetic Acid (EDTA) | 5,000 | | | |
| Formaldehyde | 100 | | | |
| Formic Acid | 5,000 | | | |
| Hydrochloric Acid | 5,000 | | | |
| Isophorone | | ✓ | ✓ | ✓ |
| Phosphoric Acid | 5,000 | | | |
| Potassium Cyanide | 10 | ✓ | ✓ | |
| Potassium Hydroxide | 1,000 | | | |
| Silver | | ✓ | ✓ | ✓ |
| Sodium Bisulfate | 5,000 | | | |
| Sodium Cyanide | 10 | ✓ | ✓ | |
| Sodium Hydroxide | 1,000 | | | |
| Sulfuric Acid | 1,000 | | | |

Abbreviations and definitions:
CWA - Clean Water Act
CWA 311 - Hazardous Substances
RQ - Reportable Quantities of CWA 311 hazardous substances
CWA 307a - Toxic Pollutants
CWA 304b - Effluent Limitations Guidelines

The NPDES permit program (40 CFR Part 122) contains regulations governing the discharge of pollutants to waters of the U.S. Forty states and one territory are authorized to administer NPDES programs that are at least as stringent as the federal program; EPA administers the program in states that are not authorized to do so. The following discussion covers federal NPDES requirements. Facilities may be required to comply with additional state requirements not covered in this document.

The NPDES program requires permits for the discharge of "pollutants" from any "point source" into "navigable waters" (except those covered by Section 404 dredge and fill permits). CWA defines all of these terms broadly, and a source is required to obtain an NPDES permit if it discharges almost anything other than dredge and fill material directly to surface waters. A source that sends its wastewater to a POTW is not required to obtain an NPDES permit, but may be required to obtain an industrial user permit from the POTW to cover its discharge.

## CWA Priority Pollutants

In addition to other NPDES permit application requirements, facilities will need to be aware of *priority pollutants* listed in 40 CFR Part 122, Appendix D; this list of 126 compounds

was developed by EPA to define a specific list of chemicals to be given priority consideration in the development of effluent limitations. Each applicant for an NPDES permit must provide quantitative data for those priority pollutants which the applicant knows or has reason to believe will be discharged in greater than trace amounts. Each applicant must also indicate whether it knows or has reason to believe it discharges any of the other hazardous substances or non-conventional pollutants listed at 40 CFR Part 122, Appendix D. Quantitative testing is not required for the other hazardous pollutants; however, the applicant must describe why it expects the pollutant to be discharged and provide the results of any quantitative data about its discharge for that pollutant. Quantitative testing is required for the non-conventional pollutants if the applicant expects them to be present in its discharge.

**CWA Effluent Limitations Guidelines**

A principal means for attaining water quality objectives under the CWA is the establishment and enforcement of technology-based effluent limitations, which are based on the pollutant control capabilities of available technologies, taking into consideration the economic achievability of these limitations and a number of other factors. Because of differences in production processes, quantities and composition of discharges, separate standards are established for discharges associated with different industry categories. These standards are referred to as technology-based effluent limitation guidelines.

The effluent limitation to be applied to a particular pollutant in a particular case depends on the following:

- Whether the pollutant is conventional, nonconventional, or toxic.
- Whether the point source is a new or existing source.
- Whether the point source discharges directly to the waters of the U.S. or to a POTW. (Facilities that discharge to POTWs must comply with the pretreatment standards.)

Existing sources must comply with either best practicable control technology currently available (BPT), best conventional control technology (BCT), or best available control technology economically practicable (BAT) standards. New facilities must comply with New Source Performance Standards. NPDES permits must also contain any more stringent permit limitations based on state water quality standards.

In the absence of effluent limitation guidelines for a facility category, permit writers establish technology-based controls using their Best Professional Judgement. In essence, the permit writer undertakes an effluent guideline-type analysis for a single facility. The permit writer will use information such as permit limits from similar facilities using similar treatment technology, performance data from actual operating facilities, and scientific literature. Best Professional Judgement may not be used in lieu of existing effluent guidelines. These guidelines apply only to direct dischargers of wastewater.

**Pretreatment Standards**

Only those facilities that discharge pollutants into waters of the U.S. need to obtain an NPDES permit. Facilities that discharge to POTWs, however, must comply with pretreatment

requirements, as set out in Section 307 of the CWA. These requirements were developed because of concern that discharger's waste containing toxic, hazardous, or concentrated conventional industrial wastes might "pass through" POTWs or that pollutants might interfere with the successful operation of the POTW.

40 CFR Part 413 contains pretreatment standards for existing sources. Existing sources are those which, since July 15, 1983, have not commenced construction of any building or facility that might result in a discharge. For the MHC step of the PWB manufacturing process, the main pollutant of concern is copper and copper compounds. Table 4.31 describes PWB pretreatment standards applicable to copper.

**Table 4.31 PWB Pretreatment Standards Applicable to Copper**

| | Maximum for 1 day (mg/l) | Average Daily Value for 4 Consecutive Days (mg/l) |
|---|---|---|
| Facilities discharging 38,000 liters or more per day - Existing Sources | 4.5 | 2.7 |
| Facilities discharging 38,000 liters or more per day - Existing Sources | 401[a] | 241[a] |
| All plants except job shops and independent PWB manufacturers - Existing Sources (metal finishing)[b] | 3.38 | 2.07 |
| New Sources[c] Limitations (metal finishing) | 3.38 | 2.07 |

[a] This category reflects mass-based standards for mg/square foot operation, and may be applied in place of the preceding category under prior agreement between a source subject to these standards and the POTW receiving such regulated wastes.

[b] "Metal finishing" applies to plants performing any of the following operations on any basis material: electroplating, electroless plating, anodizing, coating, chemical etching and milling and PWB manufacturing. Pretreatment standards have been promulgated for Total Toxic Organics (TTO) in this category; none of the chemicals evaluated in the MHC technologies are listed.

[c] Pretreatment standards for new sources applies to facilities that commenced construction after July 15, 1983.

### 4.3.2 Safe Drinking Water Act

The Federal Safe Drinking Water Act (SDWA) was first passed in 1974; it has been amended several times. The purpose of the SDWA is to make sure the drinking water supplied to the public is safe and wholesome. It requires water monitoring and limitations on the presence of chemical contaminants, viruses, and other disease-causing organisms in public water systems that serve 25 or more people. The SDWA also includes provisions for protection of groundwater resources in areas around wells that supply public drinking water. In addition, the injection of wastes into deep wells that are above or below drinking water sources are regulated by the SDWA Underground Injection Program (40 CFR Part 144). While most of the regulations under the SWDA affect public water supplies and suppliers, PWB manufacturers could be affected by the groundwater protection policies or the regulation of underground injection wells.

**SDWA National Primary and Secondary Drinking Water Regulations**

The SDWA National Primary Drinking Water Regulations (NPDWR) (40 CFR Part 141) set maximum concentrations for substances found in drinking water that may have an adverse

affect on human health. The National Secondary Drinking Water Regulations (NSDWR)(40 CFR Part 143) established guidelines for contaminants in drinking water that primarily affect the aesthetic qualities related to public acceptance of drinking water. The NSDWR are not federally enforceable but are intended as guidelines for the states. Table 4.32 presents MHC chemicals listed by these provisions of the SDWA.

**Table 4.32 SWDA Regulations That May Apply to Chemicals in MHC Technologies**

| Chemical | SWDA NPDWR | SWDA NSDWR |
|---|---|---|
| Copper (I) Chloride; Copper | ✓ | ✓ |
| Copper Sulfate | ✓ | ✓ |
| Fluoroboric Acid (as fluoride) | ✓ | ✓ |
| Silver | | ✓ |

Abbreviations and definitions:
SDWA - Safe Drinking Water Act
SDWA NPDWR - National Primary Drinking Water Rules
SDWA NSDWR - National Secondary Drinking Water Rules

### 4.3.3 Clean Air Act

The Clean Air Act (CAA), with its 1990 amendments, sets the framework for air pollution control in the U.S. The various MHC technologies produce a number of pollutants that are regulated under the CAA. Applicable provisions, as related to specific chemicals, are presented in Table 4.33; these particular provisions and process-based regulations are discussed below.

**Hazardous Air Pollutants**

Section 112 of the CAA established a program of regulation development for 189 hazardous air pollutants and directed EPA to add other compounds to the list as needed. EPA is authorized to establish Maximum Achievable Control Technology (MACT) standards for source categories that emit at least one of the pollutants on the list. Chemicals listed in Section 112(b) of the CAA that are used in PWB manufacturing are shown in Table 4.33. EPA is in the process of identifying categories of industrial facilities that emit substantial quantities of any of these 189 pollutants and will develop emissions limits for those industry categories.

Section 112(r) of the CAA deals with sudden releases of or accidents involving acutely toxic, explosive, or flammable chemicals. This provision, added by the CAA Amendments of 1990, establishes a list of substances which, if present in a process in a quantity in excess of a threshold, would require that the facility establish a Risk Management Program to prevent chemical accidents. This program would include preparing a risk management plan for submission to the state and to local emergency planning organizations.

**Table 4.33 CAA Regulations That May Apply to Chemicals in MHC Technologies**

| Chemical | CAA 111 | CAA 112b Hazardous Air Pollutants | CAA 112r |
|---|---|---|---|
| 2-Ethoxyethanol | ✓ | ✓ | |
| 1,3-Benezenediol | ✓ | | |
| 2-Butoxyethanol Acetate; Butylcellusolve Acetate | ✓ | | |
| Ammonia | | | ✓ |
| Diethylene Glycol Ethyl Ether | ✓ | | |
| Diethylene Glycol Methyl Ether | ✓ | ✓ | |
| Dimethylformamide | ✓ | ✓ | |
| Ethylene Glycol | ✓ | ✓ | |
| Fluoroboric Acid (as fluoride) | ✓ | | |
| Formaldehyde | ✓ | ✓ | ✓ |
| Formic Acid | ✓ | | |
| Hydrochloric Acid | | ✓ | ✓ |
| Isophorone | ✓ | ✓ | |
| Methanol | ✓ | ✓ | |
| p-Toluene Sulfonic Acid | ✓ | | |
| Potassium Cyanide | | ✓ | |
| Sodium Cyanide | | ✓ | |
| Sulfuric Acid | ✓ | | |

Abbreviations and definitions:
CAA - Clean Air Act
CAA 111 - Standards of Performance for New Stationary Sources of Air Pollutants-Equipment Leaks Chemical List
CAA 112b - Hazardous Air Pollutant
CAA 112r - Risk Management Program

## Minimum Standards for State Operating Permit Programs

The CAA and its implementing regulations (at 40 CFR Part 70) define the minimum standards and procedures required for state operating permit programs. The permit system is a new approach established by the 1990 Amendments that is designed to define each source's requirements and to facilitate enforcement. In addition, permit fees will generate revenue to fund implementation of the program.

Any facility defined as a "major source" is required to secure a permit. Section 70.2 of the regulations defines a source as a single point from which emissions are released or as an entire industrial facility that is under the control of the same person(s). A major source is defined as any source that emits or has the potential to emit:

- Ten tons per year (TPY) or more of any hazardous air pollutant.
- Twenty-five TPY or more of any combination of hazardous air pollutants.
- One hundred TPY of any air pollutant.

For ozone non-attainment areas, major sources are defined as sources with the potential to emit:

- One hundred TPY or more of volatile organic compounds (VOCs) in areas defined as marginal or moderate.
- Fifty TPY or more of VOCs in areas classified as serious.
- Twenty-five TPY or more of VOCs in areas classified as severe.
- Ten TPY or more of VOCs in areas classified as extreme.

In addition to major sources, all sources that are required to undergo New Source Review are subject to New Source Performance Standards, or are identified by federal or state regulations, must obtain a permit.

By November 15, 1993, each state must submit a design for an operating permit program to EPA for approval. EPA must either approve or disapprove the state's program within one year after submission. Once approved, the state program goes into effect.

Major sources, as well as the other sources identified above, must submit their permit applications to the state within one year of approval of the state program. (This was scheduled to take place near the end of 1995.) Once a source submits an application, it may continue to operate until the permit is issued. Permit issuance may take years because permit processing allows time for terms and conditions to be presented to and reviewed by the public and neighboring states as well as by EPA. Applicants should make certain that their applications contain a comprehensive declaration of all allowable emissions, because current emissions are used as the basis for calculating proposed reductions to meet future limits.

When issued, the permit will include all air requirements applicable to the facility. Among these are compliance schedules, emissions monitoring, emergency provisions, self-reporting responsibilities, and emissions limitations. Five years is the maximum permit term.

As established in 40 CFR Part 70, the states are required to develop fee schedules to ensure the collection and retention of revenues sufficient to cover permit program costs. The CAA sets a presumptive minimum annual fee of $25 per ton for all regulated pollutants (except carbon monoxide), but states can set higher or lower fees so long as they collect sufficient revenues to cover program costs.

### 4.3.4 Resource Conservation and Recovery Act

One purpose of the Resource Conservation and Recovery Act (RCRA) of 1976 (as amended in 1984) is to set up a cradle-to-grave system for tracking and regulating hazardous waste. EPA has issued regulations, found in 40 CFR Parts 260-299, which implement the federal statute. These regulations are Federal requirements. As of March 1994, 46 states have been authorized to implement the RCRA program and may include more stringent requirements in their authorized RCRA programs. In addition, non-RCRA-authorized states (Alaska, Hawaii, Iowa, and Wyoming) may have state laws that set out hazardous waste management requirements. A facility should always check with the state when analyzing which requirements apply to their activities.

To be a hazardous waste, a material must first be a solid waste, which is defined broadly under RCRA and RCRA regulations. Assuming the material is a solid waste, the first evaluation

to be made is whether it is also considered a hazardous waste. 40 CFR Part 261 addresses the identification and listing of hazardous waste. The waste generator has the responsibility for determining whether a waste is hazardous, and what classification, if any, may apply to the waste. The generator must examine the regulations and undertake any tests necessary to determine if the wastes generated are hazardous. Waste generators may also use their own knowledge and familiarity with the waste to determine whether it is hazardous. Generators may be subject to enforcement penalties for improperly determining that a waste is not hazardous.

## RCRA Hazardous Waste Codes

Wastes can be classified as hazardous either because they are listed by EPA through regulation in 40 CFR Part 261 or because they exhibit certain characteristics: toxicity, corrosivity, reactivity, or ignitability. Listed hazardous wastes are specifically named (e.g., discarded commercial toluene, spent non-halogenated solvents). Characteristic hazardous wastes are solid waste which "fail" a characteristic test, such as the RCRA test for ignitability.

There are four separate lists of hazardous wastes in 40 CFR Part 261. If any waste from a PWB facility is on any of these lists, the facility is subject to regulation under RCRA. The listing is often defined by industrial processes, but all wastes are listed because they contain particular chemical constituents (these constituents are listed in Appendix VII to Part 261). Section 261.31 lists wastes from non-specific sources and includes wastes generated by industrial processes that may occur in several different industries; the codes for such wastes always begin with the letter "F." The second category of listed wastes (40 CFR Section 261.32) includes hazardous wastes from specific sources; these wastes have codes that begin with the letter "K." The remaining lists (40 CFR Section 261.33) cover commercial chemical products that have been or are intended to be discarded; these have two letter designations, "P" and "U." Waste codes beginning with "P" are considered acutely hazardous, while those beginning with "U" are simply considered hazardous. Listed wastes from chemicals that are used in an MHC process are shown in Table 4.34. While this table is intended to be as comprehensive as possible, individual facilities may use other chemicals and generate other listed hazardous wastes that are not included in Table 4.34. Facilities may wish to consult the lists at 40 CFR 261.31-261.33.[3]

**Table 4.34 RCRA Hazardous Waste Codes That May Apply to Chemical Wastes From MHC Technologies**

| Chemical | U Waste Code | P Waste Code |
|---|---|---|
| 2-Ethoxyethanol | U359 | |
| 1,3-Benezenediol | U201 | |
| Formaldehyde | U122 | |
| Formic Acid | U123 | |
| Methanol | U154 | |
| Potassium Cyanide | | P098 |
| Sodium Cyanide | | P106 |

[3] Lists of the "F, P, K and U" hazardous wastes can also be obtained by calling the EPA RCRA/Superfund/EPCRA Hotline at (800) 424-9346.

## Generator Status

The hazardous waste generator is defined as any person, by site, who creates a hazardous waste or makes a waste subject to RCRA Subtitle C. Generators are divided into three categories:

- Large Quantity Generators (LQG) - These facilities generate at least 1,000 kg (approximately 2,200 lbs) of hazardous waste per month, or greater than 1 kg (2.2 lbs) of acutely hazardous waste per month.
- Small Quantity Generators (SQG) - These facilities generate greater than 100 kg (approximately 220 lbs) but less than 1,000 kg of hazardous waste per month, and up to 1 kg (2.2 lbs) per month of acutely hazardous waste.
- Conditionally Exempt Small Quantity Generators (CESQG) - These facilities generate no more than 100 kg (approximately 220 lbs) per month of hazardous waste and up to 1 kg (2.2 lbs) per month of acutely hazardous waste.

Large and small quantity generators must meet many similar requirements. 40 CFR Part 262 provides that SQGs may accumulate up to 6,000 kg of hazardous waste on-site at any one time for up to 180 days without being regulated as a treatment, storage, or disposal facility (TSDF) and thereby having to apply for a TSDF permit. The provisions of 40 CFR 262.34(f) allow SQGs to store waste on-site for 270 days without having to apply for TSDF status provided the waste must be transported over 200 miles. LQGs have only a 90-day window to ship wastes off-site without needing a RCRA TSDF permit. Keep in mind that most provisions of 40 CFR Parts 264 and 265 (for hazardous waste treatment, storage and disposal facilities) do not apply to generators who send their wastes off-site within the 90- or 180-day window, whichever is applicable.

Hazardous waste generators that do not meet the conditions for CESQGs must (among other requirements such as record keeping and reporting):

- Obtain a generator identification number.
- Store and ship hazardous waste in suitable containers or tanks (for storage only).
- Manifest the waste properly.
- Maintain copies of the manifest, a shipment log covering all hazardous waste shipments, and test records.
- Comply with applicable land disposal restriction requirements.
- Report releases or threats of releases of hazardous waste.

## Treatment, Storage, or Disposal Facility Status

As mentioned above, Subtitle C of RCRA (40 CFR Parts 264 and 265) outlines regulation and permit requirements for facilities that treat, store, or dispose of hazardous wastes. Any generator (except some CESQGs [see 40 CFR Part 261.5(g)]), no matter what monthly waste output, who treats, stores, or disposes of waste on site is classified as a TSDF. Every TSDF must comply with 40 CFR Part 264-267 and Part 270, including requirements to apply for a permit and meet certain stringent technical and financial responsibility requirements. Generators who discharge hazardous waste into a POTW or from a point source regulated by an

NPDES permit are not required to comply with TSDF regulations, nor are generators who store waste for short periods (see Generator Status, above).

### 4.3.5 Comprehensive Environmental Response, Compensation and Liability Act

The Comprehensive Environmental Response, Compensation and Liability Act (also known as CERCLA, or more commonly as Superfund) was enacted in 1980. CERCLA is the Act that created the Superfund hazardous substance cleanup program and set up a variety of mechanisms to address risks to public health, welfare, and the environment caused by hazardous substance releases.

**CERCLA RQs**

Substances deemed hazardous under CERCLA are listed in 40 CFR Section 302.4. Under CERCLA, EPA has assigned a reportable quantity (RQ) to most hazardous substances; regulatory RQs are either 1, 10, 100, 1,000, or 5,000 pounds (except for radionuclides). If EPA has not assigned a regulatory RQ to a hazardous substance, its RQ is one pound (Section 102). Any person in charge of a facility (or a vessel) must immediately (within a 24-hour period) notify the National Response Center as soon as a person has knowledge of a release of an amount of a hazardous substance that is equal to or greater than its RQ.[4] There are some exceptions to this requirement, including exceptions for certain continuous releases and for federally permitted releases. Table 4.35 lists RQs of substances under CERCLA that may apply to chemicals used in the MHC process.

**Table 4.35 CERCLA Reportable Quantities That May Apply to Chemicals in MHC Technologies**

| Chemical | CERCLA RQ (lbs) | Chemical | CERCLA RQ (lbs) |
|---|---|---|---|
| 1,3-Benezenediol | 5,000 | Isophorone | 5,000 |
| Ammonia | 100 | Methanol | 5,000 |
| Ammonia Chloride | 5,000 | Phosphoric Acid | 5,000 |
| Copper (I) Chloride | 10 | Potassium Cyanide | 10 |
| Copper Sulfate | 10 | Potassium Hydroxide | 1,000 |
| Dimethylformamide | 100 | Silver | 1,000 |
| Ethyl Glycol | 5,000 | Sodium Cyanide | 10 |
| Formaldehyde | 100 | Sodium Hydroxide | 1,000 |
| Formic Acid | 5,000 | Sulfuric Acid | 1,000 |
| Hydrochloric Acid | 5,000 | | |

Abbreviations and definitions:
CERCLA - Comprehensive Environmental Response, Compensation and Liability Act
CERCLA RQ - CERCLA reportable quantity

[4] The national toll-free number for the National Response Center is (800) 424-8802; in Washington, DC., call (202) 426-2675.

## CERCLA Liability

CERCLA further makes a broad class of parties liable for the costs of removal or remediation of the release or threatened release of any hazardous substance at a facility. Section 107 specifies the parties liable for response costs, including the following: 1) current owners and operators of the facility; 2) owners and operators of facility at the time hazardous substances were disposed; 3) persons who arranged for disposal or treatment, or for transportation for disposal or treatment of such substances; and 4) persons who accepted such substances for transportation for disposal or treatment. These parties are liable for: 1) all costs of removal or remedial action incurred by the federal government, a state, or an Indian tribe not inconsistent with the National Contingency Plan (NCP); 2) any other necessary costs of response incurred by any person consistent with the NCP; 3) damages for injury to natural resources; and 4) costs of health assessments.

### 4.3.6 Superfund Amendments and Reauthorization Act and Emergency Planning and Community Right-To-Know Act

CERCLA was amended in 1986 by the Superfund Amendments and Reauthorization Act (SARA). Title III of SARA is also known as the Emergency Planning and Community Right-To-Know Act (EPCRA). Certain sections of SARA and EPCRA may be applicable to MHC chemicals and PWB manufacturers. Table 4.36 lists applicable provisions as related to specific chemicals.

**Table 4.36 SARA and EPCRA Regulations That May Apply to Chemicals in MHC Technologies**

| Chemical | SARA 110 | EPCRA 302a | EPCRA 313 | Chemical | SARA 110 | EPCRA 302a | EPCRA 313 |
|---|---|---|---|---|---|---|---|
| 2-Ethoxyethanol | | | ✓ | Hydrochloric Acid | | ✓ | ✓ |
| Ammonia | ✓ | ✓ | ✓ | Hydrogen Peroxide | | ✓ | |
| Copper (I) Chloride | ✓ | | ✓ | Isopropyl Alcohol | ✓ | | ✓ |
| Copper Sulfate | ✓ | | ✓ | Methanol | | | ✓ |
| Dimethylformamide | | | ✓ | Phosphoric Acid | | | ✓ |
| Ethylene Glycol | | | ✓ | Potassium Cyanide | | ✓ | ✓ |
| EDTA | | | ✓ | Silver | ✓ | | ✓ |
| Fluoroboric Acid (as fluoride) | ✓ | | | Sodium Cyanide | | ✓ | ✓ |
| Formaldehyde | ✓ | ✓ | ✓ | Stannous Chloride (as tin) | ✓ | | |
| Formic Acid | | | ✓ | Sulfuric Acid | | ✓ | ✓ |

Abbreviations and definitions:
SARA - Superfund Amendments and Reauthorization Act
SARA 110 - Superfund Site Priority Contaminant
EPCRA - Emergency Planning & Community Right-To-Know Act
EPCRA 302a - Extremely Hazardous Substances
EPCRA 313 - Toxic Chemical Release Inventory

**SARA Priority Contaminants**

SARA Section 110 addresses Superfund site priority contaminants. This list contains the 275 highest ranking substances of the approximately 700 prioritized substances. These chemical substances, found at Superfund sites, are prioritized based on their frequency of occurrence, toxicity rating, and potential human exposure. Once a substance has been listed, the Agency for Toxic Substances and Disease Registry (ATSDR) is mandated to develop a toxicological profile that contains general health/hazard assessments with effect levels, potential exposures, uses, regulatory actions, and further research needs.

**EPCRA Extremely Hazardous Substances**

Section 302(a) of EPCRA regulates extremely hazardous substances and is intended to facilitate emergency planning for response to sudden toxic chemical releases. These chemicals, if present in quantities greater than their threshold planning quantities, must be reported to the State Emergency Response Commission and Local Emergency Planning Committee and addressed in community emergency response plans. These same substances are also subject to regulation under EPCRA Section 304, which requires accidental releases in excess of reportable quantities to be reported to the same state and local authorities.

**EPCRA Toxic Release Inventory**

Under EPCRA Section 313, a facility in SIC Codes 20-39 that has ten or more full-time employees and that manufactures, processes, or otherwise uses more than 10,000 or 25,000 pounds per year of any toxic chemical listed in 40 CFR Section 372.65 must file a toxic chemical release inventory (TRI) reporting form (EPA Form R) covering releases of these toxic chemicals (including those releases specifically allowed by EPA or state permits) with the EPA and a state agency where the facility is located. Beginning with the 1991 reporting year, such facilities must also report pollution prevention and recycling data for TRI chemicals pursuant to Section 6607 of the Pollution Prevention Act, 42 USC 13106. The threshold for reporting releases is 10,000 or 25,000 pounds, depending on how the chemical is used (40 CFR Section 372.25). Form R is filed annually, covers all toxic releases for the calendar year, and must be filed on or before the first of July of the following year.

### 4.3.7 Toxic Substances Control Act

The Toxic Substances Control Act (TSCA)(40 CFR Part 700-799), originally passed in 1976 and subsequently amended, applies to the manufacturers, importers, processors, distributors, users, and disposers of chemical substances or mixtures. Table 4.37 lists TSCA regulations that may be pertinent to the MHC process.

**Table 4.37 TSCA Regulations That May Apply to Chemicals in MHC Technologies**

| Chemical | TSCA 8d HSDR | TSCA 8a MTL | TSCA 8a PAIR | Chemical | TSCA 8d HSDR | TSCA 8a MTL | TSCA 8a PAIR |
|---|---|---|---|---|---|---|---|
| Benzotriazole | ✓ | | | Palladium Chloride | | | ✓ |
| Diethylene Glycol Methyl Ether | ✓ | | ✓ | Silver | | | ✓ |
| Dimethylformamide | ✓ | | ✓ | Sodium Cyanide | | ✓ | |
| Formaldehyde | | ✓ | | Triethanolamine | | ✓ | ✓ |
| Isophorone | ✓ | | ✓ | Vanillin | | ✓ | |
| Isopropyl Alcohol | | ✓ | ✓ | | | | |

Abbreviations and definitions:
TSCA - Toxic Substances Control Act
TSCA 8d HSDR - Health & Safety Data Reporting Rules
TSCA MTL - Master Testing List
TSCA 8a PAIR - Preliminary Assessment Information Rule

## Testing Requirements

Section 4 authorizes EPA to require the testing of any chemical substance or mixture on finding that such testing is necessary due to insufficient data from which the chemical's effects can be predicted and that the chemical either may present an unreasonable risk of injury to health or the environment or the chemical is produced in substantial quantities or may result in substantial human exposure.

The TSCA Master Testing List (MTL) is a list compiled by EPA's Existing Chemicals Program to set the Agency's testing agenda under TSCA Section 4. The major purposes are to: 1) identify chemical testing needs; 2) focus limited EPA resources on those chemicals with the highest priority testing needs; 3) identify and publicize EPA's testing priorities for existing chemicals; 4) obtain broad public comments on EPA's testing program and priorities; and 5) encourage initiatives by industry to help EPA meet those priority needs. Since 1990, EPA has: 1) added 222 specific chemicals and nine categories to the MTL; 2) deleted 45 chemicals from the MTL; 3) proposed testing for 113 chemicals via proposed rulemaking under TSCA Section 4; 4) required testing for six chemicals and one category via final TSCA Section 4 test rules, negotiated consent orders, or voluntary testing agreements; and 5) made risk assessment or management decisions on 41 chemicals based on TSCA Section 4 test results received. The MTL now contains over 320 specific chemicals and nine categories.

## Existing Chemical Requirements

Section 6 authorizes EPA, to the extent necessary to protect adequately against unreasonable risk using the least burdensome requirements, to prohibit the manufacture, processing, or distribution in commerce of a chemical substance; to limit the amounts, concentrations, or uses of it; to require labeling or record keeping concerning it; or to prohibit or otherwise regulate any manner or method of disposal, on finding there is a reasonable basis to conclude that the chemical presents or will present an unreasonable risk of injury to human health or the environment.

**Preliminary Assessment Information Rules**

Section 8(a) of TSCA, the Preliminary Assessment Information Rules (PAIR), establishes procedures for chemical manufacturers and processors to report production, use, and exposure-related information on listed chemical substances. Any person (except a "small business") who imports, manufactures, or processes chemicals identified by EPA by rule must report information on production volume, environmental releases, and/or chemical releases. Small businesses are required to report such information in some circumstances.

### 4.3.8 Occupational Safety and Health Act

**OSHA Hazard Communication Standard**

The Occupational Safety and Health Administration (OSHA) governs the exposure of workers to chemicals in the workplace. Any facility that is required by OSHA's Hazard Communication Standard (29 CFR Section 1910.1200) to have Material Safety Data Sheets (MSDSs) for certain hazardous chemicals, and that has such chemicals above certain minimum threshold levels, must provide copies of the MSDSs for these substances or a list of the substances to the State Emergency Response Commission (SERC), the Local Emergency Planning Commission (LEPC), and the local fire department. MSDSs must also be made available to workers. In addition, facilities must annually submit to the SERC, the LEPC, and the fire department a Tier I report indicating the aggregate amount of chemicals (above threshold quantities) at their facilities, classified by hazard category. If any agency that receives a Tier I report requests a Tier II report requiring additional information, facilities must submit this second report to the agency within 30 days of receiving a request for such a report. Tier II reports include an inventory of all chemicals at the facility. Most of the chemicals used in the MHC technologies industry are subject to these MSDS and Tier reporting requirements (40 CFR Part 370).

### 4.3.9 Summary of Regulations by MHC Technology

Tables 4.38 through 4.45 provide a summary of regulations that may apply to chemicals in each of the MHC technology categories. Chemicals listed in bold in the tables are used in all of the technology product lines evaluated. For example, formaldehyde is used in all of the electroless copper lines evaluated in this study, but dimethylformamide is only used in one product line. PWB manufacturers should check with their chemical supplier or review their MSDSs to determine which chemicals are present in the products they use.

Chemicals and wastes from the MHC alternatives appear to be subject to fewer overall federal environmental regulations than electroless copper. This suggests that implementing an alternative could potentially improve competitiveness by reducing compliance costs.

**Table 4.38 Summary of Regulations That May Apply to Chemicals in the Electroless Copper Technology**

| Process Chemical[a] | Chemicals Subject to Applicable Regulation | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CWA | | | | SDWA | | CAA | | | SARA 110 | EPCRA | | TSCA | | | RCRAWaste | |
| | 304b | 307a | 311 | Priority Pollutant | NPDWR | NSDWR | 111 | 112b | 112r | | 302a | 313 | 8d HSDR | MTL | 8a PAIR | P | U |
| Ammonium Chloride | | | ✓ | | | | | | | | | | | | | | |
| Benzotriazole | | | | | | ✓ | | | | | | | ✓ | | | | |
| Boric Acid | | | | | | | | | | | | | | | | | |
| **Copper (I) Chloride**[b] | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | | | ✓ | | ✓ | | | | | |
| **Copper Sulfate**[b] | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | | | ✓ | | ✓ | | | | | |
| Dimethylaminoborane | | | | | | | | | | | | | | | | | |
| Dimethylformamide | | | | ✓ | | ✓ | ✓ | ✓ | | | | ✓ | ✓ | | ✓ | | |
| Ethanolamine | | | | | | | | | | | | | | | | | |
| 2-Ethoxyethanol | | | | | | | ✓ | ✓ | | | | ✓ | | | | | 359 |
| Ethylenediaminetetraacetic Acid (EDTA) | | | ✓ | | | | | | | | | | | | | | |
| Ethylene Glycol | | | | ✓ | | | ✓ | ✓ | | | | ✓ | | | | | |
| Fluoroboric Acid (as fluoride) | ✓ | | | | ✓ | ✓ | ✓ | | | ✓ | | | | | | | |
| **Formaldehyde** | | | ✓ | | | | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | ✓ | | | 122 |
| Formic Acid | | | ✓ | ✓ | | | ✓ | | | | | ✓ | | | | | 123 |
| **Hydrochloric Acid**[c] | | | ✓ | | | | | ✓ | ✓ | | ✓ | ✓ | | | | | |
| Hydrogen Peroxide | | | | | | | | | | | ✓ | | | | | | |
| Hydroxyacetic Acid | | | | | | | | | | | | | | | | | |
| Isopropyl Alcohol, 2-Propanol | | | | | | | | | | ✓ | | ✓ | | ✓ | ✓ | | |
| m-Nitrobenzene Sulfonic Acid | | | | | | | | | | | | | | | | | |
| Magnesium Carbonate | | | | | | | | | | | | | | | | | |
| **Methanol** | | | | ✓ | | | ✓ | ✓ | | | | ✓ | | | | | 154 |

| Process Chemical[a] | Chemicals Subject to Applicable Regulation | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CWA | | | | SDWA | | CAA | | | SARA 110 | EPCRA | | TSCA | | | RCRAWaste | |
| | 304b | 307a | 311 | Priority Pollutant | NPDWR | NSDWR | 111 | 112b | 112r | | 302a | 313 | 8d HSDR | MTL | 8a PAIR | P | U |
| Palladium | | | | | | | | | | | | | | | | | |
| Peroxymonosulfuric Acid | | | | | | | | | | | | | | | | | |
| Potassium Bisulfate | | | | | | | | | | | | | | | | | |
| Potassium Cyanide | | ✓ | ✓ | ✓ | ✓ | | | ✓ | | | ✓ | ✓ | | | | 098 | |
| Potassium Hydroxide | | | ✓ | | | | | | | | | | | | | | |
| Potassium Persulfate | | | | | | | | | | | | | | | | | |
| Potassium Sodium Tartrate | | | | | | | | | | | | | | | | | |
| Potassium Sulfate | | | | | | | | | | | | | | | | | |
| Sodium Bisulfate | | | ✓ | | | | | | | | | | | | | | |
| Sodium Carbonate | | | | | | | | | | | | | | | | | |
| Sodium Chlorite | | | | | | | | | | | | | | | | | |
| Sodium Cyanide | | ✓ | ✓ | ✓ | | | | ✓ | | | ✓ | ✓ | | ✓ | | 106 | |
| **Sodium Hydroxide** | | | ✓ | | | | | | | | | | | | | | |
| Sodium Hypophosphite | | | | | | | | | | | | | | | | | |
| Sodium Sulfate | | | | | | | | | | | | | | | | | |
| Stannous Chloride | ✓ | | | | | | | | | ✓ | | | | | | | |
| **Sulfuric Acid** | | | ✓ | | | | ✓ | | | | ✓ | ✓ | | | | | |
| Tartaric Acid | | | | | | | | | | | | | | | | | |
| p-Toluene Sulfonic Acid | | | | | | | | | | | | | | | | | |
| Triethanolamine | | | | | | | | | | | | | | ✓ | ✓ | | |

[a] Chemicals in bold were in all electroless copper technologies evaluated, unless otherwise noted.
[b] Either copper (I) chloride or copper sulfate was in all electroless copper lines evaluated.
[c] Hydrochloric acid was listed on the MSDSs for five of six electroless copper lines.

**Table 4.39 Summary of Regulations That May Apply to Chemicals in the Carbon Technology**

| Process Chemical[a] | Chemicals Subject to Applicable Regulation | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CWA | | | | SDWA | | CAA | | | SARA 110 | EPCRA | | TSCA | | | RCRA Waste | |
| | 304b | 307a | 311 | Priority Pollutant | NPDWR | NSDWR | 111 | 112b | 112r | | 302a | 313 | 8d HSDR | MTL | 8a PAIR | P | U |
| Carbon Black | | | | | | | | | | | | | | | | | |
| Copper Sulfate | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | | | ✓ | | ✓ | | | | | |
| Ethanolamine | | | | | | | | | | | | | | | | | |
| Ethylene Glycol | | | | ✓ | | | ✓ | ✓ | | | | ✓ | | | | | |
| Potassium Carbonate | | | | | | | | | | | | | | | | | |
| Potassium Hydroxide | | | ✓ | | | | | | | | | | | | | | |
| Sodium Persulfate | | | | | | | | | | | | | | | | | |
| Sulfuric Acid | | | ✓ | | | | ✓ | | | ✓ | | ✓ | | | | | |

[a] Only one carbon technology was evaluated. All chemicals listed were present in that product line.

## Table 4.40 Summary of Regulations That May Apply to Chemicals in the Conductive Ink Technology

| Process Chemical[a] | Chemicals Subject to Applicable Regulation | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CWA | | | | SDWA | | CAA | | | SARA 110 | EPCRA | | TSCA | | | RCRA Waste | |
| | 304b | 307a | 311 | Priority Pollutant | NPDWR | NSDWR | 111 | 112b | 112r | | 302a | 313 | 8d HSDR | MTL | 8a PAIR | P | U |
| 2-Butoxyethanol Acetate | | | | | | | ✓ | | | | | | | | | | |
| Carbon Black | | | | | | | | | | | | | | | | | |
| Diethylene Glycol n-Butyl Ether | | | | | | | | | | | | | | | | | |
| Diethylene Glycol Ethyl Ether | | | | | | | ✓ | | | | | | | | | | |
| Diethylene Glycol Methyl Ether | | | | | | | ✓ | ✓ | | | | | ✓ | | ✓ | | |
| Graphite | | | | | | | | | | | | | | | | | |
| Isophorone | ✓ | ✓ | | ✓ | | | ✓ | ✓ | | | | | ✓ | | ✓ | | |
| Methanol | | | | | | | ✓ | ✓ | | | | ✓ | | | | | 154 |
| Silver | ✓ | ✓ | | ✓ | | ✓ | | | | ✓ | | ✓ | | | ✓ | | |

[a] Only one conductive ink technology was evaluated. All chemicals listed were present in that product line.

**Table 4.41 Summary of Regulations That May Apply to Chemicals in the Conductive Polymer Technology**

| Process Chemical[a] | Chemicals Subject to Applicable Regulation | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CWA | | | | SDWA | | CAA | | | SARA 110 | EPCRA | | TSCA | | | RCRA Waste | |
| | 304b | 307a | 311 | Priority Pollutant | NPDWR | NSDWR | 111 | 112b | 112r | | 302a | 313 | 8d HSDR | MTL | 8a PAIR | P | U |
| 1H-Pyrrole | | | | | | | | | | | | | | | | | |
| Peroxymonosulfuric Acid | | | | | | | | | | | | | | | | | |
| Phosphoric Acid | | | ✓ | | | | | | | | | ✓ | | | | | |
| Sodium Carbonate | | | | | | | | | | | | | | | | | |
| Sodium Hydroxide | | | ✓ | | | | | | | | | | | | | | |
| Sulfuric Acid | | | ✓ | | | | ✓ | | | | ✓ | ✓ | | | | | |

[a] Only one conductive polymer technology was evaluated. All chemicals listed were present in that product line.

## Table 4.42 Summary of Regulations That May Apply to Chemicals in the Graphite Technology

| Process Chemical[a] | Chemicals Subject to Applicable Regulation | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CWA | | | | SDWA | | CAA | | | SARA 110 | EPCRA | | TSCA | | | RCRA Waste | |
| | 304b | 307a | 311 | Priority Pollutant | NPDWR | NSDWR | 111 | 112b | 112r | | 302a | 313 | 8d HSDR | MTL | 8a PAIR | P | U |
| Ammonia | ✓ | | ✓ | | | | | | ✓ | ✓ | ✓ | ✓ | | | | | |
| Copper Sulfate | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | | | ✓ | | ✓ | | | | | |
| Ethanolamine | | | | | | | | | | | | | | | | | |
| **Graphite** | | | | | | | | | | | | | | | | | |
| Peroxymonosulfuric Acid | | | | | | | | | | | | | | | | | |
| Potassium Carbonate | | | | | | | | | | | | | | | | | |
| **Sodium Persulfate** | | | | | | | | | | | | | | | | | |
| **Sulfuric Acid** | | | ✓ | | | | ✓ | | | | ✓ | ✓ | | | | | |

[a] Chemicals in bold were in both graphite technologies evaluated.

**Table 4.43 Summary of Regulations That May Apply to Chemicals in the Non-Formaldehyde Electroless Copper Technology**

| Process Chemical[a] | Chemicals Subject to Applicable Regulation | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CWA | | | | SDWA | | CAA | | | SARA 110 | EPCRA | | TSCA | | | RCRA Waste | |
| | 304b | 307a | 311 | Priority Pollutant | NPDWR | NSDWR | 111 | 112b | 112r | | 302a | 313 | 8d HSDR | MTL | 8a PAIR | P | U |
| Copper Sulfate | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | | | ✓ | | ✓ | | | | | |
| Hydrochloric Acid | | | ✓ | | | | | ✓ | ✓ | | ✓ | ✓ | | | | | |
| Hydrogen Peroxide | | | | | | | | | | | ✓ | | | | | | |
| Isopropyl Alcohol (2-propanol) | | | | | | | | | | ✓ | | ✓ | | ✓ | ✓ | | |
| Potassium Hydroxide | | | ✓ | | | | | | | | | | | | | | |
| Potassium Persulfate | | | | | | | | | | | | | | | | | |
| Sodium Chlorite | | | | | | | | | | | | | | | | | |
| Sodium Hydroxide | | | ✓ | | | | | | | | | | | | | | |
| Stannous Chloride | | | | | | | | | | ✓ | | | | | | | |
| Sulfuric Acid | | | ✓ | | | | ✓ | | | | ✓ | ✓ | | | | | |

[a] Only one non-formaldehyde electroless copper technology was evaluated. All chemicals listed were present in that product line.

**Table 4.44 Summary of Regulations That May Apply to Chemicals in the Organic-Palladium Technology**

| Process Chemical[a] | Chemicals Subject to Applicable Regulation | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CWA | | | | SDWA | | CAA | | | SARA 110 | EPCRA | | TSCA | | | RCRA Waste | |
| | 304b | 307a | 311 | Priority Pollutant | NPDWR | NSDWR | 111 | 112b | 112r | | 302a | 313 | 8d HSDR | MTL | 8a PAIR | P | U |
| Hydrochloric Acid | | | ✓ | | | | | ✓ | ✓ | | ✓ | ✓ | | | | | |
| Sodium Bisulfate | | | ✓ | | | | | | | | | | | | | | |
| Sodium Carbonate | | | | | | | | | | | | | | | | | |
| Sodium Bicarbonate | | | | | | | | | | | | | | | | | |
| Sodium Hypophosphite | | | | | | | | | | | | | | | | | |
| Sodium Persulfate | | | | | | | | | | | | | | | | | |
| Trisodium Citrate 5,5-Hydrate or Sodium Citrate | | | | | | | | | | | | | | | | | |

[a] Only one organic-palladium technology was evaluated. All chemicals listed were present in that product line.

## Table 4.45 Summary of Regulations That May Apply to Chemicals in the Tin-Palladium Technology

| Process Chemical[a] | Chemicals Subject to Applicable Regulation | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CWA | | | | SDWA | | CAA | | | SARA | EPCRA | | TSCA | | | RCRA Waste | |
| | 304b | 307a | 311 | Priority Pollutant | NPDWR | NSDWR | 111 | 112b | 112r | 110 | 302a | 313 | 8d HSDR | MTL | 8a PAIR | P | U |
| 1,3-Benzenediol | | | | | | | ✓ | | | | | | | | | | 201 |
| **Copper (I) Chloride[b]** | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | | | ✓ | | ✓ | | | | | |
| **Copper Sulfate[b]** | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | | | | ✓ | | ✓ | | | | | |
| Dimethylaminoborane | | | | | | | | | | | | | | | | | |
| Ethanolamine | | | | | | | | | | | | | | | | | |
| Fluoroboric Acid (as fluoride) | | | | | ✓ | ✓ | ✓ | | | ✓ | | | | | | | |
| **Hydrochloric Acid[c]** | | | ✓ | | | | | ✓ | ✓ | | ✓ | ✓ | | | | | |
| Hydrogen Peroxide | | | | | | | | | | | ✓ | | | | | | |
| Isopropyl Alcohol (2-propanol) | | | | | | | | | | ✓ | | ✓ | | ✓ | ✓ | | |
| Lithium Hydroxide | | | | | | | | | | | | | | | | | |
| **Palladium[d]** | | | | | | | | | | | | | | | | | |
| **Palladium Chloride[d]** | | | | | | | | | | | | | | | ✓ | | |
| Phosphoric Acid | | | ✓ | | | | | | | | | ✓ | | | | | |
| Potassium Carbonate | | | | | | | | | | | | | | | | | |
| Sodium Bisulfate | | | ✓ | | | | | | | | | | | | | | |
| Sodium Chloride | | | | | | | | | | | | | | | | | |
| Sodium Hydroxide | | | ✓ | | | | | | | | | | | | | | |
| Sodium Persulfate | | | | | | | | | | | | | | | | | |
| **Stannous Chloride[e]** | | | | | | | | | | ✓ | | | | | | | |
| **Sulfuric Acid[c]** | | | ✓ | | | | ✓ | | | | ✓ | ✓ | | | | | |
| Triethanolamine | | | | | | | | | | | | | | ✓ | ✓ | | |
| Vanillin | | | | | | | | | | | | | | ✓ | | | |

[a] Chemicals in bold were in all tin-palladium technologies evaluated, unless otherwise noted.
[b] Either copper (I) chloride or copper sulfate was listed on the MSDSs for four of five tin-palladium lines evaluated.
[c] Hydrochloric and sulfuric acid were listed on the MSDSs for four of five tin-palladium lines evaluated.
[d] Palladium or palladium chloride was listed on the MSDS for three of five tin-palladium lines evaluated. The MSDSs for the two other lines did not list a source of palladium.
[e] Stannous chloride was listed on the MSDSs for four of the five tin-palladium lines evaluated. The MSDSs for the remaining tin-palladium product line did not list a source of tin or palladium.

## 4.4 INTERNATIONAL INFORMATION

Several alternatives to the electroless copper process are being adopted more quickly abroad than in the U.S. This section discusses the world market for PWBs and the international use of MHC alternatives. It also discusses factors driving the international use of MHC alternatives, including economic, environmental and regulatory considerations.

### 4.4.1 World Market for PWBs

The total world market for PWBs is approximately $21 billion (EPA, 1995c). The U.S. and Japan are the leading suppliers of PWBs but Hong Kong, Singapore, Taiwan, and Korea are increasing their market share. In 1994 the U.S. provided 26 percent of the PWBs in the world market, Japan 28 percent, and Europe 18 percent (EPA, 1995c). IPC estimates that domestic PWB imports are approximately $500 to $600 million annually (EPA, 1995c). Taiwan comprises approximately 30 to 35 percent of the import market with Japan, Hong Kong, Korea, and Thailand comprising 10 percent each. Domestic PWB exports were approximately $100 million in 1993, which represents two to three percent of total domestic production (EPA, 1995c).

### 4.4.2 International Use of MHC Alternatives

The alternatives to the traditional electroless copper MHC process are in use in many countries abroad, including England, Italy, France, Spain, Germany, Switzerland, Sweden, Japan, China, Hong Kong, Singapore, Taiwan, and Canada. In addition, most of the suppliers of these alternatives have manufacturing facilities located in the countries to which they sell. One company provides its palladium alternative to Japan, France, Sweden, the UK, Canada, and Germany (Harnden, 1996). Another company, which provides a palladium alternative to electroless copper, provides both processes to England, Italy, France, Spain, Germany, Switzerland, China, Hong Kong, Singapore, and Taiwan. Presently, that company's electroless copper process is used more frequently than the palladium alternative (Nargi-Toth, 1996). However, restrictions on EDTA in Germany are making the use of the palladium alternative almost equal to the use of the traditional electroless copper process. Similarly, in Taiwan and China the use of the palladium process is increasing relative to the electroless copper process due to the high cost of water (Nargi-Toth, 1996). Internationally, one company reports its conductive polymer and organic-palladium processes make up approximately five percent of the world market (Boyle, 1996).

Another company provides its graphite alternative in Germany, England, France, Japan, Taiwan and Hong Kong, and is opening manufacturing facilities in both China and Malaysia within a few months (Carano, 1996). The company's graphite process is reportedly used more frequently in Europe than is its electroless copper process. However, in Asia, the electroless copper process is used more frequently (Carano, 1996).

Several suppliers have indicated that the use of their particular MHC alternative to electroless copper is increasing throughout the international arena. Some suppliers have indicated that the international usage of the electroless copper process is also on the rise but that the MHC alternatives are increasing in usage more rapidly than traditional electroless copper

processes (Carano, 1996). A pollution prevention and control survey performed under the DfE PWB Project confirmed that the electroless copper is the predominate method employed in the U.S. The survey was conducted of 400 PWB manufacturers in the U.S.; 40 responses were received, representing approximately 17 percent of the total U.S. PWB production (EPA, 1995d). Eighty-six percent of survey respondents use the electroless copper for most of their products, 14 percent use palladium alternatives, and one respondent uses a graphite system (EPA, 1995d). The Pollution Prevention and Control Survey is discussed further in Chapter 1 of the CTSA.

**Reasons for Use of Particular Alternatives Internationally**

For the most part, the alternatives to the electroless copper process appear to be employed due to reasons other than environmental pressures. According to international manufacturers who participated in the Performance Demonstration Project, the most common reason for use of an alternative is economics. According to suppliers, some of the alternatives are in fact less costly than the traditional electroless copper process (see Section 4.2 for an analysis of the comparative costs of alternatives developed for the CTSA). An example of this is one company's graphite process, which reportedly costs less than the company's comparable electroless copper process (Carano, 1996). Furthermore, several of the performance demonstration participants in Europe indicated that their use of an alternative MHC process has resulted in increased throughput and decreased manpower requirements.

Some of the economic drivers for adopting alternatives to the electroless copper process internationally also relate to environmental issues. Several of the countries adopting the MHC alternatives have high population densities as compared to the U.S., making water a scarcer resource. As a result, these companies face high costs to buy and treat their wastewater. In Germany, for example, companies pay one cent per gallon to have water enter the plant and then must pay 1.2 cents per gallon to dispose of wastewater (Obermann, 1996). As a result, any alternative that offers a reduction in the use of wastewater is potentially more attractive from a cost-effectiveness standpoint. Several MHC alternatives allow wastewater to be reused a number of times, something that is not available when using the electroless copper process due to the high levels of chelators and copper that cannot be removed from the water except through chemical treatment (Obermann, 1996). Therefore, the costs of buying the water and paying to have it treated are reduced through the use of less water-intensive alternatives.

In some countries there are "pressures" rather than environmental regulations that have led to the adoption of an alternative to the electroless copper MHC process. Some countries have identified the use of EDTA and formaldehyde as areas of potential concern. For instance, in Germany there are restrictions on the use of the chelator EDTA that are making the adoption of non-EDTA using alternatives more attractive (Nargi-Toth, 1996). Some alternatives do not use formaldehyde and as such are used with more frequency than the electroless copper process in countries that are attempting to limit the use of formaldehyde (Harnden, 1996).

**Barriers to Trade and Supply Information**

The alternatives to the electroless copper process do not suffer from any readily apparent barriers to trade or tariff restrictions that would make their increased adoption more costly. The alternatives discussed above are all made from readily available materials. Therefore, if the

demand for these alternatives should increase there should be no problem with meeting the increased demand. Most of the suppliers of these alternatives have manufacturing facilities located in the countries to which they sell and so they face no tariffs from importing these chemicals. The companies that wish to use the particular alternative simply contact the manufacturer in their country to purchase the alternatives. Therefore, there are no trade barriers in the form of tariffs making one alternative more attractive to a potential purchaser (Carano, 1996; Nargi-Toth, 1996; Harnden, 1996). As was indicated above, most alternatives are available in the same countries so they all appear to be on equal footing in terms of availability and susceptibility to trade barriers.

### 4.4.3 Regulatory Framework

Most of the driving forces leading to the use of an alternative to electroless copper are related to the cost-effectiveness of the alternative. However, there are several regulatory mechanisms in place internationally that favor alternatives to traditional electroless copper processes. These include wastewater effluent requirements and water consumption issues, discussed below.

**Wastewater Effluent Requirements**

Suppliers and international performance demonstration participants report that economics, not chemical bans or restrictions on specific chemicals, are the leading cause for the adoption of an MHC alternative. However, wastewater effluent requirements for certain chemicals found in electroless copper processes are also speeding the adoption of other MHC processes. For example, in Germany the chemical EDTA is restricted so that it must be removed from wastewater before the wastewater is discharged to an off-site wastewater treatment facility. This restriction led one manufacturer to replace his electroless copper process with an organic-palladium process (Schwansee, 1996). This restriction is a national one so that all companies must adhere to it.

Also in Germany, the wastewater leaving a plant cannot contain copper in amounts in excess of 0.5 mg/L or any ammonia (Obermann, 1996). The German regulation on copper discharges is much more stringent than comparable regulations in the U.S., where facilities must at least comply with federal effluent regulations and are sometimes subjected to more stringent regulations from the states (EPA, 1995d). The federal effluent guidelines for copper discharges are 3.38 mg/l maximum and 2.07 mg/l average monthly concentration (EPA, 1995d). According to the Pollution Prevention and Control Survey discussed previously, 63 percent of the respondents must meet discharge limitations that are more stringent than the federal effluent limitations (EPA, 1995d). However, only 15 percent of the respondents had to meet effluent limitations that were as stringent as, or more stringent than, the German regulation (EPA, 1995d).

**Water Consumption**

As indicated above, water usage is a main concern in many of the international arenas that use these alternatives. While there are few direct regulations on the amount of water that can be used in a MHC process, the cost of buying and treating the water make a more water-intensive process less economical. In Germany, the high cost of purchasing water and discharging

wastewater greatly influences the decision of whether or not to use an alternative. The less water a process uses, the more likely it is that process will be used. In addition, in certain parts of Germany, local authorities examine plans for the MHC process and issue permits to allow use of the line. If the process that is proposed for use is too water-intensive, a permit will not be issued by the local authorities (Carano, 1996). In addition, local authorities sometimes give specific time limits in which an older more water-intensive process must be phased out (Carano, 1996). For example, one international participant in the Performance Demonstration Project uses an older electroless copper process for some of its products. The local authorities have given the company four years to cease operation of the line because it uses too much water (Obermann, 1996).

### 4.4.4 Conclusions

The information set forth above indicates that the cost-effectiveness of an alterative has been the main driver causing PWB manufacturers abroad to switch from an electroless copper process to one of the newer alternatives. In addition to the increased capacity and decreased labor requirements of some of the MHC alternatives over the non-conveyorized electroless copper process, environmental concerns also affected the process choice. For instance, the rate at which an alternative consumes water and the presence or absence of strictly regulated chemicals are two factors which have a substantial affect on the cost-effectiveness of MHC alternatives abroad. Finally, in some parts of Germany, local authorities can deny a permit for a new MHC process line if it is deemed too water-intensive, or require an existing MHC process to be replaced. While environmental regulations do not seem to be the primary forces leading toward the adoption of the newer alternatives, it appears that the companies that supply these alternatives are taking environmental regulations and concerns into consideration when designing alternatives to the electroless copper process.

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# Chapter 5
# Conservation

Businesses are finding that by conserving natural resources and energy they can cut costs, improve the environment, and improve their competitiveness. And due to the substantial amount of rinse water consumed and wastewater generated by traditional electroless copper processes, water conservation is an issue of particular concern to printed wiring board (PWB) manufacturers and to the communities in which they are located. This chapter of the Cleaner Technologies Substitutes Assessment (CTSA) evaluates the comparative resource consumption and energy use of the making holes conductive (MHC) technologies. Section 5.1 presents a comparative analysis of the resource consumption rates of MHC technologies, including the relative amounts of rinse water consumed by the technologies and a discussion of factors affecting process and wastewater treatment chemicals consumption. Section 5.2 presents a comparative analysis of the energy impacts of MHC technologies, including the relative amount of energy consumed by each MHC process, the environmental impacts of this energy consumption, and factors affecting energy consumption during other life-cycle stages, such as chemical manufacturing or MHC waste disposal.

## 5.1 RESOURCE CONSERVATION

Resource conservation is an increasingly important goal for all industry sectors, particularly as global industrialization increases demand for limited resources. A PWB manufacturer can conserve resources through his or her selection of an MHC process and the manner in which it is operated. By reducing the consumption of resources, a manufacturer will not only minimize process costs and increase process efficiency, but will also conserve resources throughout the entire life-cycle chain. Resources typically consumed by the operation of the MHC process include water used for rinsing panels, process chemicals used on the process line, energy used to heat process baths and power equipment, and wastewater treatment chemicals. The focus of this section is to perform a comparative analysis of the resource consumption rates of the baseline and alternative MHC technologies. Section 5.1.1 discusses the types and quantities of natural resources (other than energy) consumed during MHC operation. Section 5.1.2 presents conclusions of this analysis.

### 5.1.1 Natural Resource Consumption

To determine the effects that alternatives have on the rate of natural resource consumption during the operation of the MHC process, specific data were gathered through the Performance Demonstration Project, information from chemical suppliers, and dissemination of the IPC Workplace Practices Questionnaire to industry. Natural resource data gathered through these means include the following:

- Process specifications (i.e., type of process, facility size, process throughput, etc.).
- Physical process parameters and equipment description (i.e., automation level, bath size, rinse water system configuration, pollution prevention equipment, etc.).

- Operating procedures and employee practices (i.e., process cycle-time, individual bath dwell times, bath maintenance practices, chemical disposal procedures, etc.).
- Resource consumption data (i.e., rinse water flow rates, frequency of bath replacement, criteria for replacement, bath formulations, frequency of chemical addition, etc.).

Using the collected data, a comparative analysis of the water consumption rates for each of the MHC alternatives was developed. For both process chemical and treatment chemical consumption, however, statistically meaningful conclusions could not be drawn from the compiled data. Differences in process chemicals and chemical product lines, bath maintenance practices, and process operating procedures, just to name a few possibilities, introduced enough uncertainty and variability to prevent the formulation of quantifiable conclusions. A qualitative analysis of these data is therefore presented and factors affecting the chemical consumption rates are identified. Table 5.1 summarizes the types of resources consumed during the MHC operation and the effects of the MHC alternatives on resource conservation. Water, process chemicals, and treatment chemicals consumption are discussed below.

**Table 5.1 Effects of MHC Alternatives on Resource Consumption**

| Resource | Effects of MHC Alternative on Resource Consumption |
|---|---|
| Water | Water consumption can vary significantly according to MHC alternative and level of automation. Other factors such as water and sewage costs and operating practices also affect water consumption rates. |
| Process Chemicals | Reduction in the number of chemical baths comprising MHC substitutes typically leads to reduced chemical consumption. The quantity of process chemicals consumed is also dependent on other factors such as expected bath lives (e.g., the number of surface square feet (ssf) processed before a bath must be replaced or chemicals added), process throughput, and individual facility operating practices. |
| Energy | Energy consumption rates can differ substantially among the baseline and alternatives. Energy consumption is discussed in Section 5.2. |
| Treatment Chemicals | Water consumption rates and the associated quantities of wastewater generated as well as the elimination of chelators from the MHC process can result in differences in the type and quantity of treatment chemicals consumed. |

## Water Consumption

The MHC process line consists of a series of chemical baths which are typically separated by one, and sometimes several, water rinse steps. These water rinse steps account for virtually all of the water consumed during the operation of the MHC process. The water baths dissolve or displace residual chemicals from the panel surface, preventing contamination of subsequent baths, while creating a clean panel surface for future chemical activity. The number of rinse stages recommended by chemical suppliers for their MHC processes range from two to seven, but can actually be much higher depending on facility operating practices. The number of rinse stages reported by respondents to the IPC Workplace Practices Questionnaire ranged from two to fifteen separate water rinse stages.

The flow rate required by each individual rinse tank to fulfill its role in the process is dependent on several factors, including the time of panel submersion, the type and amount of chemical residue to be removed, the type of agitation used in the rinse stage, and the purity of

rinse water. Because proper water rinsing is critical to the MHC process, manufacturers often use more water than is required to ensure that panels are cleaned sufficiently. Other methods, such as flow control valves and sensors, are available to ensure that sufficient water is available to rinse PWB panels, while minimizing the amount of water consumed by the process.

PWB manufacturers often use multiple rinse water stages between chemical process steps to facilitate better rinsing. The first rinse stage removes the majority of residual chemicals and contaminants, while subsequent rinse stages remove any remaining chemicals. Counter-current or cascade rinse systems minimize water use by feeding the water effluent from the cleanest rinse tank, usually at the end of the cascade, into the next cleanest rinse stage, and so on, until the effluent from the most contaminated, initial rinse stage is sent for treatment or recycle. Other water reuse or recycle techniques include ion exchange, reverse osmosis, as well as reusing rinse water in other plant processes. A detailed description of methods to reduce water consumption, including methods to reuse or recycle contaminated rinse water, is presented in Chapter 6 of this CTSA.

To assess the water consumption rates of the different process alternatives, data from chemical suppliers and the IPC Workplace Practices Questionnaire were used and compared for consistency. Estimated water consumption rates for each alternative were provided by chemical suppliers for each MHC process. Consumption rates were reported for three categories of manufacturing facilities based on board surface area processed in ssf per day: small (2,000 to 6,000), medium (6,000 to 15,000), and large (15,000 +). Water consumption rates for each alternative were also calculated using data collected from the IPC Workplace Practices Questionnaire. An average water flow rate per rinse stage was calculated for both non-conveyorized (1,840 gal/day per rinse stage) and conveyorized processes (1,185 gal/day per rinse stage) from the data collected. The average flow rate was then multiplied by the number of rinse stages in the standard configuration for each process (see Section 3.1, Source Release Assessment) to generate a water consumption rate per day for each MHC alternative. The number of rinse stages in a standard configuration of an alternative, the daily rinse water flow rate calculated from the IPC Workplace Practices Questionnaire, and the daily water flow rate reported by chemical suppliers for each MHC alternative are presented in Table 5.2.

To determine the overall amount of rinse water consumed by each alternative, the rinse water flow rate in Table 5.2 was multiplied by the amount of time needed for each alternative to manufacture 350,000 ssf of board (the average MHC throughput of respondents to the IPC Workplace Practices Questionnaire). The operating time required to produce the panels was simulated using a computer model developed for each MHC alternative. For the purposes of this evaluation it was assumed that the water flow to the rinse stages was turned off during periods of MHC process shutdown (e.g., bath replacements). The results of the simulation along with a discussion of the data and parameters used to define each alternative are presented in Section 4.2, Cost Analysis. The days of MHC operation required to manufacture 350,000 ssf from the simulation, the total amount of rinse water consumed for each MHC alternative, and the water consumption per ssf of board produced are presented in Table 5.3. The amount of rinse water consumed for each alternative is also displayed in Figure 5.1.

**Table 5.2 Rinse Water Flow Rates for MHC Process Alternatives**

| MHC Process Alternative | No. of Rinse Stages[a] | MHC Rinse Water Flow Rate (gal/day) | |
|---|---|---|---|
| | | IPC Workplace Practices Questionnaire[b] | Supplier Data Sheet[c] |
| Electroless Copper, non-conveyorized (BASELINE) | 7 | 12,880 | 5,700 - 12,500 |
| Electroless Copper, conveyorized | 7 | 8,300 | 3,840 |
| Carbon, conveyorized | 4 | 4,740 | ND |
| Conductive Polymer, conveyorized | 4 | 4,740 | ND |
| Graphite, conveyorized | 2 | 2,370 | 1,400 - 3,800 |
| Non-Formaldehyde Electroless Copper, non-conveyorized | 5 | 9,200 | ND |
| Organic-Palladium, non-conveyorized | 5 | 9,200 | ND |
| Organic-Palladium, conveyorized | 5 | 5,930 | ND |
| Tin-Palladium, non-conveyorized | 4 | 7,360 | 4,300 - 9,400 |
| Tin-Palladium, conveyorized | 4 | 4,740 | 2,900 - 7,200 |

[a] Data reflects the number of rinse stages required for the standard configuration of each MHC alternative as reported in Section 3.1, Source Release Assessment. Multiple rinse tanks in succession were considered to be cascaded and thus were counted as a single rinse stage with respect to water usage.

[b] Rinse water flow rate was calculated by averaging water flow data per stage from both questionnaire and performance demonstrations data (non-conveyorized = 1,840 gal/day per rinse stage; conveyorized = 1,185 gal/day per rinse stage) and then multiplying by the number of rinse stages in each process.

[c] Data ranges reflect estimates provided by chemical suppliers for facilities with process throughputs ranging from 2,000 to 15,000 ssf per day.

ND: No Data.

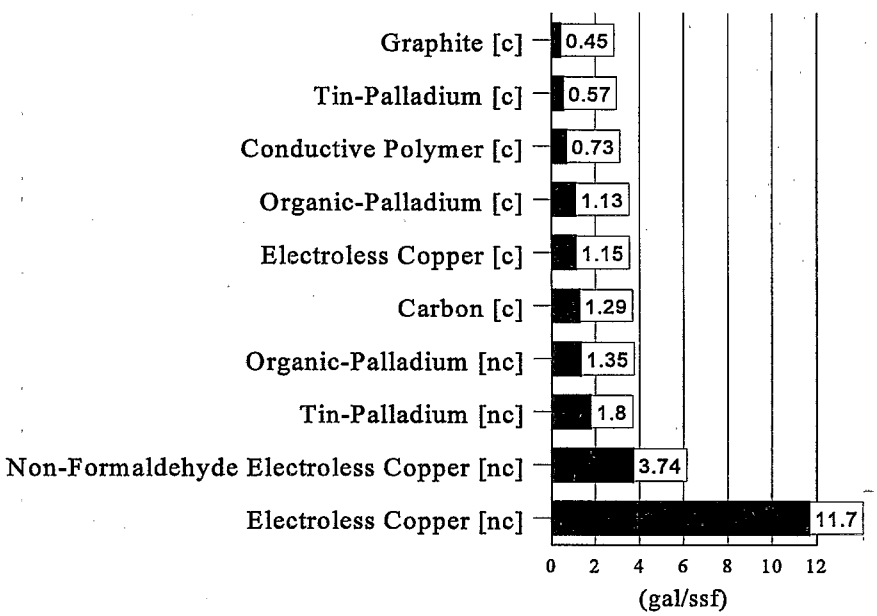
An analysis of the data shows that the type of MHC process, as well as the level of automation, have a profound effect on the amount of water that a facility will consume during normal operation of the MHC line. All of the MHC alternatives have been demonstrated to consume less water during operation than the traditional non-conveyorized electroless copper process. The reduction in water usage is primarily attributable to the decreased number of rinse stages required by many of the alternative processes and the decreased operating time required to process a set number of boards. The table also demonstrates that the conveyorized version of a process typically consumes less water during operation than the non-conveyorized version of the same process, a result attributed to the decreased number of rinse steps required and the greater efficiency of conveyorized processes. Some companies have gone a step farther by developing equipment systems that monitor water quality and usage in order to optimize water rinse performance, a pollution prevention technique recommended to reduce water consumption and, thus, wastewater generation. The actual water usage experienced by manufacturers employing such a system may be less than that calculated in Table 5.3.

**Table 5.3 Total Rinse Water Consumed by MHC Process Alternatives by Board Production Rate**

| MHC Process Alternative | Process Operating Time[a] (days) | Rinse Water Consumed (gal/350,000 ssf) | Water Consumption Rate (gal/ssf) |
|---|---|---|---|
| Electroless Copper, non-conveyorized (BASELINE) | 317.5 | $4.09 \times 10^6$ | 11.7 |
| Electroless Copper, conveyorized | 48.4 | $4.02 \times 10^5$ | 1.15 |
| Carbon, conveyorized | 95.6 | $4.53 \times 10^5$ | 1.29 |
| Conductive Polymer, conveyorized | 53.9 | $2.55 \times 10^5$ | 0.73 |
| Graphite, conveyorized | 66.1 | $1.57 \times 10^5$ | 0.45 |
| Non-Formaldehyde Electroless Copper, conveyorized | 142.8 | $1.31 \times 10^6$ | 3.74 |
| Organic-Palladium, non-conveyorized | 51.5 | $4.74 \times 10^5$ | 1.35 |
| Organic-Palladium, conveyorized | 67.0 | $3.97 \times 10^5$ | 1.13 |
| Tin-Palladium, non-conveyorized | 85.5 | $6.29 \times 10^5$ | 1.80 |
| Tin-Palladium, conveyorized | 41.8 | $1.98 \times 10^5$ | 0.57 |

[a] Operating time is reported in the number of days required to produce 350,000 ssf of board with a day equal to 6.8 hours of process operating time. Rinse water was assumed to be turned off during periods of process shutdown, thus the simulated operating time for each alternative was adjusted to exclude these periods of shutdown. For a more detailed description of the simulation model see Section 4.2, Cost Analysis.

**Figure 5.1 Water Consumption Rates of MHC Alternatives**




c: conveyorized
nc: non-conveyorized

A study of direct metallization processes conducted by the City of San Jose, California also identified reduced rinse water consumption as one of the many advantages of MHC alternatives (City of San Jose, 1996). The study, performed by the city's Environmental Services Department, included a literature search of currently available MHC alternatives, a survey of PWB manufacturing facilities in the area, and a comparative analysis of the advantages of MHC alternatives to electroless copper. The study report also presents several case studies of companies that have already implemented MHC alternatives. The study found that 14 out of 46 (30 percent) survey respondents cited reduced water usage as a prominent advantage of replacing their electroless copper MHC process with an alternative. On a separate survey question another five survey respondents indicated that high water use was a prominent disadvantage of operating an electroless copper MHC process. Although a couple of the companies studied reported little reduction in water usage, several other companies implementing MHC alternatives indicated decreases in water consumption. The study concluded that the magnitude of the reduction in water consumption is site-specific depending on the facility's former process set-up and operating practices.

## Process Chemicals Consumption

Some of the resources consumed through the operation of the MHC process are the chemicals that comprise the various chemical baths or process steps. These chemicals are consumed through the normal operation of the MHC process line by either deposition onto the panels or degradation caused by chemical reaction. Process chemicals are also lost through volatilization, bath depletion, or contamination as PWBs are cycled through the MHC process. Process chemicals are incorporated onto the panels, lost through drag-out to the following process stages, or become contaminated through the build-up of impurities requiring the replacement of the chemical solution. Methods for limiting unnecessary chemical loss and thus minimizing the amount of chemicals consumed are presented in Chapter 6 in this CTSA.

Performing a comparative analysis of the process chemical consumption rates is difficult due to the variability and site-specific nature of many of the factors that contribute to process chemical consumption. Factors affecting the rate at which process chemicals are consumed through the operation of the MHC process include:

- Characteristics of the process chemicals (i.e., composition, concentration, volatility, etc.).
- Process operating parameters (i.e., number of chemical baths, process throughput, automation, etc.).
- Bath maintenance procedures (i.e., frequency of bath replacement, replacement criteria, frequency of chemical additions, etc.).

The chemical characteristics of the process chemicals do much to determine the rate at which chemicals are consumed in the MHC process. A chemical bath containing a highly volatile chemical or mixture of chemicals can experience significant chemical losses to the air. A more concentrated process bath will lose a greater amount of process chemicals in the same volume of drag-out than a less concentrated bath. These chemical characteristics not only vary among MHC alternatives, but can also vary considerably among MHC processes offered by different chemical suppliers within the same MHC alternative category.

The physical operating parameters of the MHC process is a primary factor affecting the consumption rate of process chemicals. One such parameter is the number of chemical baths that comprise the MHC process. Many of the MHC alternatives have reduced the number of chemical process baths, not counting rinse stages, through which a panel must be processed to perform the MHC function. The number of chemical baths in an MHC technology category range from eight for electroless copper to four in the graphite substitute. The process throughput, or quantity of PWBs being passed through the MHC process, also affects chemical usage since the higher the throughput, the more process chemicals are consumed. However, conveyorized processes tend to consume less chemicals per ssf than non-conveyorized versions of the same process due to the smaller bath sizes and higher efficiencies of the automated processes.

The greatest impact on process chemical consumption can result from the bath maintenance procedures of the facility operating the process. The frequency with which baths are replaced and the bath replacement criteria used are key chemical consumption factors. Chemical suppliers typically recommend that chemical baths be replaced using established testing criteria such as concentration thresholds of bath constituents (e.g., 2 g/L of copper content). Other bath replacement criteria include ssf of PWB processed and elapsed time since the last bath replacement. The practice of making regular adjustments to the bath chemistry through additions of process chemicals consumes process chemicals, but extends the operating life of the process baths. Despite the supplier recommendations, project data showed a wide range of bath replacement practices and criteria for manufacturing facilities operating the same, as well as different, MHC technologies.

A quantitative analysis of the consumption of process chemicals could not be performed due to the variability of factors that affect the consumption of this resource. Chemical bath concentration and composition differs significantly among MHC alternatives, but can also differ considerably among chemical product lines within an MHC alternative category. Facilities operating the same MHC alternative may have vast differences in both their MHC operating parameters and bath maintenance procedures which can vary significantly from shop-to-shop and from process-to-process. Because chemical consumption can be significantly affected by so many factors not directly attributable to the type of MHC alternative (i.e., process differences within an alternative, facility operating practices, bath maintenance procedures, etc.) it is difficult to perform any quantitative analysis of chemical consumption among alternatives. Further analysis of these issues is beyond the scope of this project and is left to future research efforts.

**Wastewater Treatment Chemicals Consumption**

The desire to eliminate chelating agents from the MHC process has been a factor in the movement away from electroless copper processes and toward the development of substitute MHC processes. Chelators are chemical compounds that inhibit precipitation by forming chemical complexes with metals, allowing the metals to remain soluble in solution well past their normal solubility limits. The elimination of chelating compounds from MHC wastewater greatly simplifies the chemical precipitation process required to effectively treat the streams. A detailed description of the treatment process for both chelated and non-chelated wastes, as well as a discussion of the effect of MHC alternatives on wastewater treatment, is presented in Section 6.2, Recycle, Recovery, and Control Technologies Assessment.

The extent to which the consumption of treatment chemicals will be reduced, if any, is dependant on several factors, some of which include the rate at which wastewater is generated (e.g., the amount of rinse water consumed), the type of treatment chemicals used, composition of waste streams from other plant processes, percentage of treatment plant throughput attributable to the MHC process, the resulting reduction in MHC waste volume realized, and the extent to which the former MHC process was optimized for waste reduction. Because many of the above factors are site-specific and not dependent on the type of MHC process a quantitative evaluation would not be meaningful. However, the San Jose study mentioned previously addressed this issue qualitatively.

The San Jose study found that 21 out of 46 (46 percent) survey respondents cited ease of waste treatment as a prominent advantage of MHC alternatives. In response to a separate question, 8 out of 46 (17 percent) respondents cited copper-contaminated wastewater as a prominent disadvantage of electroless copper. Most of the facilities profiled in the study reported mixed results with regard to the effects of MHC alternatives on wastewater treatment chemical usage. Although several companies reported a decrease in the amount of treatment chemicals consumed, others reported no effect or a slight increase in consumption. It was concluded that the benefits of the reduction or elimination of chelators and their impact on the consumption of treatment chemicals is site-specific (City of San Jose, 1996).

### 5.1.2 Conclusions

A comparative analysis of the water consumption rates was performed for the MHC process alternatives. The daily water flow rate was developed for the baseline and each alternative using survey data provided by industry. A computer simulation was used to determine the operating time required to produce 350,000 ssf of PWB for each technology and a water consumption rate was determined. Calculated water consumption rates ranged from a low of 0.45 gal/ssf for the graphite process to a high of 11.7 gal/ssf for the non-conveyorized electroless copper process. The results indicate all of the alternatives consume significantly less water than the traditional non-conveyorized electroless copper process. Conveyorized processes were found to consume less water than non-conveyorized versions of the same process.

A quantitative analysis of both process chemicals and treatment chemicals consumption could not be performed due to the variability of factors that affect the consumption of these resources. The role the MHC process has in the consumption of these resources was presented and the factors affecting the consumption rates were identified.

## 5.2 ENERGY IMPACTS

Energy conservation is an important goal for PWB manufacturers, as companies strive to cut costs and seek to improve environmental performance and global competitiveness. Energy use has become an important consideration in the manufacture of PWBs as much of the manufacturing process requires potentially energy-intensive operations, such as the addition of heat to process baths. This is especially true in the operation of the MHC process, where energy is consumed by immersion heaters, fluid pumps, air blowers, agitation devices such as vibrating motors, and by conveyorized transport systems. The focus of this section is to perform a comparative analysis of the relative energy consumption rates of the baseline MHC process and process alternatives and to qualitatively assess their relative energy impacts throughout the product life cycle.

Data collected for this analysis focus on the use of MHC chemical products in PWB manufacturing. Although a quantitative life-cycle analysis is beyond the scope and resources of this project, a qualitative discussion of other life-cycle stages is presented, including a discussion of the energy impacts of manufacturing or synthesizing the chemical ingredients of MHC products, as well as a discussion of the relative life-cycle environmental impacts resulting from energy consumption during the use of MHC chemicals. Section 5.2.1 discusses energy consumption during MHC process operation. Section 5.2.2 discusses the environmental impacts of this energy consumption, while Section 5.2.3 discusses energy consumption of other life-cycle stages. Section 5.2.4 presents conclusions of the comparative energy analysis.

### 5.2.1 Energy Consumption During MHC Process Operation

To determine the relative rates of energy consumption during the operation of the MHC technologies, specific data were collected regarding energy consumption through the Performance Demonstration project and through dissemination of the Workplace Practices Survey to industry members. Energy data collected include the following:

- Process specifications (i.e., type of process, facility size, etc.).
- Physical process parameters (i.e., number of process baths, bath size, bath conditions such as temperature and mixing, etc.).
- Process automation (i.e., conveyorized, computer-controlled hoist, manual, etc.).
- Equipment description (i.e., heater, pump, motor, etc.).
- Equipment energy specifications (i.e., electric load, duty, nominal power rating, horsepower, etc.).

Each of the MHC process alternatives consist of a series of chemical baths which are typically separated by one or more water rinse steps. In order for the process to perform properly, each chemical bath should be operated within specific supplier recommended parameters, such as parameters for bath temperature and mixing. Maintaining these chemical baths within the desired parameters often requires energy-consuming equipment such as immersion heaters, fluid circulation pumps, and air blowers. In addition, the degree of process automation affects the relative rate of energy consumption. Clearly, conveyorized equipment requires energy to operate the system, but also non-conveyorized systems require additional equipment not found in conveyorized systems, such as panel agitation equipment.

Table 5.4 lists the types of energy-consuming equipment used in MHC process lines and the function of the equipment. In some cases, one piece of equipment may be used to perform a function for the entire process line. For example, panel vibration is typically performed by a single motor used to rock an apparatus that extends over all of the process tanks. The apparatus provides agitation to each individual panel rack that is connected to it, thus requiring only a single motor to provide agitation to every bath on the process line that may require it. In other cases, each process bath or stage may require a separate piece of energy-consuming equipment.

**Table 5.4 Energy-Consuming Equipment Used in MHC Process Lines**

| Type of Equipment | Function |
|---|---|
| Conveyor Drive Motor | Powers the conveyor system required to transport PWB panels through the MHC process. |
| Immersion Heater | Raise and maintain temperature of a process bath to the optimal operating temperature. |
| Fluid Pump | Circulate bath fluid to promote flow of bath chemicals through drilled through-holes and to assist filtering of impurities from bath chemistries. |
| Air Pump | Compress and blow air into process baths to promote agitation of bath to ensure chemical penetration into drilled through-holes. Also provides compressed air to processes using air knife to remove residual chemicals from PWB panels. |
| Panel Agitation Motor | Agitate apparatus used to gently rock panel racks back and forth in process baths. Not required for conveyorized processes. |
| Gas Heater | Heat PWB panels to promote drying of residual moisture remaining on the panel surface. |
| Ventilation Equipment | Provides ventilation required for MHC bath chemistries and to exhaust chemical fumes. |

To assess the energy consumption rate of each of the MHC alternatives, an energy use profile was developed for each MHC technology that identified typical sources of energy consumption during the operation of the MHC process. The number of MHC process stages that result in the consumption of energy during their operation was determined from Performance Demonstration and Workplace Practices Survey data. This information is listed in Table 5.5 according to the function of the energy-consuming equipment. For example, a typical non-conveyorized electroless copper process consists of four heated process baths, two baths requiring fluid circulation, and a single process bath that is air sparged. The panel vibration is typically performed by a single motor used to rock an apparatus that extends over all of the process tanks. Ventilation equipment is not presented in Table 5.5 because the necessary data were not collected during the Performance Demonstration or in the Workplace Practices Survey. However, the amount of ventilation required varies according to the type of chemicals, bath operating conditions, and the configuration of the process line. Because they are enclosed, the ventilation equipment for conveyorized processes are typically more energy efficient than non-conveyorized processes.

**Table 5.5 Number of MHC Process Stages that Consume Energy by Function of Equipment**

| Process Type | Function of Equipment[a] | | | | | |
|---|---|---|---|---|---|---|
| | Conveyor | Bath Heat | Fluid Circulation | Air Sparging[b] | Panel Agitation[c] | Panel Drying |
| Electroless Copper, non-conveyorized (BASELINE) | 0 | 4 | 2 | 1 | 1 | 0 |
| Electroless Copper, conveyorized | 1 | 5 | 7 | 0 | 0 | 0 |
| Carbon, conveyorized | 1 | 2 | 6 | 0 | 0 | 2 |
| Conductive Polymer, conveyorized | 1 | 2 | 4 | 0 | 0 | 0 |
| Graphite, conveyorized | 1 | 1 | 4 | 0 | 0 | 1 |
| Non-Formaldehyde Electroless Copper, non-conveyorized | 0 | 5 | 2 | 0 | 1 | 0 |
| Organic-Palladium, non-conveyorized | 0 | 3 | 3 | 0 | 1 | 0 |
| Organic-Palladium, conveyorized | 1 | 3 | 7 | 0 | 0 | 0 |
| Tin-Palladium, non-conveyorized | 0 | 3 | 3 | 1 | 1 | 0 |
| Tin-Palladium, conveyorized | 1 | 3 | 9 | 0 | 0 | 0 |

[a] Table entries for each MHC alternative represent the number of process baths requiring each specific function. All functions are supplied by electric equipment, except for drying, which is performed by gas-fired oven.
[b] Air sparging is used selectively by some manufacturers to enhance bath performance. Sparging may not be required for all product lines or facilities using an alternative.
[c] Processes reporting panel agitation for one or more baths are entered as one in the summary regardless of the number since a single motor can provide agitation for the entire process line.

The electrical energy consumption of MHC line equipment as well as equipment specifications (power rating, average duty, and operating load), were collected during the Performance Demonstration. In cases where electricity consumption data were not available, the electricity consumption rate was calculated using the following equation and equipment specifications:

$$EC = NPR \times OL \times AD \times (1kW/0.746\ HP)$$

where:

EC = electricity consumption rate (kWh/day)
NPR = nominal power rating (HP)
OL = operating load (%), or the percentage of the maximum load or output of the equipment that is being used
AD = average duty (h/day), or the amount of time per day that the equipment is being operated at the operating load

Electricity consumption data for each equipment category were averaged to determine the average amount of electricity consumed per hour of operation for each type of equipment per process. The natural gas consumption rate for a drying oven was supplied by an equipment vendor. Electricity and natural gas consumption rates for MHC equipment per process stage are presented in Table 5.6.

**Table 5.6 Energy Consumption Rates for MHC Equipment**

| Function of Equipment | Type of Equipment | Energy Consumption Rates Per Process Stage | |
|---|---|---|---|
| | | Electricity[a] (kW/hr) | Natural Gas[b] ($ft^3$/hr) |
| Conveyorized Automation | Conveyor System | 14.1 | - |
| Non-Conveyorized Process Line[c] | Panel Agitation Motor | 3.1 | - |
| Heat | Immersion Heater | 4.8 | - |
| Fluid Circulation | Fluid Pump | 0.7 | - |
| Air Sparging | Air Pump | 3.5 | - |
| Drying Oven | Gas Heater | - | 90 |

[a] Electricity consumption rates for each type of equipment were calculated by averaging energy consumption data per stage from the performance demonstrations. If required, consumption data were calculated from device specifications and converted to total kW/hr per bath using 1 HP = 0.746 kW.
[b] Natural gas consumption rate for the gas heater was estimated by an equipment vendor (Exair Corp.).
[c] Non-conveyorized process lines are assumed to be manually operated with no automated panel transport system. The electricity consumption rate reported includes the electricity consumed by a panel agitation motor.

The total electricity consumption rate for each MHC alternative was calculated by multiplying the number of process stages that consume electricity (Table 5.5) by the appropriate electricity consumption rate (Table 5.6) for each equipment category, then summing the results. The calculations are described by the following equation:

$$ECR_{total} = \sum_{i=1}^{n} [NPS_i \times ECR_i]$$

where:

$ECR_{total}$ = total electricity consumption rate (kW/h)
$NPS_i$ = number of process stages requiring equipment i
$ECR_i$ = energy consumption rate for equipment i (kW/h)

Natural gas consumption rates were calculated using a similar method. The individual energy consumption rates for both natural gas and electricity were then converted to British Thermal Units (Btu) per hour and summed for each alternative to give the total energy consumption rate for each MHC alternative. The individual consumption rates for both natural gas and electricity, as well as the hourly energy consumption rate calculated for each of the MHC process alternatives are listed in Table 5.7.

These energy consumption rates only consider the types of equipment listed in Table 5.4, which are commonly recommended by chemical suppliers to successfully operate an MHC process. However, equipment such as ultrasonics, automated chemical feed pumps, vibration units, panel feed systems, or other types of electrically powered equipment may be part of the MHC process line. The use of this equipment may improve the performance of the MHC line, but is not required in a typical process for any of the MHC technologies.

**Table 5.7 Hourly Energy Consumption Rates for MHC Alternatives**

| Process Type | Energy Consumption Rates | | Hourly Consumption Rate[a] (Btu/hr) |
|---|---|---|---|
| | Electricity (kW/hr) | Natural Gas ($ft^3$/hr) | |
| Electroless Copper, non-conveyorized (BASELINE) | 27.2 | - | 92,830 |
| Electroless Copper, conveyorized | 43 | - | 146,750 |
| Carbon, conveyorized | 27.2 | 180 | 276,430 |
| Conductive Polymer, conveyorized | 26.5 | - | 90,440 |
| Graphite, conveyorized | 21.7 | 90 | 165,860 |
| Non-Formaldehyde Electroless Copper, non-conveyorized | 28.5 | - | 97,270 |
| Organic-Palladium, non-conveyorized | 19.6 | - | 66,890 |
| Organic-Palladium, conveyorized | 33.4 | - | 113,990 |
| Tin-Palladium, non-conveyorized | 23.1 | - | 78,840 |
| Tin-Palladium, conveyorized | 34.8 | - | 118,770 |

[a] Electrical energy was converted at the rate of 3,413 Btu per kilowatt hour where a kWh = 1 kW/hr. Natural gas consumption was converted at the rate of 1,020 Btu per cubic feet of gas consumed.

To determine the overall amount of energy consumed by each technology, the hourly energy consumption rate from Table 5.7 was multiplied by the amount of time needed for each alternative to manufacture 350,000 ssf of board (the average MHC throughput of respondents to the Workplace Practices Survey). Because insufficient survey data exist to accurately estimate the amount of time required for each process to produce the 350,000 ssf of board, the operating time was simulated using a computer model developed for each alternative. The results of the simulation along with a discussion of the data and parameters used to define each alternative are presented in Section 4.2, Cost Analysis. The hours of MHC operation required to produce 350,000 ssf of board from the simulation, the total amount of energy consumed, and the energy consumption rate for each alternative per ssf of board produced are presented in Table 5.8.

Table 5.8 shows that all of the alternatives are more energy efficient than the traditional non-conveyorized electroless copper process. This is primarily attributable to a process operating time for non-conveyorized electroless copper that is two to eight times greater than the operating times of the alternatives. Other processes with high energy consumption rates include non-formaldehyde electroless copper due to its long operating time and both carbon and graphite due to their high hourly consumption rates. The three processes consuming the least energy per unit of production are the organic-palladium non-conveyorized system and the conductive polymer and tin-palladium conveyorized systems.

The performance of specific MHC processes with respect to energy is primarily dependent on the hourly energy consumption rate (Table 5.7) and the overall operating time for the process (Table 5.8). Non-conveyorized processes typically have lower hourly consumption rates than conveyorized processes because the operation of conveyorized equipment is more energy-intensive. Although conveyorized processes typically have higher hourly consumption rates, these differences are more than offset by the shorter operating times that are required to produce an equivalent quantity of PWBs.

**Table 5.8 Energy Consumption Rate per ssf of Board Produced for MHC Alternatives**

| Process Type | Process Operating Time[a] (hours) | Total Energy Consumed (Btu/350,000 ssf) | Energy Consumption Rate (Btu/ssf) |
|---|---|---|---|
| Electroless Copper, non-conveyorized (BASELINE) | 2,160 | $2.01 \times 10^8$ | 573 |
| Electroless Copper, conveyorized | 329 | $4.83 \times 10^7$ | 138 |
| Carbon, conveyorized | 650 | $1.80 \times 10^8$ | 514 |
| Conductive Polymer, conveyorized | 367 | $3.31 \times 10^7$ | 94.7 |
| Graphite, conveyorized | 450 | $7.46 \times 10^7$ | 213 |
| Non-Formaldehyde Electroless Copper, non-conveyorized | 971 | $9.44 \times 10^7$ | 270 |
| Organic-Palladium, non-conveyorized | 350 | $2.34 \times 10^7$ | 66.9 |
| Organic-Palladium, conveyorized | 456 | $5.19 \times 10^7$ | 148 |
| Tin-Palladium, non-conveyorized | 581 | $4.58 \times 10^7$ | 131 |
| Tin-Palladium, conveyorized | 284 | $3.38 \times 10^7$ | 96.4 |

[a] Times listed represent the operating time required to manufacture 350,000 ssf of board by each process as simulated by computer model.

When MHC processes with both non-conveyorized and conveyorized versions are compared, the conveyorized versions of the alternatives are typically more energy efficient. Table 5.8 shows this to be true for both the electroless copper and tin-palladium processes. The organic-palladium processes are the exceptions. The non-conveyorized configuration of this process not only has a better hourly consumption rate than the conveyorized, but also benefits from a faster operating time, a condition due to the low number of process baths and its short rate-limiting step.[1] These factors combine to give the non-conveyorized organic-palladium process a lower energy consumption rate than the conveyorized version and make it the most energy efficient process evaluated.

Finally, it should be noted that the overall energy use experienced by a facility will depend greatly upon the operating practices and the energy conservation measures adopted by that facility. To minimize energy use, several simple energy conservation opportunities are available and should be implemented. These include insulating heated process baths, using thermostats on heaters, and turning off equipment when not in use.

### 5.2.2 Energy Consumption Environmental Impacts

The production of energy results in the release of pollution into the environment, including pollutants such as carbon dioxide ($CO_2$), sulfur oxides ($SO_x$), carbon monoxide (CO), sulfuric acid ($H_2SO_4$), and particulate matter. The type and quantity of pollution depends on the method of energy production. Typical energy production facilities in the U.S. include hydroelectric, nuclear, and coal-fired generating plants.

[1] The rate-limiting step is the process step that requires more time than the other steps, thus limiting the feed rate for the system.

The environmental impacts attributable to energy production resulting from the differences in energy consumption among MHC alternatives were evaluated using a computer program developed by EPA National Risk Management Research Laboratory called *P2P- version 1.50214* (EPA, 1994). This program can, among other things, estimate the type and quantity of pollutant releases resulting from the production of energy as long as the differences in energy consumption and the source of the energy used (i.e., does the energy come from a coal-fired generating plant, or is it thermal energy from a oil-fired boiler, etc.) are known. The program uses data reflecting the "national average" pollution releases per kilowatt-hour derived from particular sources. Electrical power derived from the average national power grid was selected as the source of electrical energy, while natural gas was used as the source of thermal energy for this evaluation. Energy consumption rates from Table 5.7 were multiplied by the operating time required to produce 350,000 ssf of board reported for each alternative in Table 5.8. These totals were then divided by 350,000 to get the electrical and thermal energy consumed per ssf of board, which were then used as the basis for the analysis. Results of the environmental impact analysis from energy production have been summarized and are presented in Table 5.9. Appendix H contains printouts from the P2P program for each alternative.

Although the pollutant releases reported in Table 5.9 are combined for all media (i.e. air, water, and land), they often occur in one or more media where they may present different hazards to human health or the environment. To allow a comparison of the relative effects of any pollution that may occur, it is necessary to identify the media of releases. Table 5.10 displays the pollutants released during the production of energy, the media into which they are released, and the environmental and human health concerns associated with each pollutant.

The information presented in Tables 5.9 and 5.10 show that the generation of energy is not without environmental consequences. Pollutants released to air, water, and soil resulting from energy generation can pose direct threats to both human health and the environment. As such the consumption of energy by the MHC process contributes directly to the type and magnitude of these pollutant releases. Primary pollutants released from the production of electricity include carbon dioxide, solid wastes, sulfur oxides and nitrogen oxides. These pollutants contribute to a wide range of environmental and human health concerns. Natural gas consumption results primarily in releases of carbon dioxide and hydrocarbons which typically contribute to environmental problems such as global warming and smog. Because all of the MHC alternatives consume less energy than the traditional non-conveyorized electroless copper process, they all decrease the quantity of pollutants released into the environment resulting from the generation of the energy consumed during the MHC process.

**Table 5.9 Pollution Resulting From the Generation of Energy Consumed by MHC Technologies**

| MHC Alternative | Types of Pollutants Released (g/ssf)[a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Carbon Dioxide ($CO_2$) | Carbon Monoxide (CO) | Dissolved Solids | Hydrocarbons | Nitrogen Oxides ($NO_x$) | Particulates | Solid Wastes | Sulfur Oxides ($SO_x$) | Sulfuric Acid ($H_2SO_4$) |
| Electroless Copper, non-conveyorized (BASELINE) | 120 | 0.160 | 0.022 | 0.140 | 0.510 | 0.190 | 14.0 | 1.00 | 0.086 |
| Electroless Copper, conveyorized | 28 | 0.040 | 0.005 | 0.034 | 0.120 | 0.047 | 3.4 | 0.25 | 0.021 |
| Carbon, conveyorized | 56 | 0.059 | 0.008 | 0.260 | 0.180 | 0.060 | 4.3 | 0.32 | 0.026 |
| Conductive Polymer, conveyorized | 19 | 0.027 | 0.004 | 0.024 | 0.084 | 0.032 | 2.3 | 0.17 | 0.014 |
| Graphite, conveyorized | 27 | 0.031 | 0.004 | 0.098 | 0.094 | 0.033 | 2.4 | 0.18 | 0.014 |
| Non-Formaldehyde Electroless Copper, non-conveyorized | 55 | 0.078 | 0.010 | 0.067 | 0.240 | 0.092 | 6.7 | 0.48 | 0.041 |
| Organic-Palladium, non-conveyorized | 14 | 0.019 | 0.003 | 0.017 | 0.060 | 0.023 | 1.7 | 0.12 | 0.010 |
| Organic-Palladium, conveyorized | 30 | 0.043 | 0.006 | 0.037 | 0.130 | 0.051 | 3.7 | 0.27 | 0.022 |
| Tin-Palladium, non-conveyorized | 27 | 0.038 | 0.005 | 0.033 | 0.120 | 0.045 | 3.2 | 0.23 | 0.020 |
| Tin-Palladium, conveyorized | 20 | 0.028 | 0.004 | 0.024 | 0.086 | 0.033 | 2.4 | 0.17 | 0.015 |

[a] Pollutant totals calculated using the computer program *P2P version 1.50214* developed by EPA's National Risk Management Research Laboratory.

**Table 5.10 Pollutant Environmental and Human Health Concerns**

| Pollutant | Medium of Release | Environmental and Human Health Concerns |
|---|---|---|
| Carbon Dioxide ($CO_2$) | Air | Global warming |
| Carbon Monoxide (CO) | Air | Toxic organic,[a] smog |
| Dissolved Solids | Water | Dissolved solids[b] |
| Hydrocarbons | Air | Odorant, smog |
| Nitrogen Oxides ($NO_x$) | Air | Toxic inorganic,[a] acid rain, corrosive, global warming, smog |
| Particulates | Air | Particulates[c] |
| Solid Wastes | Soil | Land disposal capacity |
| Sulfur Oxides ($SO_x$) | Air | Toxic inorganic,[a] acid rain, corrosive |
| Sulfuric Acid ($H_2SO_4$) | Water | Corrosive, dissolved solids[b] |

[a] Toxic organic and inorganic pollutants can result in adverse health effects in humans and wildlife.
[b] Dissolved solids are a measure of water purity and can negatively affect aquatic life as well as the future use of the water (e.g., salinity can affect the water's effectiveness at crop irrigation).
[c] Particulate releases can promote respiratory illness in humans.

### 5.2.3 Energy Consumption in Other Life-Cycle Stages

When performing a comparative evaluation among MHC technologies, the energy consumed throughout the entire life cycle of the chemical products in the technology should be considered. The product use phase is only one aspect of the environmental performance of a product. A life-cycle analysis considers all stages of the life of a product, beginning with the extraction of raw materials from the environment, and continuing on through the manufacture, transportation, use, recycle, and ultimate disposal of the product.

Each stage within this life cycle consumes energy. It is possible for a product to be energy efficient during the use phase of the life cycle, yet require large amounts of energy to manufacture or dispose of the product. The manufacture of graphite is an example of an energy-intensive manufacturing process. Graphite is manufactured by firing carbon black particles to temperatures over 3000 °F for several hours, which is required to give a crystalline structure to the otherwise amorphic carbon black particles (Thorn, 1996). There are also energy consumption differences in the transportation of wastes generated by an MHC line. The transportation of large quantities of sludge resulting from the treatment of processes with chelated waste streams (i.e., electroless copper) will consume more energy than the transportation of smaller quantities of sludge resulting from processes that do not use chelators. These examples show that energy use from other life-cycle stages can be significant and should be considered when evaluating the energy performance of a product. However, a comprehensive assessment of other life-cycle stages was beyond the scope of this study.

### 5.2.4 Conclusions

A comparative analysis of the relative energy consumption rates was performed for the MHC technologies. An hourly energy consumption rate was developed for the baseline and each alternative using data collected from industry through a survey. A computer simulation was used to determine the operating time required to produce 350,000 ssf of PWB and an energy

consumption rate per ssf of PWB was calculated. The energy consumption rates ranged from 66.9 Btu/ssf for the non-conveyorized organic-palladium process to 573 Btu/ssf for the non-conveyorized electroless copper process. The results indicate all of the MHC alternatives are more energy efficient than the traditional non-conveyorized electroless copper process. It was also found that for alternatives with both types of automation, the conveyorized version of the process is typically the more energy efficient, with the notable exception of the organic-palladium process.

An analysis of the impacts directly resulting from the production of energy consumed by the MHC process showed that the generation of the required energy is not without environmental consequence. Pollutants released to air, water, and soil can result in damage to both human health and the environment. The consumption of natural gas tends to result in releases to the air which contribute to odor, smog and global warming, while the generation of electricity can result in pollutant releases to all media with a wide range of possible affects. Since all of the MHC alternatives consume less energy than electroless copper, they all result in less pollutant releases to the environment from energy production.

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# Chapter 6
# Additional Environmental Improvement Opportunities

This chapter of the Cleaner Technologies Substitute Assessment (CTSA) identifies and qualitatively discusses techniques that can be used by printed wiring board (PWB) manufacturing facilities to prevent pollution, minimize waste, recycle and recover valuable resources, and control releases. The Pollution Prevention Act of 1990 set forth the following hierarchy to waste management in order of desirability:

- Pollution prevention at the source.
- Recycling in an environmentally safe manner.
- Treatment in an environmentally safe manner.
- Disposal or other release into the environment only as a last resort and in an environmentally safe manner.

This hierarchy has been adopted by EPA as the preferred method of waste management to reduce or eliminate potential releases by industry. The hierarchy reflects the common sense notion that preventing pollution is preferable to any subsequent response, be it recycling, treatment, or disposal. By preventing pollution we also eliminate potential transfers of the pollution across media (Kling, 1995).

The hierarchy also recognizes that pollution prevention is not always feasible and that other waste management methods are often required. When pollution prevention is not feasible, we should turn in order to recycling, treatment, and finally disposal if no other option remains. A manufacturing facility often combines pollution prevention techniques with these other approaches to effectively reduce emissions from a production process. While pollution prevention is clearly the most desirable, all of these methods contribute to overall environmental improvement (Kling, 1995).

This chapter focuses on the application of the waste management hierarchy to potential waste streams generated by the making holes conductive (MHC) process of the PWB industry. Techniques are identified, organized, and presented in an order corresponding to the hierarchy. Pollution prevention techniques are presented in Section 6.1, while methods for minimizing waste, recycling or recovering resources, and controlling releases are presented in Section 6.2. While the focus of this chapter is on the MHC line, many of the techniques described here can be applied to other processes used in PWB manufacturing. A series of pollution prevention case studies developed by the EPA DfE Program for the PWB industry present examples of the successful implementation of techniques available to industry (EPA, 1995a; EPA, 1995b; EPA, 1996a; EPA, 1996b; EPA, 1996c).

## 6.1 POLLUTION PREVENTION

Pollution prevention, defined in the Pollution Prevention Act of 1990, is the reduction in the amounts or hazards of pollution at the source and is often referred to as source reduction. Source reduction, also defined in the Pollution Prevention Act, is any practice which: 1) reduces the amount of any hazardous substance, pollutant, or contaminant entering any waste stream or otherwise released into the environment (including fugitive emissions) prior to recycling, treatment, or disposal; and 2) reduces the hazards to public health and the environment associated with the release of such substances, pollutants, or contaminants. Source reduction includes equipment or technology modification, process or procedure modifications, reformulation or redesign of products, substitution of raw materials, and improvements in housekeeping, maintenance, training, or inventory control.

Current pollution prevention practices within the PWB industry were identified and data were collected through contact with industry personnel, extensive review of published accounts, and through the design and dissemination of two information requests to PWB manufacturers. The IPC Workplace Practices Questionnaire, conducted as part of this CTSA, specifically focused on the MHC process to identify important process parameters and operating practices for the various MHC technologies. For a breakdown of respondents by alternative, refer to Section 1.3.4 of the Introduction. Facility characteristics of respondents are presented in Section 3.2, Exposure Assessment. The questionnaire used in the IPC Workplace Practices Questionnaire is presented in Appendix A.

The Pollution Prevention and Control Technology Survey (hereafter referred to as the Pollution Prevention Survey) was designed to collect information about past and present pollution prevention procedures and control technologies for the entire PWB manufacturing process. This Survey was performed by the DfE PWB Project and is documented in the EPA publication, *Printed Wiring Board Pollution Prevention and Control: Analysis of Survey Results* (EPA, 1995c). The Survey results presented periodically throughout this chapter are compiled from responses to the Pollution Prevention Survey unless otherwise indicated. Results from the Pollution Prevention Survey pertaining to recycle or control technologies are presented in Section 6.2 of this chapter.

Opportunities for pollution prevention in PWB manufacturing were identified in each of the following areas:

- Management and personnel practices.
- Materials management and inventory control.
- Process improvements.

The successful implementation of pollution prevention practices can lead to reductions in waste treatment, pollution control, environmental compliance, and liability costs. Cost savings can result directly from pollution prevention techniques that minimize water usage, chemical consumption, and process waste generation.

### 6.1.1 Management and Personnel Practices

Pollution prevention is an ongoing activity that requires the efforts of both management and employees to achieve the best results. While management's commitment to reducing pollution is the foundation upon which a successful pollution prevention program is built, any pollution prevention measures taken are ultimately implemented by the process employees, making them an integral part of any pollution prevention effort. Management and employees must work together to form an effective pollution prevention program.

Approximately half (52.6 percent) of the PWB companies responding to the Pollution Prevention Survey reported having a formal pollution prevention policy statement while half (50 percent) of the survey respondents reported having a pollution prevention program. Over two thirds (68.4 percent) of PWB companies surveyed reported conducting employee education for pollution prevention.

The scope and depth of pollution prevention planning and the associated activities will vary with the size of the facility. While larger facilities may go through an entire pollution prevention planning exercise (as described below), smaller facilities may require as little as a commitment by the owner to pollution prevention along with cooperation and assistance from employees to meet any stated goals. A list of management and personnel practices that promote pollution prevention, along with their benefits, are listed in Table 6.1.

**Table 6.1 Management and Personnel Practices Promoting Pollution Prevention**

| Method | Benefits |
|---|---|
| Create a company pollution prevention and waste reduction policy statement. | Communicates to employees and states publicly the company commitment to achieving pollution prevention and waste reduction goals. |
| Develop a written pollution prevention and waste reduction plan. | Communicates to employees how to accomplish the goals identified in the company's policy statement. Identifies in writing specific implementation steps for pollution prevention. |
| Provide periodic employee training on pollution prevention. | Educates employees on pollution prevention practices. |
| Make employees accountable for their pollution prevention performance and provide feedback on their performance. | Provides incentives to employees to improve pollution prevention performance. |
| Promote internal communication between management and employees. | Informs employees and facilitates input on pollution prevention from all levels of the company. |
| Implement total cost accounting or activity-based accounting system. | Identifies true costs of waste generation and the benefits of pollution prevention. |

A company's commitment to pollution prevention begins with a pollution prevention and waste reduction policy statement. This statement, which is the company's public proclamation of its dedication to preventing pollution and reducing waste, should clearly state why a program is being undertaken, include specific pollution prevention and waste reduction goals, and assign responsibility for accomplishing those goals. The statement details to the public and to its employees the depth of the company's commitment to pollution prevention.

A pollution prevention plan is needed to detail how the pollution prevention and waste reduction goals described in the company's policy statement will be achieved. The pollution prevention plan builds on the company's policy statement by:

- Creating a list of waste streams and their point sources.
- Identifying opportunities for pollution prevention.
- Evaluating and prioritizing waste reduction options.
- Developing an implementation strategy for options that are feasible.
- Creating a timetable for pollution prevention implementation.
- Detailing a plan for measuring and evaluating pollution prevention and waste reduction progress.

The plan is best developed with input drawn from the experiences of a team of people selected from levels throughout the company. The team approach provides a variety of perspectives to pollution prevention and helps to identify pollution prevention opportunities and methods for implementing them. Team members should include representatives from management, supervisory personnel, and line workers who are familiar with the details of the daily operation of the process. The direct participation of employees in the development of the pollution prevention plan is important since it is the employees who are responsible for implementing the plan.

Data should be collected by performing a waste minimization assessment on the company or process being targeted. Once identified, pollution prevention options should be evaluated and prioritized based on their cost, feasibility of implementation, and their overall effectiveness of reducing waste. After an implementation strategy and timetable is established, the plan, along with expected benefits, should be presented to the remaining company employees to communicate the company's commitment to pollution prevention.

Once the pollution prevention plan has been finalized and implementation is ready to begin, employees must be given the skills to implement the plan. Training programs play an important role in educating process employees about current pollution prevention practices and opportunities. The goal of the training program is to educate each employee on how waste is generated, its effects on worker safety and the environment, possible methods for waste reduction, and on the overall benefits of pollution prevention.

Employee training should begin at the time of new employee orientation, introducing them to the company's pollution prevention plan, thus highlighting the company's dedication to reducing waste. More advanced training focusing on process operating procedures, potential sources of release, and pollution prevention practices already in place should be provided after a few weeks of work or when an employee starts a new position. Retraining employees periodically will keep them focused on the company's goal of pollution prevention.

Effective communication between management and employees is an important part of a successful pollution prevention program. Reports to employees on the progress of implementing pollution prevention recommendations, as well as the results of actions already taken, reiterate management's commitment to reducing waste, while keeping employees informed and intimately

involved in the process. Employee input should also be solicited both during and after the creation of the pollution prevention plan to determine if any changes in the plan are warranted.

Assigning responsibility for each source of waste is an important step in closing the pollution prevention loop. Making individual employees and management accountable for chemical usage and waste generated within their process or department provides incentive for employees to reduce waste. The quantity of waste generated should be tracked and the results reported to employees who are accountable for the process generating the waste. Progress in pollution prevention should be an objective upon which employees will be evaluated during performance reviews, once again emphasizing the company's commitment to waste reduction.

Employee initiative and good performance in pollution prevention areas should be recognized and rewarded. Employee suggestions that prove feasible and cost effective should be implemented and the employee recognized either with a company commendation or with some kind of material award. These actions will ensure continued employee participation in the company's pollution prevention efforts.

Implementing an activity-based or total cost accounting system will identify the costs of waste generation that are typically hidden in overhead costs by standard accounting systems. These cost accounting methods identify cost drivers (activities) within the manufacturing process and assign the costs incurred through the operation of the process to the cost drivers. By identifying the cost drivers, manufacturers can correctly assess the true cost of waste generation and the benefits of any pollution prevention efforts.

### 6.1.2 Materials Management and Inventory Control

Materials management and inventory control focuses on how chemicals and materials flow through a facility in order to identify opportunities for pollution prevention. A proper materials management and inventory control program is a simple, cost-effective approach to preventing pollution. Table 6.2 presents materials management and inventory control methods that can be used to prevent pollution.

**Table 6.2 Materials Management and Inventory Control Pollution Prevention Practices**

| Practice | Benefits |
|---|---|
| Minimize the amount of chemicals kept on the floor at one time. | Provides incentives to employees to use less chemicals. |
| Manage inventory on a first-in, first-out basis. | Reduces materials and disposal costs of expired chemicals. |
| Centralize responsibility for storing and distributing chemicals. | Provides incentives to employees to use less chemicals. |
| Store chemical products in closed, clearly marked containers. | Reduces materials loss; increases worker safety by reducing worker exposure. |
| Use a pump to transfer chemical products from stock to transportation container. | Reduces potential for accidental spills; reduces worker exposure. |

Controlling inventory levels and limiting access to inventory are widely used practices in the PWB manufacturing industry (78.9 percent of Pollution Prevention Survey respondents). Keeping track of chemical usage and limiting the amount of chemicals on the process floor provides process operators an incentive to use the minimum quantity of chemical required to do the job. Using chemicals on a first-in/first-out basis reduces the time chemicals spend in storage and the amount of expired chemical that is disposed. Some companies have contracted with a specific chemical supplier to provide all of their process chemicals and manage their inventory. In exchange for the exclusive contract, the chemical supplier assumes many of the inventory management duties including managing the inventory, material safety data sheets (MSDSs), ordering the chemicals, distributing the chemicals throughout the plant, and disposing of spent chemicals and packaging (Brooman, 1996).

Chemical storage and handling practices also provide pollution prevention opportunities. Ensuring that all chemical containers are kept closed when not in use minimizes the amount of chemical lost through evaporation or volatilization. When transferring chemicals from container to container, utilizing a hand pump can reduce the amount of chemical spillage. These simple techniques not only result in less chemical usage representing a cost savings, but also result in reduced worker exposure and an improved worker environment.

### 6.1.3 Process Improvements

Improving the efficiency of a production process can significantly reduce waste generation at the source. Process improvements include process or procedural changes in operations carried out by employees, process equipment modification or automation, and redesign of the process altogether. Process improvements that lead to pollution prevention in the MHC process are categorized by the following goals:

- Extend chemical bath life.
- Reduce water consumption.
- Improve process efficiency through automation.

Pollution prevention through process improvement does not always have to be expensive. In fact, some of the most cost-effective pollution prevention techniques are simple, inexpensive changes in production procedures. Process improvements that help achieve the goals listed above, along with their benefits, are discussed in detail in the sections below.

**Extend Chemical Bath Life**

The MHC process involves the extensive use of chemicals, many of which are costly and pose a hazard to human health and the environment. Improvements in the efficient usage of these chemicals can occur by accomplishing the following:

- Reducing chemical bath contamination.
- Reducing chemical bath drag-out.
- Improving bath maintenance.

Inefficiencies in the use of chemicals can result in increased chemical usage, higher operating costs, increased releases to the environment, and increased worker exposure. Techniques to improve the efficient use of chemicals by the MHC and other PWB process steps are discussed in detail below.

**Reduce Bath Contaminants.** The introduction of contaminants to a chemical bath will affect its performance and significantly shorten the life of the chemical bath. Bath contaminants include chemicals dragged-in from previous chemical baths, chemical reaction by-products, and particulate matter which may be introduced to the bath from the air. Process baths are replaced when impurities reach a level where they degrade product quality to an unacceptable level. Any measure that prevents the introduction of impurities will not only result in better bath performance, but also will reduce chemical usage and generate less waste. Table 6.3 presents pollution prevention methods for reducing bath contamination.

**Table 6.3 Pollution Prevention Practices to Reduce Bath Contaminants**

| Practices | Benefits |
|---|---|
| Improve the efficiency of the water rinse system. | Rinses off any residual bath chemistries and dislodges any particulate matter from panels and racks. |
| Use distilled or deionized water during chemical bath make-up. | Reduces chemical contamination resulting from water impurities. |
| Maintain and rebuild panel racks. | Prevents the build-up of deposits and corrosion that can dislodge or dissolve into chemical baths. |
| Clean process tanks efficiently before new bath make-up. | Prevents contamination of the new bath from residual spent bath chemistries. |
| Utilize chemical bath covers when process baths are not in operation. | Reduces the introduction of unwanted airborne particulate matter; prevents evaporation or volatilization of bath chemistries. |
| Filter contaminants continuously from process baths. | Prevents the build-up of any contaminants. |

Thorough and efficient water rinsing of process panels and the racks that carry them is crucial to preventing harmful chemical drag-in and to prolonging the life span of the chemical baths. The results of the IPC Workplace Practices Questionnaire indicate that nearly every chemical bath in the MHC process is preceded by at least one water rinse tank. Improved rinsing can be achieved by using spray rinses, panel and/or water agitation, warm water, or by several other methods that do not require the use of a greater volume of water. A more detailed discussion of these methods is presented in the reduced water consumption portion in this section.

A rack maintenance program is also an important part of reducing chemical bath contamination and is practiced by 87 percent of the respondents to the Pollution Prevention Survey. By cleaning panel racks regularly and replacing corroded metal parts, preferably with parts of plastic or stainless steel, chemical deposition and build-up can be minimized. Respondents to the IPC Workplace Practices Questionnaire typically perform rack cleaning using a chemical solution, usually acid. Mechanical methods, such as peeling or filing away the

majority of any metal deposits before applying a weak acid solution, can be used to prevent pollution by reducing the quantity of acid required. An added benefit is that the reclaimed metal can be sold or reused in the process.

According to the IPC Workplace Practices Questionnaire, 42 percent of the respondents reported using bath covers on at least some of their baths during periods when the MHC process was not operating. Respondents were not specifically questioned about the other methods for reducing bath contamination described above; consequently, no information was collected.

**Chemical Bath Drag-Out Reduction.** The primary loss of bath chemicals during the operation of the MHC process comes from chemical bath drag-out (Bayes, 1996). This loss occurs as the rack full of panels is being removed from the bath, dragging with it a film of chemical solution still coating the panels. The drag-out is then typically rinsed from the panels by a water rinse tank, making bath drag-out the primary source of chemical contaminant introduction into the MHC rinse water. In some cases, however, the panels are deposited directly into the next process bath without first being rinsed (e.g., predip followed directly by palladium catalyst in tin-palladium process).

Techniques that minimize bath drag-out also prevent the premature reduction of bath chemical concentration, extending the useful life of a bath. In addition to extended bath life, minimizing or recovering drag-out losses also has the following effects:

- Requires less rinse water.
- Minimizes bath chemical usage.
- Reduces chemical waste.
- Requires less water treatment chemical usage.

Methods for reducing or recovering chemical bath drag-out are presented in Table 6.4 and then discussed below.

The most common methods of drag-out control employed by respondents to the Pollution Prevention Survey are slow panel removal from the bath (52.6 percent) and increased panel drainage time (76.3 percent). Removing the panels slowly from the bath allows the surface tension of the solution to remove much of the residual chemical from the panels. Most of the remaining chemicals can be removed from the panel surfaces by increasing the time allowed for the panels to drain over the process bath. Briefly agitating the panels directly after being removed from the tank can also help dislodge chemicals trapped in panel through-holes and result in better drainage. All three methods require no capital investment and when practiced individually or in combination, these techniques are effective methods for reducing drag-out.

Drain boards catch drag-out chemicals that drip from panels as they are transported to the next process step. The chemicals are then returned to the original process bath. Chemical loss due to splashing can be prevented by the use of drip shields, which are plastic panels that extend the wall height of the process tank. Both drain boards and drip shields are inexpensive, effective drag-out control options. Unlike drip shields, however, space between process steps is required to install drain boards, making them impractical where process space is an issue.

**Table 6.4 Methods for Reducing Chemical Bath Drag-Out**

| Methods | Benefits |
|---|---|
| Remove panels slowly from process baths. | Reduces the quantity of residual chemical on panel surfaces. |
| Increase panel drainage time over process bath. | Allows a greater volume of residual bath chemistries to drip from the panel back into the process bath. |
| Agitate panels briefly while draining. | Dislodges trapped bath chemistries from drilled through-holes. |
| Install drain boards. | Collects and returns drag-out to process baths. |
| Install drip shields between process baths. | Prevents bath chemical loss due to splashing. |
| Add static drag-out tanks/drip tanks to process line where needed. | Recovers chemical drag-out for use in bath replenishment. |
| Utilize non-ionic wetting agents in the process bath chemistries. | Reduces surface tension of bath solutions, thereby reducing residual chemicals on panel surfaces. |
| Utilize air knives directly after process bath in conveyorized system.[a] | Blows residual process chemistries from process panels which are recaptured and returned to process bath. |
| Decrease process bath viscosity. | Reduces quantity of chemical that adheres to panel surface. |
| Employ fog rinses/spray rinses over heated baths. | Rinses drag-out from the panels as they are removed from the solution. |

[a] May not be a viable pollution prevention technique unless system is fully enclosed to prevent worker exposure to bath chemicals introduced to the air.

Much of the chemical solution lost to drag-out can be recovered through the use of either static drag-out tanks or drip tanks. A static drag-out tank is a batch water bath that immediately follows the process bath from which the drag-out occurs. The panels are submerged and agitated in the static rinse water, washing the residual chemicals from the panel's surface. When sufficiently concentrated, the rinse water and chemical mixture can be used to replenish the original bath. Drip tanks are similar to static drag-out tanks except that they contain no water. The drip tank collects chemical drag-out which can then be returned to the process bath. Static drag-out tanks are most suitably used in conjunction with heated process baths which lose water by evaporation, requiring frequent replacement.

Bath viscosity can be lowered by increasing bath temperature, decreasing bath concentration, or both. Both of these methods may negatively affect overall process performance if done in excess, however, and the chemical supplier should be consulted. In addition, increased bath temperatures can increase chemical volatilization and worker exposure. Energy implications of higher temperature baths should also be considered and are discussed in Section 5.2.

**Bath Maintenance Improvements.** The MHC process and other wet chemistry processes in PWB manufacturing are series of complex, carefully balanced and formulated chemical mixtures, each one designed to operate at specific conditions, working together to perform an overall function. A bath testing and control program is essential in preventing the

chemical breakdown of process baths, thus extending their useful lives and preventing their premature disposal. The premature disposal of process chemistries results in increased chemical costs for both bath and treatment chemicals, prolonged process down-time, and increased process waste.

Bath maintenance, or control, refers to maintaining a process bath in peak operating condition by identifying and controlling key operating parameters, such as bath temperature, individual chemical concentrations, pH, and the concentration of contaminants. Proper control of bath operating parameters will result in more consistent bath operation, less water usage, and better, more consistent quality of work.

According to Pollution Prevention Survey respondents, the majority of PWB manufacturing facilities (92.1 percent) have a preventative bath maintenance program already in place. Typical bath maintenance methods and their benefits are presented in Table 6.5 below.

**Table 6.5 Bath Maintenance Improvement Methods To Extend Bath Life**

| Methods | Benefits |
|---|---|
| Monitor bath chemistries by testing frequently. | Determines if process bath is operating within recommended parameters. |
| Replace process baths according to chemical testing. | Prevents premature chemical bath replacement of good process baths. |
| Maintain operating chemical balance through chemical additions according to testing. | Maintains recommended chemical concentrations through periodic chemical replenishment as required. |
| Filter process baths continuously. | Prevents the build-up of harmful impurities that may shorten bath life. |
| Employ steady state technologies. | Maintains steady state operating conditions by filtering precipitates or regenerating bath solutions continuously. |
| Install automated/statistical process control system. | Provides detailed analytical data of process operating parameters, facilitating more efficient process operation. |
| Utilize temperature control devices. | Regulates bath temperatures to maintain optimum operating conditions. |
| Utilize bath covers. | Reduces process bath losses to evaporation and volatilization. |

Frequent monitoring and adjustment of the various chemical concentrations within a process bath are the foundations on which a good bath maintenance program is built. Monitoring is done by regularly testing the bath concentrations of key chemicals to ensure that the bath is chemically balanced. If chemical concentrations are outside of the operating levels recommended by the supplier, a volume of chemical is added to the bath to bring it back into balance. When the concentration of contaminants reaches an established critical level, or some other criteria reported by the supplier, the bath is disposed of and replaced with a new bath.

Bath testing and adjustment can be performed manually or with an automated system that can perform both functions. Either way, controlling the bath through regular testing and bath additions is an inexpensive, effective method for extending bath life and reducing pollution. Nearly all of the PWB facilities surveyed (97.4 percent) report testing chemical bath concentrations.

Bath replacement should be based upon chemical testing, instead of some other predetermined criteria. Predetermined criteria, such as times or production volumes, are often given by suppliers as safe guidelines for bath replacement for facilities that do not regularly test their process baths. These criteria are conservative estimates of the effective life of the process bath, but can be exceeded with a proper bath testing and maintenance program. By replacing the process bath only when chemical testing indicates it is required, bath life can be extended while chemical usage and waste are reduced. Most (92.1 percent) of the surveyed PWB facilities reported replacing their process baths only when testing indicated.

The build-up of contaminants in a process bath will eventually require the bath to be replaced. Bath contaminants can be solid matter, such as particulate matter and precipitates, or undesired chemical species in solution, such as reaction byproducts or drag-in chemicals. An effective method of extending bath life is to continuously filter the process bath to remove undesired bath constituents. Installing standard cartridge or bag filters which remove solid impurities from the bath is another inexpensive, yet effective method to extend bath life.

Some baths may be maintained at steady state conditions using readily obtainable systems capable of regenerating or filtering process bath chemistries. For example, a system that continuously filters the copper sulfate precipitate from peroxide-sulfuric microetch baths can be used to maintain the microetch bath on a MHC process line, providing a recyclable precipitate. Regeneration techniques can be used to continuously regenerate both alkaline and cupric chloride etchants. Maintaining steady state conditions keeps a bath within the optimal operating conditions resulting in extended bath life (Edwards, 1996).

Statistical process control (SPC) is a method of analyzing the current and past performance of a process bath, using chemical testing results and operating condition records to optimize future bath performance. SPC will lead to more efficient bath operation and extended bath life by indicating when a bath needs maintenance through the tracking and analysis of individual operating parameters and their effect on past performance (Fehrer, 1996). Only one quarter (26.3 percent) of the survey respondents reported using a SPC system.

Many of the MHC process baths are heated, making temperature control an important necessity for proper bath operation. If bath temperature is not controlled properly, the bath may not be hot enough to perform its function, or may become too hot, leading to chemical and water losses due to evaporation or volatilization. The bath chemicals that remain become more concentrated, resulting in increased chemical loss to drag-out. By installing thermostats on all heated process baths, solution temperature will be kept constant, reducing waste generation and chemical and energy use, and saving money through decreased energy use, chemical use, and waste treatment costs.

Another method of limiting evaporative losses from process baths is to cover the surface of the solution with floating plastic balls that will not react with the process solution. The plastic balls, which do not interfere with the work pieces being processed, prevent the evaporation of the bath solution by limiting the surface area of solution exposed to the air. One facility uses ping pong balls which are made from polystyrene to minimize losses from the electroless copper bath. Hexagonal-shaped balls are now available that leave even less surface area exposed to the air (Brooman, 1996). This method is especially effective for higher temperature process baths where evaporative losses tend to be high. This method is inexpensive, easy to utilize, and will decrease the air emissions from the bath, limiting the amount of operator exposure to the chemicals.

## Reduced Water Consumption

Contaminated rinse water is the primary source of heavy metal ions discharged to waste treatment processes from the MHC process and other wet chemistry process lines (Bayes, 1996). These contaminants, which are introduced to the rinse water through chemical drag-out, must be treated and removed from the water before it can be reused in the process or discharged to the sewer. Because rinsing is often an uncontrolled portion of the process, large quantities of water are consumed and treated unnecessarily. Reducing the amount of water used by the MHC process has the following benefits:

- Decreases water and sewage costs.
- Reduces wastewater treatment requirements, resulting in less treatment chemical usage and reduced operating costs.
- Reduces the volume of sludge generated from wastewater treatment.
- Improves opportunities to recover process chemicals from more concentrated waste streams.

The MHC process line consists of a series of chemical baths, which are typically separated by at least one, and sometimes more, water rinse steps. These water rinse steps account for virtually all of the water used during the operation of the MHC line. The water baths act as a buffer, dissolving or displacing any residual drag-in chemicals from the panels surface. The rinse baths prevent contamination of subsequent baths while creating a clean surface for future chemical activity.

Improper rinsing does not only lead to shortened bath life through increased drag-in, as discussed previously, but can also lead to a host of problems affecting product quality, such as peeling, blistering and staining. Insufficient rinsing of panels can lead to increased chemical drag-in quantities and will fail to provide a clean panel surface for subsequent chemical activity. Excessive water rinsing, done by exposing the panels too long to water rinsing, can lead to oxidation of the copper surface and may result in peeling, blistering, and staining. To avoid insufficient rinsing, manufacturers often use greater water flow rates than are necessary, instead of using more efficient rinsing methods that reduce water consumption but may be more expensive to implement. These practices were found to be true among survey respondents, where facilities with low water and sewage costs typically used much larger amounts of water than comparable facilities with high water and sewer costs.

Many techniques are available that can reduce the amount of water consumed while rinsing. These techniques are categorized by the following:

- Methods to control water flow.
- Techniques to improve water rinse efficiency.
- Good housekeeping practices.

Flow control methods focus on controlling the flow of water, either by limiting the maximum rate that water is allowed to flow into the rinse system, or by stopping and starting the water flow as it is needed. These methods seek to limit the total water usage while ensuring that sufficient water is made available to cleanse the PWB panels. Examples of these techniques include the use of flow restrictors or smaller diameter piping to limit the maximum flow of water, and control valves that provide water to the rinse baths only when it is needed. Control valves can be either manually operated by an employee, or automated using some kind of sensing device such as conductivity meters, pH meters, or parts sensors. All of the methods are effective water reduction techniques that can be easily installed.

Pollution prevention techniques directed at improving water efficiency in the rinse system seek to control or influence the physical interaction between the water and the panels. This can be done by increasing bath turbulence, improving water quality, or by using a more efficient rinse configuration. All of these methods, discussed below, seek to improve rinsing performance while using less water.

Increasing bath turbulence can be accomplished through the use of ultrasonics, panel agitation, or air sparging. All of these agitation methods create turbulence in the bath, increasing contact between the water and the part, thereby accelerating the rate that residual chemicals are removed from the surface. Agitating the bath also keeps the water volume well mixed, distributing contaminants throughout the bath and preventing concentrations of contaminants from becoming trapped. However, agitating the bath can also increase air emissions from the bath unless pollution prevention measures are used to reduce air losses.

Water quality can be improved by using distilled or deionized water for rinsing instead of tap water that may include impurities such as carbonate and phosphate precipitates, calcium, fluoride, and iron. Finally, utilizing more efficient rinse configurations such as countercurrent rinse stages, spray rinses, or fog rinses will increase the overall efficiency of the MHC rinse system while reducing the volume of wastewater generated. PWB manufacturers often use multiple rinse water stages between chemical process steps to facilitate better rinsing. The first rinse stage removes the majority of residual chemicals and contaminants, while subsequent rinse stages remove any remaining chemicals. Counter-current or cascade rinse systems minimize water use by feeding the water effluent from the cleanest rinse tank, usually at the end of the cascade, into the next cleanest rinse stage, and so on, until the effluent from the most contaminated, initial rinse stage is sent for treatment or recycle.

Good housekeeping practices focus on keeping the process equipment in good repair and fixing or replacing leaky pipes, pumps, and hoses. These practices can also include installing devices such as spring loaded hose nozzles that shut off when not in use, or water control timers that shut off water flow in case of employee error. These practices often require little investment

and are effective in preventing unnecessary water usage. For a more detailed discussion on methods of improving water rinse efficiency and reducing water consumption, refer to Section 5.1, Resource Conservation.

**Improve Process Efficiency Through Automation**

The operation of the MHC process presents several opportunities for important and integral portions of the process to become automated. By automating important functions, operator inconsistencies can be eliminated allowing the process to be operated more efficiently. Automation can lead to the prevention of pollution by:

- Gaining a greater control of process operating parameters.
- Performing the automated function more consistently and efficiently.
- Eliminating operator errors.
- Making the process compatible with newer and cleaner processes designed to be operated with an automated system.

Automating a part of the MHC process can be expensive. The purchase of some automated equipment can require a significant initial investment, which may prevent small companies from automating. Other costs that may be incurred include installing the equipment, training employees, any lost production due to process down-time, and the cost of redesigning other processes to be compatible with the new system. Although it may be expensive, the benefits of automation on productivity and waste reduction will result in a more efficient process that can save money over the long run.

Installation of automated equipment such as a rack or panel transportation system, chemical sampling equipment, or an automated system to make chemical additions can have a major impact on the quantity of pollution generated during the day-to-day operation of the MHC process and can also reduce worker exposure. MHC process steps or functions that can be automated effectively include:

- Rack transportation.
- Bath maintenance.
- Water flow control.

Rack transportation systems present an excellent opportunity for automation, due to the repetitive nature of transporting panel racks. Various levels of automation are available ranging from a manually operated vertical hoist to a computer controlled robotic arm. All of these methods allow for greater process control over panel movement through the MHC process line. By building in drag-out reduction methods such as slower panel withdraw and extended drainage times into the panel movement system, bath chemical loss and water contamination can be greatly reduced.

Automating bath maintenance testing and chemical additions can result in longer bath life and reduced waste. These systems monitor bath solutions by regularly testing bath chemistries for key contaminants and concentrations. The system then adjusts the process bath by making small chemical additions, as needed, to keep contaminant build-up to a minimum and the process

bath operating as directed. The resulting process bath operates more efficiently, resulting in prolonged bath life, less chemical waste, reduced chemical cost, and reduced drag-out.

Controlling rinse water flow is an inexpensive process function to automate. Techniques for controlling rinse water flow were discussed previously. The reduction in fresh water usage as a result of automating these techniques will not only reduce water costs, but will also result in reduced treatment chemical usage and less sludge.

A conveyorized system integrates many of the methods described above into a complete automated MHC system. The system utilizes a series of process stages connected by a horizontal conveyor to transport the PWB panels through the MHC process. Drag-out is greatly reduced due, in part, to the separate process stages, and to the vertical alignment of the drilled holes that trap less chemicals. Since drag-out is reduced, much less rinse water is required to cleanse the panel surfaces, resulting in reduced water and treatment costs. A single water tank is sufficient between process baths where multiple stages may be required in a non-conveyorized process, thus dramatically reducing the number of process stages required, resulting in a much shorter cycle time and reduced floor space requirements. The enclosed process stages limit evaporative losses, reducing chemical costs, while also reducing the amount of chemical to which an employee is exposed. Several MHC alternative chemistry processes have been designed to operate effectively using this type of conveyorized system.

A conveyorized system should also take advantage of other pollution prevention techniques, such as water flow controllers, bath maintenance techniques and other methods discussed throughout this module, to further reduce waste. By integrating all of these methods together into a single MHC system, the process operates more efficiently, reducing water and chemical consumption, resulting in less process waste and employee exposure.

**Segregate Wastewater Streams to Reduce Sludge Generation.** Another type of process improvement to prevent pollution relates to segregating the wastewater streams generated by MHC and other PWB manufacturers process steps. The segregation of wastewater streams is a simple and cost-effective pollution prevention technique for the MHC process. In a typical PWB facility, wastewater streams from different process steps are often combined and then treated by an on-site wastewater treatment process to comply with local discharge limits.

Some waste streams from the MHC process, however, may contain chelating agents. These chelators, which permit metal ions to remain dissolved in solution at high pH levels, must first be broken down chemically before the waste stream can be treated and the heavy metal ions removed. Treatment of waste containing chelators requires extra treatment steps or more active chemicals to break down the chelating agents and precipitate out the heavy metal ions from the remaining water effluent. Because the chelator-bearing streams are combined with other non-chelated streams before being treated, a larger volume of waste must be treated for chelators than is necessary, which also results in a larger volume of sludge.

To minimize the amount of treatment chemical used and sludge produced, the chelated waste streams should be segregated from the other non-chelated wastes and collected in a storage tank. When enough waste has been collected, the chelated wastes should be batch treated to breakdown the chelator and remove the heavy metals. The non-chelated waste streams can then

be treated by the on-site wastewater treatment facility without additional consideration. By segregating and batch treating the chelated heavy metal wastes from other non-hazardous waste streams, the volume of waste undergoing additional treatment is minimized and treatment chemical usage and sludge generation reduced.

## 6.2 RECYCLE, RECOVERY, AND CONTROL TECHNOLOGIES ASSESSMENT

While pollution prevention is the preferred method of waste management, the waste management hierarchy recognizes that pollution prevention is not always feasible. Companies often supplement their pollution prevention efforts with additional waste management techniques to further reduce emissions. These techniques, presented in order of preference, include recycling, treatment, and disposal. This section presents waste management techniques typically used by the PWB industry in the MHC process to minimize waste, recycle or recover valuable process resources, and to control emissions to water and air.

### 6.2.1 Recycle and Resource Recovery Opportunities

PWB manufacturers have begun to reevaluate the merits of recycle and recovery technologies because of more stringent effluent pretreatment regulations. Recycling is the in-process recovery of process material effluent, either on-site or off-site, which would otherwise become a solid waste, air emission, or a wastewater stream. Metals recycling and recovery processes have become more economical to operate due to the increased cost of managing sludge containing heavy metals under stricter regulatory requirements. Technologies that recycle water from waste streams concentrate the final effluent making subsequent treatment more efficient, thus reducing the volume of waste generated along with overall water and sewer costs. As a result, these technologies are being used more frequently by industry to recycle or recover valuable process resources while also minimizing the volume of waste that is sent to disposal. This trend was supported by the respondents of the *Printed Wiring Board Pollution Prevention and Control: Analysis of Survey Results* (EPA, 1995c), 76 percent of whom reported using some type of recycle or resource recovery technology.

Recycle and resource recovery technologies include those that recover materials from waste streams before disposal or recycle waste streams for reuse in another process. Opportunities for both types of technologies exist within the MHC process. Rinse water can be recycled and reused in further rinsing operations while copper can be recovered from waste streams before disposal and sold to a metals reclaimer. These recycle and recovery technologies may be either in-line (dedicated and built into the process flow of a specific process line) or at-line (employed at the line as desired as well as other places in the plant) technologies depending on what is required (Brooman, 1996). Each individual waste stream that cannot be prevented should be evaluated to determine its potential for effective recycle or resource recovery.

The decision on whether to purchase a recycle or resource recovery process should be based on several factors. Economic factors such as process operating costs and effluent disposal costs for the current system must be compared with those estimated for the new technology. The initial capital investment of the new technology along with any potential cost savings and the length of the payback period must also be considered. Other factors such as the characteristics of the waste stream(s) considered for treatment, the ability of the process to accept reused or recycled materials, and the effects of the recycle or recovery technology on the overall waste treatment process should also be considered.

The entire PWB manufacturing process must be considered when assessing the economic feasibility of a recycle or resource recovery process. An individual recovery process can recover

copper from a single stream originating from the MHC process, or it may recover the metal from streams that originate from other processes as well. Only by considering the new technology's impact on the entire process, can an accurate and informed decision be made. While this section focuses on technologies that could be used to recycle or recover resources from the waste streams that are generated from the MHC process, many of these technologies are applicable to other PWB process lines. Workplace practices that can lead to the recycle or reuse of resources (e.g., manually recovering copper from panel racks, water recycle using cascade water rinse systems) are discussed in Section 6.1.

## Reverse Osmosis

Reverse osmosis is a recovery process used by the PWB industry to regenerate rinse waters and to reclaim process bath drag-out for return to the process (EPA, 1990). It relies on a semi-permeable membrane to separate the water from metal impurities allowing bath solutions to be reused. It can be used as a recycling or recovery technology to reclaim or regenerate a specific solution, or it can be part of an overall waste treatment process to concentrate metals and impurities before final treatment.

The reverse osmosis process uses a semi-permeable membrane which permits only certain components to pass through it and a driving force to separate these components at a useful rate. The membrane is usually made of a polymer compound (e.g., nylon) with hole sizes ranging from 0.0004 to 0.06 microns in diameter. High pressure pumping of the waste stream, at pressures typically ranging from 300 to 1,500 pounds per square inch (psi) force the solution through the membrane (Capsule Environmental Engineering, Inc., 1993). The membrane allows the water to pass while inhibiting the metal ions, collecting them on the membrane surface. The concentrated metal ions are allowed to flow out of the system where they are reused as bath make-up solution or are sent to treatment. The relatively pure water can be recycled as rinse water or directly sewered.

The reverse osmosis process has some limitations. The types of waste streams suitable for processing are limited to the ability of the plastic membranes to withstand the destructive nature of the given waste stream. The membranes are sensitive to solutions with extreme pH values, either low or high, which can degrade the polymer membranes. Pure organic streams are likewise not treatable. Waste streams with suspended solids should be filtered prior to separation to keep the solids from fouling the membrane, thus reducing the efficiency of the process. Process membranes may also have a limited life due to the long-term pressure of the solution on the membrane (Coombs, 1993). Data regarding the usage of reverse osmosis technology by industry was not collected by the Pollution Prevention Survey.

## Ion Exchange

Ion exchange is a process used by the PWB industry mainly to recover metal ions, such as copper or palladium, from rinse waters and other solutions. This process uses an exchange resin to remove the metal from solution and concentrate it on the surface of the resin. It is particularly suited to treating dilute solutions, because it removes the metal species from the solution instead of removing the solution from the metal. As a result, the relative economics of the process improve as the concentration of the feed solution decreases. Aside from recovering copper, ion

exchange can also be used for treating wastewater, deionizing feed water, and recovering chemical solutions.

Ion exchange relies on special resins, either cationic or anionic, to remove the desired chemical species from solution. Cation exchange resins are used to remove positively charged ions such as copper. When a feed stream containing copper is passed through a bed of cation exchange resin, the resin removes the copper ions from the stream, replacing them with hydrogen ions from the resin. For example, a feed stream containing copper sulfate ($CuSO_4$) is passed through the ion exchange resin where the copper ions are removed and replaced by hydrogen ions to form sulfuric acid ($H_2SO_4$). The remaining water effluent is either further processed using an anion exchange resin and then recirculated into the rinse water system, or pH neutralized and then directly sewered. Ion exchange continues until the exchange resin becomes saturated with metal ions and must be regenerated.

Special chelating resins have been designed to capture specific metal ions that are in the presence of chelating agents, such as metal ions in electroless plating baths. These resins are effective in breaking down the chemical complexes formed by chelators that keep metal ions dissolved in solution, allowing them to be captured by the resin. They ignore hard water ions, such as calcium and magnesium that would otherwise be captured, creating a more pure concentrate. Chelating resins require that the feed stream be pH adjusted to reduce acidity and filtered to remove suspended solids that will foul the exchange bed (Coombs, 1993).

Regeneration of the cation or chelating exchange resin is accomplished using a moderately concentrated (e.g., ten percent) solution of a strong acid, such as sulfuric acid. Regeneration reverses the ion exchange process by stripping the metal ions from the exchange resin and replacing them with hydrogen ions from the acid. The concentration of metal ions in the remaining regenerant depends on the concentration of the acid used, but typically ranges from 10 to 40 g/L or more (Coombs, 1993).

Ionic exchange can be combined with electrowinning (electrolytic recovery) to recover metal from solutions that would not be cost-effective to recover using either technology alone. It can be used to concentrate a dilute solution of metal ions for electrolytic recovery that would otherwise be uneconomical to recover. For example, a dilute copper chloride solution can be treated by an ion exchange unit which is regenerated using sulfuric acid, producing a concentrated copper sulfate solution. The electrowinning unit can then be used to recover the copper from the solution while regenerating the acid, which could then be used for the next regeneration cycle.

A benefit of ion exchange is the ability to control the type of metallic salt that will be formed by selecting the type of acid used to regenerate the resin. In the previous example, the copper chloride was converted to copper sulfate while being concentrated by the ion exchange system. This is particularly useful when electrowinning is used, since it cannot process solutions containing the chlorine ion without generating toxic chlorine gas.

Twenty-six percent of the respondents to the Pollution Prevention Survey reported using an ion exchange process as a water recycle/chemical recovery technology. The average capital

cost of a unit, which is related to its capacity, reported by the respondents was $47,500 with a low of $5,000 and a high of $100,000.

**Electrolytic Recovery**

Electrolytic recovery, also known as electrowinning, is a common metal recovery technology employed by the PWB industry. Operated either in continuous or batch mode, electrowinning can be applied to various process fluids including spent microetch, drag-out rinse water, and ion exchange regenerant. An advantage of electrowinning, which uses an electrolytic cell to recover dissolved copper ions from solution, is its ability to recover only the metal from solution without recovering the other impurities that are present. The recovered copper can then be sold as scrap or reused in the process.

Process waste solutions containing chlorine ions in any form should not be processed using electrolytic recovery methods since the electrolysis of these solutions could generate chlorine gas. Solutions containing copper chloride salts should first be converted using ion exchange methods to a non-chloride copper salt (e.g., copper sulfate) solutions before undergoing electrowinning to recover the copper content (Coombs, 1993).

Electrowinning is most efficient with concentrated solutions. Dilute solutions with less than 100 mg/L of copper become uneconomical to treat due to the high power consumption relative to the amount of copper recovered (Coombs, 1993). Waste streams that are to be treated should be segregated to prevent dilution and to prevent the introduction of other metal impurities. Already diluted solutions can be concentrated first using ion exchange or evaporation techniques to improve the efficiency and cost-effectiveness of metal recovery.

The electrolytic cell is comprised of a set of electrodes, both cathodes and anodes, placed in the copper laden solution. An electric current, or voltage, is applied across the electrodes and through the solution. The positively charged metal ions are drawn to the negatively charged cathode where they deposit onto the surface. The solution is kept thoroughly mixed using air agitation, or other proprietary techniques, which allow the process to use higher current densities (the amount of current per surface area of cathode) that speed deposition time and improve efficiency. As copper recovery continues, the concentration of copper ions in solution becomes depleted, requiring the current density to be reduced to maintain efficiency. When the concentration of copper becomes too low for its removal to be economically feasible, the process is discontinued and the remaining solution is sent to final treatment.

The layers of recovered copper can be sold as scrap to a metals reclaimer. Copper removal efficiencies of 90 to 95 percent have been achieved using electrolytic methods (EPA, 1990). The remaining effluent will still contain small amounts of copper and will be acidic in nature (i.e., low pH). Adjusting the pH may not be sufficient for the effluent to meet the standards of some POTW authorities; therefore, further treatment may be required.

Eighteen percent of the Pollution Prevention Survey respondents reported using electrowinning as a resource recovery technology with nearly all (89 percent) being satisfied. The median cost of a unit reported by the respondents was $15,000; however, electrowinning capital costs are dependant on the capacity of the unit.

### 6.2.2 Control Technologies

If the release of a hazardous material cannot be prevented or recycled, it may be possible to treat or reduce the impact of the release using a control technology. Control technologies are engineering methods that minimize the toxicity and volume of released pollutants. Most of these methods involve altering either the physical or chemical characteristics of a waste stream to isolate, destroy, or alter the concentration of target chemicals. While this section focuses on technologies that are used to control on-site releases from the MHC process, many of these technologies are also applicable to other PWB process lines.

Control technologies are typically used to treat on-site releases to both water and air from the operation of the MHC process. Wastewater containing concentrations of heavy metal ions, along with chelators and complexing agents, are of particular concern. Water effluent standards require the removal of most heavy metals and toxic organics from the plant effluent before it can be disposed to the sewer. On-site releases to air of concern include formaldehyde vapors, as well as acid and solvent fumes. The desire to eliminate both formaldehyde and chelating agents has led to the development of alternative MHC processes. This section identifies the control technologies used by PWB manufacturers to treat or control wastewater and air emissions released by the operation of the MHC process.

**Wastewater Treatment**

**Chemical Precipitation.** In the PWB industry, the majority of facilities surveyed (61 percent) reported using a conventional chemical precipitation system to accomplish the removal of heavy metal ions from wastewater. Chemical precipitation is a process for treating wastewater that depends on the water solubility of the various compounds formed during treatment. Heavy metal cations that are present in the wastewater are reacted with certain treatment chemicals to form metal hydroxides, sulfides, or carbonates that all have relatively low water solubilities. The resulting heavy metal compounds are then precipitated from the solution as an insoluble sludge that is subsequently recycled to reclaim the metals content or sent to disposal. The chemical precipitation process can be operated as a batch process, but is typically operated in a continuous process to treat wastewater.

In the chemical precipitation treatment of wastewater from PWB manufacturing, the removal of heavy metals may be carried out by a unit sequence of rapid mix precipitation, flocculation, and clarification. The process begins with the dispersion of treatment chemicals into the wastewater input stream under rapid mixing conditions. The initial mixing unit is designed to create a high intensity of turbulence in the reactor vessel, promoting encounters between the metal ions and the treatment chemical species, which then react to form metal compounds that are insoluble in water. The type of chemical compounds formed depends on the treatment chemical employed; this is discussed in detail later in this section. These insoluble compounds form a fine precipitate at low pH levels that remains suspended in the wastewater.

The wastewater then enters the flocculation tank. The purpose of the flocculation step is to transform smaller precipitation particles into large particles that are heavy enough to be removed from the water by gravity settling in the clarification step. This particle growth is accomplished in a flocculation tank using slow mixing to promote the interparticle collisions of

precipitate particles suspended in the wastewater. The degree of flocculation is enhanced through the use of flocculating chemicals such as cationic or anionic polymers. These chemicals promote interparticle adhesion by adding charged particles to the wastewater that attach themselves to the precipitate, thereby increasing the growth rate of the precipitate particles.

Clarification is the final stage of the wastewater treatment process. The wastewater effluent from the flocculation stage is fed into a clarification tank where the water is allowed to collect undisturbed. The precipitate then settles out of the water by gravity, forming a blanket of sludge at the bottom of the clarification tank. A portion of the sludge, typically 10 to 25 percent, is often recirculated to the head of the flocculation step to reduce chemical requirements, as well as to enhance the rate of precipitation (Frailey, 1996). The sludge particles provide additional precipitation nuclei that increase the probability of particle collisions, resulting in a more dense sludge deposit. When a dense layer of sludge has been formed, the sludge is removed from the tank and is either dewatered or sent for recycle or disposal. The precipitate-free water is then either recycled or sewered.

Other process steps are sometimes employed in the case of unusually strict effluent guidelines. Filtration, reverse osmosis, ion exchange, or additional precipitation steps are sometimes employed to further reduce the concentration of chemical contaminants present in the wastewater effluent.

The heavy metal sludge generated by the wastewater treatment process is often concentrated, or dewatered, before being sent to recycle or disposal. Sludge can be dewatered in several methods including sludge thickening, press filtration, and sludge drying. Through the removal of water, sludge volume can be minimized, thus reducing the cost of disposal.

**Treatment of Non-Chelated Wastewater.** The absence of complexing chemicals (e.g., ammonia) or chelating agents (e.g., EDTA) in the wastewater stream simplifies the removal of heavy metal ions by precipitation. Heavy metal removal from such waste streams is accomplished through simple pH adjustment using hydroxide precipitation. Caustic soda (NaOH) is typically used while other treatment chemicals include calcium hydroxide and magnesium hydroxide. The heavy metal ions react with the caustic soda to form insoluble metal hydroxide compounds that precipitate out of solution at a high pH level. After the precipitate is removed by gravity settling, the effluent is pH adjusted to a pH of seven to nine and then sewered. The treatment can be performed in a chemical precipitation process similar to the one described above, resulting in a sludge contaminated with metals that is then sent to recycling or disposal.

**Treatment of Wastewater Containing Chelated Metals.** The presence of complexing chemicals or chelators require a more vigorous effort to achieve a sufficient level of heavy metal removal. Chelators are chemical compounds that inhibit precipitation by forming chemical complexes with the metals, allowing them to remain in solution beyond their normal solubility limits. These chemicals are found in spent MHC plating baths, in cleaners, and in the water effluent from the rinse tanks following these baths. Treatment chemicals enhance the removal of chelated metals from water by breaking the chelant-to-metal bond, destroying the soluble complex. The freed metal ions then react to form insoluble metal compounds, such as metal hydroxides, that precipitate out of solution. Several different chemicals are currently being used

to effectively treat chelator-contaminated wastewater resulting from the manufacture of PWBs. Some common chemicals used in the treatment of wastewater produced by the MHC process are briefly described in Table 6.6. For a more information regarding individual treatment chemicals and their applicability to treating specific wastes, consult the supplier of the treatment chemical.

**Table 6.6 Treatment Chemicals Used to Remove Heavy Metals From Chelated Wastewater**

| Chemical | Description |
|---|---|
| Ferrous Sulfate | Inexpensive treatment that requires iron concentrations in excess of 8:1 to form an insoluble metal hydroxide precipitate (Coombs, 1993). Ferrous sulfate is first used as a reducing agent to breakdown the complexed copper structures under acidic conditions before forming the metal hydroxide during subsequent pH neutralization. Drawbacks include the large volumes of sludge generated and the presence of iron which reduces the value of sludge to a reclaimer. |
| DTC (Dimethyl-dithiocarbamate) | Moderately expensive chemical that acts as a complexing agent, exerting a stronger reaction to the metal ion than the chelating agent, effectively forming an insoluble heavy metal complex. The sludge produced is light in density and difficult to gravity separate (Guess, 1992; Frailey, 1996). |
| Sodium Sulfide | Forms heavy metal sulfides with extremely low solubilities that precipitate even in the presence of chelators. Produces large volume of sludge that is slimy and difficult to dewater (Guess, 1992). |
| Polyelectrolyte | Polymers that remove heavy metals effectively without contributing to the volume of sludge. Primary drawback is the high chemical cost (Frailey, 1996). |
| Sodium Borohydride | Strong reducing agent reduces heavy metal ions which then precipitate out of solution forming a compact, low volume sludge. Drawbacks include its high chemical cost and the evolution of potentially explosive hydrogen gas (Guess, 1992; Frailey, 1996). |
| Ferrous Dithionite | Reduces heavy metal ions under acidic conditions to form metallic particles that are recovered by gravity separation. Excess iron is regenerated instead of being precipitated producing a low volume sludge (Guess, 1992). |

**Effects of MHC Alternatives On Wastewater Treatment.** The strong desire to remove both formaldehyde and complexing chemicals, such as chelators, from the MHC process has led the drive away from traditional electroless copper and toward the development of alternative MHC processes. These processes eliminate the use of chelating agents that inhibit the precipitation of heavy metal ions in wastewater. Also eliminated is the need for expensive treatment chemicals, which are designed to breakdown chelators and which can add to the quantity of sludge produced. The resulting treatment of the non-chelated waste stream produces less sludge at a lower chemical treatment cost than it would if chelators were present. A detailed description of the treatment for both chelated and non-chelated wastes is presented elsewhere in this chapter.

While MHC alternative processes may reduce or eliminate the presence of chelators in the wastewater, they do not create any additional treatment concerns that would require any

physical changes in the treatment process. The treatment of wastewater generated from the operation of a MHC alternative can be accomplished using the traditional chemical precipitation stages of rapid mix precipitation, flocculation, and clarification.

**Alternative Treatment Processes.** Although chemical precipitation is the most common process for treating wastewater by PWB manufacturers, other treatment processes exist as well. Survey respondents reported the use of both ion exchange (33 percent) and/or electrowinning (12 percent) to successfully treat wastewater generated from the manufacture of PWBs. These processes operate separately, or in combination, to efficiently remove heavy metal ions from chelated or non-chelated waste streams, typically yielding a highly concentrated sludge for disposal. These processes were discussed in Section 6.2.1.

**Batch Treatment of Process Baths.** Most spent process baths can be mixed with other wastewater and treated by the on-site wastewater treatment process using chemical precipitation. Chemical suppliers, however, recommend that some process baths be treated separately from the usual waste treatment process. The separate treatment of these baths is usually recommended due to the presence of strong chelating agents, high heavy metal concentrations, or other chemicals, such as additives or brighteners, that require additional treatment measures before they can be disposed of properly. Spent bath solution requiring special treatment measures can be processed immediately, but is typically collected and stored until enough has accumulated to warrant treatment. Batch treatment of the accumulated waste is then performed in a single tank or drum, following the specific treatment procedures provided by the chemical supplier for that bath.

Despite the supplier's recommendations, PWB facilities sometimes treat individual process baths using their typical wastewater treatment process. Spent bath solutions can be mixed slowly, in small quantities, with other wastewater before being treated, thus diluting the concentration of the chemical species requiring treatment. However, the introduction of concentrated wastes to the wastewater could result in increased treatment chemical consumption and more sludge produced than if batch treated separately. Also the introduction of a chemical species not typically found in the wastewater may adversely affect the treatment process or require more vigorous treatment chemicals or processes. Factors affecting the success of such treatment include the type of treatment chemicals used, the contaminant concentrations in the wastewater, and the overall robustness of the treatment process.

## Air Pollution Control Technologies

Air pollution control technologies are often used by the PWB industry to cleanse air exhaust streams of harmful fumes and vapors. Exactly half (50 percent) of the PWB facilities surveyed have installed air scrubbers to control air emissions from various manufacturing processes, and almost a quarter of the facilities (23 percent) scrub air releases from the MHC process. The first step of any air control process is the effective containment of fugitive air emissions at their source of release. This is accomplished using fume hoods over the process areas from which the air release of concern is emanating. These hoods may be designed to continuously collect air emissions for treatment by one of the methods described below.

**Gas Absorption.** One method for removing pollutants from an exhaust stream is by gas absorption in a technique sometimes referred to as air scrubbing. Gas absorption is defined as the transfer of material from a gas to a contacting liquid, or solvent. The pollutant is chemically absorbed and dispersed into the solvent leaving the air free of the pollutant. The selection of an appropriate solvent should be based upon the liquid's solubility for the solute, and the cost of the liquid. Water is used for the absorption of water soluble gases while alkaline solutions are typically used for the absorption of acid gases. Air scrubbers are used by the PWB industry to treat wet process air emissions, such as formaldehyde and acid fumes, and emissions from other processes outside the MHC process.

Gas absorption is typically carried out in a packed gas absorption tower, or scrubber. The gas stream enters the bottom of the tower, and passes upward through a wetted bed of packing material before exiting the top. The absorbing liquid enters the top of the tower and flows downward through the packing before exiting at the bottom. Absorption of the air pollutants occurs during the period of contact between the gas and liquid. The gas is either physically or chemically absorbed and dispersed into the liquid. The liquid waste stream is then sent to water treatment before being discharged to the sewer. Although the most common method for gas absorption is the packed tower, other methods exist such as plate towers, sparged towers, spray chambers, or venturi scrubbers (Cooper, 1990).

**Gas Adsorption.** The removal of low concentration organic gases and vapors from an exhaust stream can be achieved by the process of gas adsorption. Adsorption is the process in which gas molecules are retained on the interface surfaces of a solid adsorbent by either physical or chemical forces. Activated carbon is the most common adsorbent but zeolites such as alumina and silica are also used. Adsorption is used primarily to remove volatile organic compounds from air, but is also used in other applications such as odor control and drying process gas streams (Cooper, 1990). In the MHC process it can be used to recover volatile organic compounds, such as formaldehyde.

Gas adsorption occurs when the vapor-laden air is collected and then passed through a bed of activated carbon, or another adsorbent material. The gas molecules are adsorbed onto the surface of the carbon, while the clean vapor-free air is exhausted from the system. The adsorbent material eventually becomes saturated with organic material and must be replaced or regenerated. Adsorbent canisters, which are replaced on a regular basis, are typically used to treat small gas flow streams. Larger flows of organic pollutants require packed beds of adsorbent material, which must be regenerated when the adsorbent becomes saturated (Cooper, 1990).

Regeneration of the adsorbent is typically accomplished by a steam stripping process. The adsorbent is contacted with low pressure steam which desorbs the adsorbed gas molecules from the surface of the packed bed. Following condensation of the steam, the organic material is recovered from the water by either decanting or distillation (Campbell, 1990).

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# Chapter 7
# Choosing Among MHC Technologies

This chapter of the Cleaner Technologies Substitutes Assessment (CTSA) organizes data collected or developed throughout the assessment of the baseline non-conveyorized electroless copper process and alternatives in a manner that facilitates decision-making. First, risk, competitiveness, and conservation data are summarized in Section 7.1. This information is used in Section 7.2 to assess the net benefits and costs to society of implementing an alternative as compared to the baseline. Section 7.3 provides summary profiles for the baseline and alternatives.

Information is presented for eight technologies for performing the making holes conductive (MHC) function. These technologies are electroless copper, carbon, conductive ink, conductive polymer, graphite, non-formaldehyde electroless copper, organic-palladium, and tin-palladium. All of these technologies are wet chemistry processes, except the conductive ink technology, which is a screen printing technology.[1] The wet chemistry processes can be operated using vertical, immersion-type, non-conveyorized equipment or horizontal, conveyorized equipment.[2] Table 7.1 presents the processes (alternatives and equipment configurations) evaluated in the CTSA.

**Table 7.1 MHC Processes Evaluated in the CTSA[a]**

| MHC Technology | Equipment Configuration | |
|---|---|---|
| | Non-Conveyorized | Conveyorized |
| Electroless Copper (BASELINE) | ✓ | ✓ |
| Carbon | | ✓ |
| Conductive Polymer | | ✓ |
| Graphite | | ✓ |
| Non-Formaldehyde Electroless Copper | ✓ | |
| Organic-Palladium | ✓ | ✓ |
| Tin-Palladium | ✓ | ✓ |

[a] The human health and aquatic toxicity hazards and chemical safety hazards of the *conductive ink technology* were also evaluated, but risk was not characterized.

[1] Only limited analyses were performed on the conductive ink technology for two reasons: 1) the process is not applicable to multi-layer boards, which were the focus of the CTSA; and 2) sufficient data were not available to characterize the risk, cost, and energy and natural resources consumption of all of the relevant process steps (e.g., preparation of the screen for printing, the screen printing process itself, and screen reclamation).

[2] Conveyorized MHC equipment is a relatively new innovation in the industry, and is usually more efficient than non-conveyorized equipment. Many of the newer technologies are only being used with conveyorized equipment, while most facilities in the U.S. still use a non-conveyorized electroless copper process to perform the MHC function.

The results of the CTSA suggest that the alternatives not only have environmental and economic benefits compared to the non-conveyorized electroless copper process, but also perform the MHC function as well as the baseline. While there appears to be enough information to show that a switch away from traditional electroless copper processes has reduced risk benefits, there is not enough information to compare the alternatives to this process among themselves for all their environmental and health consequences. This is due to a lack of proprietary chemical data from some suppliers[3] and because toxicity values are not available for some chemicals. In addition, it is important to note that there are additional factors beyond those assessed in this CTSA which individual businesses may consider when choosing among alternatives. None of these sections make value judgements or recommend specific alternatives. The actual decision of whether or not to implement an alternative is made outside of the CTSA process.

## 7.1 RISK, COMPETITIVENESS, AND CONSERVATION DATA SUMMARY

Earlier sections of the CTSA evaluated the risk, performance, cost, and resource requirements of the baseline MHC technology as well as the alternatives. This section summarizes the findings associated with the analysis of MHC technologies. Relevant data include the following:

- Risk information: occupational health risks, public health risks, ecological hazards, and process safety concerns.
- Competitiveness information: technology performance, cost and regulatory status, and international information.
- Conservation information: energy and natural resource use.

Sections 7.1.1 through 7.1.3 present risk, competitiveness, and conservation summaries, respectively.

### 7.1.1 Risk Summary

This risk characterization uses a health-hazard based framework and a model (generic) facility approach to compare the health risks of one MHC process technology to the health risks associated with switching to an alternative technology. As much as possible, reasonable and consistent assumptions are used across alternatives. Data to characterize the model facility and exposure patterns for each process alternative were aggregated from a number of sources, including printed wiring board (PWB) shops in the U.S. and abroad, supplier data, and input from PWB manufacturers at project meetings. Thus, the model facility is not entirely

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

representative of any one facility, and actual risk could vary substantially, depending on site-specific operating conditions and other factors.

When using the results of the risk characterization to compare health effects among alternatives, it is important to remember that it is a screening level rather than a comprehensive risk characterization, both because of the predefined scope of the assessment and because of exposure and hazard data limitations. It should also be noted that this approach does not result in any absolute estimates or measurements of risk, and even for comparative purposes there are several important uncertainties associated with this assessment (see Section 3.4).

The exposure assessment for the risk characterization used, whenever possible, a combination of central tendency and high-end assumptions (i.e., 90 percent of actual values are expected to be less) to yield an overall high-end exposure estimate. Some values used in the exposure calculations, however, are better characterized as "what-if,"[4] especially pertaining to bath concentrations, use of gloves, and process area ventilation rates for a model facility. Because some part of the exposure assessment for both inhalation and dermal exposures qualifies as a "what-if" descriptor, the entire assessment should be considered "what-if."

As with any risk characterization, there are a number of uncertainties involved in the measurement and selection of hazard data, and in the data, models, and scenarios used in the exposure assessment. Uncertainties arise both from factors common to all risk characterizations (e.g., extrapolation of hazard data from animals to humans, extrapolation from the high doses used in animal studies to lower doses to which humans may be exposed, missing toxicity data, including data on the cumulative or synergistic effects of chemical exposure), and other factors that relate to the scope of the risk characterization (e.g., the MHC characterization is a screening level characterization rather than a comprehensive risk assessment). Key uncertainties in this characterization include the following:

- The risk characterization of products supplied by Enthone-OMI, MacDermid, Shipley, and, to some degree, Atotech, is based on publicly-available bath chemistry data, which do not include the identity or concentrations of chemicals considered trade secrets by chemical suppliers.[5]
- The risk estimates for occupational dermal exposure are based on limited dermal toxicity data, using oral toxicity data with oral to dermal extrapolation when dermal toxicity data were unavailable. Coupled with the high uncertainty in estimating dermal absorption rates, this could result in either over- or under-estimates of exposure and risk.

[4] A "what-if" description represents an exposure estimate based on postulated questions, making assumptions based on limited data where the distribution is unknown.

[5] Electrochemicals, LeaRonal, and Solution Technology Systems provided information on proprietary chemical ingredients to the project for evaluation in the risk characterization. Atotech provided information on one proprietary ingredient. Risk results for proprietary ingredients in chemical products submitted by these suppliers, but not chemical identities or concentrations, are included in this CTSA.

- The risk characterization is based on modeled estimates of average, steady-state chemical concentrations in air, rather than actual monitoring data of average and peak air concentrations.
- The risk characterization does not account for any side reactions occurring in the baths, which could either underestimate exposures to toxic reaction products or overestimate exposures to toxic chemicals that react in the bath to form more benign chemicals.
- Due to resource constraints, the risk characterization does not address all types of exposures that could occur from MHC processes or the PWB industry, including short-term or long-term exposures from sudden releases due to fires, spills, or periodic releases.

The Risk Characterization section of the CTSA (Section 3.4) discusses the uncertainties in this characterization in detail.

**Occupational Health Risks**

Health risks to workers were estimated for inhalation exposure to vapors and aerosols from MHC baths and for dermal exposure to MHC bath chemicals. Inhalation exposure estimates are based on the assumptions that emissions to indoor air from conveyorized lines are negligible, that the air in the process room is completely mixed and chemical concentrations are constant over time, and that no vapor control devices (e.g., bath covers) are used in non-conveyorized lines. Dermal exposure estimates are based on the assumption that workers do not wear gloves[6] and that all non-conveyorized lines are operated by manual hoist. Dermal exposure to line operators on non-conveyorized lines could occur from routine line operation and maintenance (e.g., bath replacement, filter replacement, etc.). Dermal exposure to line operators on conveyorized lines was assumed to occur from bath maintenance activities alone.

Risk results indicate that alternatives to the non-conveyorized electroless copper process pose lower occupational risks due to reduced cancer risks and to the reduced number of inhalation and dermal risk concerns for the alternatives. However, there are occupational inhalation risk concerns for some chemicals in the non-formaldehyde electroless copper and tin-palladium non-conveyorized processes. In addition, there are occupational risk concerns for dermal contact with some chemicals in the conveyorized electroless copper process, the non-conveyorized non-formaldehyde electroless copper process, and tin-palladium and organic-palladium processes for either conveyorized or non-conveyorized equipment. Finally, occupational health risks could not be quantified for one or more of the chemicals used in each of the MHC technologies. This is due to the fact that proprietary chemicals in the baths were not identified by some suppliers and to missing toxicity or chemical property data for some chemicals known to be present in the baths.

Table 7.2 presents chemicals of concern for potential occupational risk from inhalation. Table 7.3 presents chemicals of concern for potential occupational risk from dermal contact.

[6] Many PWB manufacturers report that their employees routinely wear gloves in the process area. However, risk from dermal contact was estimated assuming workers do not wear gloves to account for those workers who do not wear proper personal protective equipment.

## Table 7.2 MHC Chemicals of Concern for Potential Occupational Inhalation Risk

| Chemical[a] | Non-Conveyorized Process[b] | | |
|---|---|---|---|
| | Electroless Copper | Non-Formaldehyde Electroless Copper | Tin-Palladium |
| Alkene Diol | ✔ | | |
| Copper Chloride | ✔ | | |
| Ethanolamine | ✔ | | ✔ |
| 2-Ethoxyethanol | ✔ | | |
| Ethylene Glycol | ✔ | | |
| **Formaldehyde** | ✔ | | |
| Formic Acid | ✔ | | |
| **Methanol** | ✔ | | |
| Sodium Hydroxide | ✔ | | |
| **Sulfuric Acid[c]** | ✔ | ✔ | ✔ |

[a] For technologies with more than one chemical supplier (e.g., electroless copper and tin-palladium), chemicals of concern that are present in all of the product lines evaluated are indicated in bold.

[b] Occupational inhalation exposure from conveyorized lines was assumed to be negligible.

[c] Sulfuric acid was listed on the MSDSs for all of the electroless copper lines evaluated and four of the five tin-palladium lines evaluated.

## Table 7.3 MHC Chemicals of Concern for Potential Occupational Dermal Risk

| Chemical[a] | Electroless Copper | | | Non-Formaldehyde Electroless Copper | Tin-Palladium | | | Organic-Palladium | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Line Operator | | Lab Tech (NC or C) | Line Operator (NC) | Line Operator | | Lab Tech (NC or C) | Line Operator | | Lab Tech (NC or C) |
| | NC | C | | | NC | C | | NC | C | |
| Copper Chloride | ✔ | ✔ | ✔ | | ✔ | ✔ | ✔ | | | |
| Fluoroboric Acid | ✔ | ✔ | ✔ | | ✔ | ✔ | ✔ | | | |
| **Formaldehyde** | ✔ | ✔ | | | | | | | | |
| Nitrogen Heterocycle | ✔ | ✔ | | | | | | | | |
| **Palladium[b]** | ✔ | ✔ | ✔ | | ✔ | ✔ | ✔ | | | |
| **Palladium Chloride[b]** | | | | | ✔ | ✔ | ✔ | | | |
| Palladium Salt | | | | | | | | ✔ | ✔ | ✔ |
| Sodium Carboxylate | ✔ | ✔ | | | | | | | | |
| Sodium Chlorite | ✔ | ✔ | | ✔ | | | | | | |
| **Stannous Chloride[c]** | ✔ | | | ✔ | ✔ | ✔ | | | | |
| Tin Salt | | ✔ | | | | | | | | |

[a] For technologies with more than one chemical supplier (e.g., electroless copper and tin-palladium), chemicals of concern that are present in all of the product lines evaluated are indicated in bold.

[b] Palladium or palladium chloride was listed on the MSDSs for three of the five tin-palladium lines evaluated. The MSDSs for the two other lines did not list a source of palladium. Palladium and palladium chloride are not listed on the MSDSs for all of the electroless copper lines evaluated.

[c] Stannous chloride was listed on the MSDSs for four of the five tin-palladium lines evaluated. The MSDSs for the remaining line did not list a source of tin. Stannous chloride is not listed on the MSDSs for all of the electroless copper lines evaluated.

NC: Non-Conveyorized.

C: Conveyorized.

The non-conveyorized electroless copper process contains the only non-proprietary chemical for which an occupational cancer risk has been estimated (for formaldehyde). Formaldehyde has been classified by EPA as Group B1, a Probable Human Carcinogen. The upper bound excess individual cancer risk estimate for line operators in the non-conveyorized electroless copper process from formaldehyde inhalation may be as high as one in 1,000, but may be 50 times less, or one in 50,000.[7] Risks to other workers were assumed to be proportional to the amount of time spent in the process area, which ranged from three percent to 61 percent of the risk for a line operator.

Inhalation cancer risk was also estimated for one proprietary chemical, alkyl oxide, in the non-conveyorized electroless copper process. The line operator inhalation exposure estimate for alkyl oxide results in an estimated upper bound excess individual life time cancer risk of $3 \times 10^{-7}$ (one in three million) based on high end exposure. Cancer risks less than $1 \times 10^{-6}$ (one in one million) are generally considered to be of low concern.

Additionally, dermal cancer risks were estimated for two proprietary chemicals, cyclic ether and alkyl oxide, in the graphite and electroless copper processes. For the conveyorized graphite process, the dermal cancer risks for a line operator may be as high as $8 \times 10^{-8}$ (about one in ten million) for the alkyl oxide and $1 \times 10^{-7}$ (one in ten million) for the cyclic ether. The upper bound cancer risks for a laboratory technician were much less than the cancer risks for a line operator. The cancer risks for a laboratory technician were $6 \times 10^{-9}$ (one in 200 million) for alkyl oxide and $9 \times 10^{-9}$ (one in 100 million) for cyclic ether.

For non-conveyorized electroless copper, the dermal cancer risks for the line operator may be as high as $4 \times 10^{-7}$ (one in two million) for cyclic ether and $1 \times 10^{-8}$ (one in 100 million) for alkyl oxide. The estimated upper bound cancer risks for a laboratory technician were much less than the cancer risks for a line operator. The estimated cancer risks for a laboratory technician were $9 \times 10^{-9}$ (one in 100 million) for cyclic ether and $1 \times 10^{-10}$ (one in ten billion) for alkyl oxide.

For conveyorized electroless copper, the dermal cancer risk for a line operator may be as high as $8 \times 10^{-8}$ (about one in ten million) for cyclic ether and $4 \times 10^{-9}$ (one in 200 million) for alkyl oxide. The estimated upper bound cancer risks for a laboratory technician were much less than the cancer risks for a line operator. The estimated cancer risks for a laboratory technician were $9 \times 10^{-9}$ (one in 100 million) for cyclic ether and $1 \times 10^{-10}$ (one in ten billion) for alkyl oxide.

Other non-proprietary chemicals in the MHC processes are suspected carcinogens. Dimethylformamide and carbon black have been determined by the International Agency for Research on Cancer (IARC) to possibly be carcinogenic to humans (IARC Group 2B). Like formaldehyde, the evidence for carcinogenic effects is based on animal data. However, unlike

[7] To provide further information on the possible variation of formaldehyde exposure and risk, an additional exposure estimate was provided in the Risk Characterization (Section 3.4) using average and median values (rather than high-end) as would be done for a central tendency exposure estimate. This results in approximately a 35-fold reduction in occupational formaldehyde exposure and risk from the estimates presented here.

formaldehyde, slope factors are not available for either chemical. There are potential cancer risks to workers from both chemicals, but they cannot be quantified. Dimethylformamide is used in the electroless copper process. Workplace exposures have been estimated but cancer potency and cancer risk are unknown. Carbon black is used in the carbon and conductive ink processes. Occupational exposure due to air emissions from the carbon baths in the carbon process is expected to be negligible because this process is typically conveyorized and enclosed. There may be some airborne carbon black, however, from the drying oven steps. Exposures from conductive ink were not characterized. One proprietary chemical used in the electroless copper process, trisodium acetate amine B, was determined to possibly be carcinogenic to humans but does not have an established slope factor.

**Public Health Risks**

Public health risk was estimated for inhalation exposure only for the general populace living near a facility. Environmental releases and risk from exposure to contaminated surface water were not quantified due to a lack of data; chemical constituents and concentrations in wastewater could not be adequately characterized. Public health risk estimates are based on the assumption that emissions from both conveyorized and non-conveyorized process configurations are steady-state and vented to the outside. Risk was not characterized for short-term exposures to high levels of hazardous chemicals when there is a spill, fire, or other releases.

The risk indicators for ambient exposures to humans, although limited to airborne releases, indicate low concern from all MHC technologies for nearby residents. The upper bound excess individual cancer risk from formaldehyde inhalation for nearby residents from the non-conveyorized electroless copper process was estimated to be from approaching zero to $1 \times 10^{-7}$ (one in ten million), and from approaching zero to $3 \times 10^{-7}$ (one in three million) for the conveyorized electroless copper process. Formaldehyde has been classified by EPA as Group B1, a Probable Human Carcinogen. The risk characterization for ambient exposure to MHC chemicals also indicates low concern from the estimated air concentrations for chronic non-cancer effects. The upper bound excess individual cancer risk for nearby residents from alkyl oxide in the conveyorized graphite process was estimated to be from approaching zero to $9 \times 10^{-11}$ (one in 11 billion); in the non-conveyorized electroless copper process from approaching zero to $1 \times 10^{-11}$ (one in 100 billion); and in the conveyorized electroless copper process from approaching zero to $3 \times 10^{-11}$ (one in 33 billion). All hazard quotients are less than one for ambient exposure to the general population, and all MOEs for ambient exposure are greater than 1,000 for all processes, indicating low concern from the estimated air concentrations for chronic non-cancer effects.

**Ecological Hazards**

The CTSA methodology typically evaluates ecological risks in terms of risks to aquatic organisms in streams that receive treated or untreated effluent from manufacturing processes. Stream concentrations of MHC chemicals were not available, however, and could not be estimated because of insufficient chemical characterization of constituents and their

concentrations in facility wastewater.[8] To qualitatively assess risk to aquatic organisms, MHC chemicals were ranked based on aquatic toxicity values according to established EPA criteria for aquatic toxicity of high, moderate, or low concern (see Section 3.3.3).

Table 7.4 presents the number of MHC chemicals evaluated for each alternative, the number of chemicals in each alternative with aquatic toxicity of high, moderate, or low concern, the chemicals with the lowest concern concentration (CC) by alternative, and the bath concentrations of the chemicals with the lowest CC. The aquatic toxicity concern level could not be evaluated for some chemicals that have no measured aquatic toxicity data or established structure-activity relationships to estimate their aquatic toxicity. Aquatic toxicity rankings are based only on chemical toxicity to aquatic organisms, and are not an expression of risk.

**Table 7.4 Aquatic Hazard Data**

| Alternative | No. of Chemicals Evaluated[a] | No. of Chemicals by Aquatic Hazard Concern Level[a] | | | Chemical with Lowest CC | Bath Concentration of Chemical With Lowest CC[b] |
|---|---|---|---|---|---|---|
| | | High | Moderate | Low | | |
| Electroless Copper | 50[c] | 9 | 19 | 21 | copper sulfate (0.00002 mg/l) | 4.8 to 12 g/l |
| Carbon | 8[c] | 2 | 2 | 3 | copper sulfate (0.00002 mg/l) | 5.0 g/l |
| Conductive Ink | 11[c] | 2 | 1 | 7 | silver (0.000036 mg/l) | NA |
| Conductive Polymer | 6 | 0 | 1 | 5 | peroxymonosulfuric acid (0.030 mg/l) | 26.85 g/l |
| Graphite | 13 | 3 | 3 | 7 | copper sulfate (0.00002 mg/l) | 2.7 g/l |
| Non-Formaldehyde Electroless Copper | 10 | 3 | 3 | 4 | copper sulfate (0.00002 mg/l) | 22 g/l |
| Organic-Palladium | 7 | 2 | 3 | 2 | sodium hypophosphite (0.006 mg/l) | 75 g/l[d] |
| Tin-Palladium | 26[c] | 9 | 6 | 10 | copper sulfate (0.00002 mg/l) | 0.2 to 13 g/l |

[a] This includes chemicals from both publicly-available and proprietary data. This indicates the number of unique chemicals; there is some overlap between public and proprietary lists for electroless copper. For technologies with more than one chemical supplier (e.g., electroless copper, graphite, and tin-palladium), all chemicals may not be present in any one product line.

[b] Bath concentrations are shown as a range for technologies supplied by more than one chemical supplier and are based on publicly-available bath chemistry data.

[c] No aquatic hazard data available for one chemical.

[d] Chemical is in microetch bath. Concentration in bath may be overestimated, because MSDS reports both chemicals in bath (sodium persulfate and sodium bisulfate) are present in concentrations < 75 percent (< 75 g/l).

NA: Not Applicable.

[8] There are well-documented copper pollution problems associated with discharges to surface waters and many of the MHC alternatives contain copper compounds. However, there were no data available to estimate the relative concentration of copper in different MHC line effluents. In addition, no data were available for surface water concentrations of other chemicals, especially chemicals in alternatives to electroless copper processes. Thus, risk to aquatic organisms were not characterized.

A CC is the concentration of a chemical in the aquatic environment which, if exceeded, may result in significant risk to aquatic organisms. CCs were determined by dividing acute or chronic toxicity values by an assessment factor (ranging from one to 1,000) that incorporates the uncertainty associated with toxicity data. CCs are discussed in more detail in Section 3.3.3.

The number of chemicals with a high aquatic hazard concern level include nine in the electroless copper process, two in carbon, two in conductive ink, none in conductive polymer, three in graphite, three in non-formaldehyde electroless copper, two in organic-palladium, and nine in tin-palladium. However, for technologies supplied by more than one chemical supplier (e.g., electroless copper, graphite, and tin-palladium), all chemicals of high aquatic toxicity concern may not be present in any one product line. The lowest CC is for copper sulfate, which is found in five of the MHC technology categories: carbon, electroless copper, graphite, non-formaldehyde electroless copper, and tin-palladium. Bath concentrations of copper sulfate vary, ranging from a high of 22 g/l for the non-formaldehyde electroless copper technology to a low of 0.2 g/l in one of the tin-palladium processes (and, based on MSDS data, not present in the conductive ink, organic-palladium, or conductive polymer processes).

## Process Safety

Workers can be exposed to two types of hazards affecting occupational safety and health: chemical hazards and process hazards. Workers can be at risk through exposure to chemicals and because they work in proximity to automated equipment. In order to evaluate the chemical safety hazards of the various MHC technologies, MSDSs for chemical products used with each of the MHC technologies were reviewed. Table 7.5 summarizes the hazardous properties of MHC chemical products.

**Table 7.5 Hazardous Properties of MHC Chemical Products**

| MHC Technology | No. of MSDSs Reviewed[b] | Number of Chemical Products with Hazardous Properties[a] | | | | | |
|---|---|---|---|---|---|---|---|
| | | Flammable | Combustible | Explosive | Fire Hazard | Corrosive | Oxidizer |
| Electroless Copper | 68 | 7 | 1 | 1 | 1 | 29 | 6 |
| Carbon | 11 | 7 | 0 | 0 | 0 | 5 | 2 |
| Conductive Ink | 5 | 0 | 0 | 5 | 0 | 0 | 0 |
| Conductive Polymer[c] | 8 | 1 | 0 | 0 | 0 | 5 | 0 |
| Graphite | 12 | 0 | 0 | 0 | 1 | 4 | 1 |
| Non-Formaldehyde Electroless Copper | 19 | 3 | 0 | 0 | 0 | 4 | 3 |
| Organic-Palladium[c] | 8 | 0 | 0 | 0 | 0 | 0 | 0 |
| Tin-Palladium | 38 | 2 | 1 | 1 | 1 | 12 | 0 |

[a] For technologies with more than one chemical supplier (e.g., electroless copper, graphite, and tin-palladium), all chemicals with hazardous properties may not be present in any one product line.

[b] Reflects the combined number of MSDSs for all product lines evaluated in a technology category.

[c] Based on German equivalent of MSDS, which may not have as stringent reporting requirements as U.S. MSDS.

**Table 7.5 Hazardous Properties of MHC Chemical Products (cont.)**

| MHC Technology | No. of MSDSs Reviewed[b] | Number of Chemical Products with Hazardous Properties[a] | | | | | |
|---|---|---|---|---|---|---|---|
| | | Reactive | Unstable | Sensitizer | Acute Health Hazard | Chronic Health Hazard | Eye Damage |
| Electroless Copper | 68 | 16 | 1 | 0 | 14 | 10 | 34 |
| Carbon | 11 | 2 | 0 | 0 | 11 | 9 | 12 |
| Conductive Ink | 5 | 0 | 0 | 0 | 0 | 0 | 2 |
| Conductive Polymer[c] | 8 | 0 | 0 | 0 | 0 | 0 | 6 |
| Graphite | 12 | 0 | 1 | 0 | 8 | 4 | 4 |
| Non-Formaldehyde Electroless Copper | 19 | 4 | 0 | 0 | 9 | 5 | 7 |
| Organic-Palladium[c] | 8 | 0 | 1 | 0 | 0 | 0 | 4 |
| Tin-Palladium | 38 | 3 | 0 | 2 | 9 | 5 | 22 |

[a] For technologies with more than one chemical supplier (e.g., electroless copper, graphite, and tin-palladium), all chemicals with hazardous properties may not be present in any one product line.
[b] Reflects the combined number of MSDSs for all product lines evaluated in a technology category.
[c] Based on German equivalent of MSDS, which may not have as stringent reporting requirements as U.S. MSDS.

Other potential chemical hazards can occur because of hazardous decomposition of chemical products, or chemical product incompatibilities with other chemicals or materials. With few exceptions, most chemical products used in MHC technologies can decompose under specific conditions to form potentially hazardous chemicals. In addition, all of the MHC processes have chemical products with incompatibilities that can pose a threat to worker safety if the proper care is not taken to prevent such occurrences.

Work-related injuries from equipment, improper use of equipment, bypassing equipment safety features, failure to use personal protective equipment, and physical stresses that may appear gradually as a result of repetitive motion are all potential process safety hazards to workers. Regardless of the technology used, of critical importance is an effective and ongoing safety training program. Characteristics of an effective worker health and safety program include:

- An employee training program.
- Employee use of personal protective equipment.
- Proper chemical storage and handling.
- Safe equipment operating procedures.

Without appropriate training, the number of worker accidents and injuries is likely to increase, regardless of the technology used. A key management responsibility is to ensure that training is not compromised by pressure to meet production demands or by cost-cutting efforts.

### 7.1.2 Competitiveness Summary

The competitiveness summary provides information on basic issues traditionally important to the competitiveness of a business: the performance characteristics of its products relative to industry standards; the direct and indirect costs of manufacturing its products; its need or ability to comply with environmental regulations; and factors influencing world-wide markets for its products or technologies that may affect its competitiveness. The final evaluation of a technology involves considering these traditional competitiveness issues along with issues that business leaders now know are equally important competitiveness issues: the health and environmental impacts of alternative products, processes, and technologies.

**Performance**

The performance of the MHC technologies was tested using production run tests. In order to complete this evaluation, PWB panels, designed to meet industry "middle-of-the-road" technology, were manufactured at one facility, run through individual MHC lines at 26 facilities, then electroplated at one facility. The panels were electrically prescreened, followed by electrical stress testing and mechanical testing, in order to distinguish variability in the performance of the MHC interconnect. The test methods used to evaluate performance were intended to indicate characteristics of a technology's performance, not to define parameters of performance or to substitute for thorough on-site testing; the study was intended to be a "snapshot" of the technologies. The Performance Demonstration was conducted with extensive input and participation from PWB manufacturers, their suppliers, and PWB testing laboratories.

The technologies tested included electroless copper (the baseline), carbon, conductive ink[9], conductive polymer, graphite, non-formaldehyde electroless copper, and palladium.[10] The test vehicle was a 24 x 18" 0.062" 8-layer panel. (See Section 4.1 for a detailed description of the test vehicle.) Each test site received three panels for processing through the MHC line.

Test sites were submitted by suppliers of the technologies, and included production facilities, testing facilities (beta sites), and supplier testing facilities. Because the test sites were not chosen randomly, the sample may not be representative of all PWB manufacturing facilities (although there is no specific reason to believe that they are not representative). In addition, the number of test sites for each technology ranged from one to ten. Due to the smaller number of test sites for some technologies, results for these technologies could more easily be due to chance than the results from technologies with more test sites. Statistical relevance could not be determined.

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[9] The conductive ink test panels were processed through the MHC process and sent for testing. The supplier of the technology felt that because the test vehicle used was incompatible with the capabilities of the conductive ink technology, the test results were not indicative of the capabilities of the technology. Therefore, the results of the conductive ink technology are not reported.

[10] The Performance Demonstration included both organic and tin-palladium processes in the overall palladium category.

Product performance for this study was divided into two functions: plated-through hole (PTH) cycles to failure and the integrity of the bond between the internal lands (post) and PTH (referred to as "post separation"). The PTH cycles to failure observed in this study is a function of both electrolytic plating and the MHC process. The results indicate that each MHC technology has the capability to achieve comparable (or superior) levels of performance to electroless copper. Post separation results indicated percentages of post separation that were unexpected by many members of the industry. It was apparent that all MHC technologies, including electroless copper, are susceptible to this type of failure.

## Cost

Comparative costs were estimated using a hybrid cost model which combined traditional costs with simulation modeling and activity-based costs. The cost model was designed to determine the total cost of processing a specific amount of PWB through a fully operational MHC line, in this case, 350,000 surface square feet (ssf). Total costs were divided by the throughput (350,000 ssf) to determine a unit cost in $/ssf. The cost model did not estimate start-up costs for a facility switching to an MHC alternative or the cost of other process changes that may be required to implement an MHC alternative.

The cost components considered include capital costs (primary equipment, installation, and facility costs), materials costs (limited to chemical costs), utility costs (water, electricity, and natural gas costs), wastewater cost (limited to wastewater discharge cost), production costs (production labor and chemical transport costs), and maintenance costs (tank cleanup, bath setup, sampling and analysis, and filter replacement costs). Other cost components may contribute significantly to overall costs, but were not quantified because they could not be reliably estimated. These include wastewater treatment cost, sludge recycling and disposal cost, other solid waste disposal costs, and quality costs. However, Performance Demonstration results indicate that each MHC technology has the capability to achieve comparable levels of performance to electroless copper. Thus, quality costs are not expected to differ among the alternatives.

Table 7.6 presents results of the cost analysis, which indicate all of the alternatives are more economical than the non-conveyorized electroless copper process. In general, conveyorized processes cost less than non-conveyorized processes. Costs ranged from $0.51/ssf for the baseline process to $0.09/ssf for the conveyorized conductive polymer process. Seven process alternatives cost less than or equal to $0.20/ssf (conveyorized carbon at $0.18/ssf, conveyorized conductive polymer at $0.09/ssf, conveyorized electroless copper at $0.15/ssf, conveyorized organic-palladium at $0.17/ssf, non-conveyorized organic-palladium at $0.15/ssf, and conveyorized and non-conveyorized tin-palladium at $0.12/ssf and $0.14/ssf, respectively). Three processes cost more than $0.20/ssf; all of these processes are non-conveyorized (non-conveyorized electroless copper at $0.51/ssf, non-conveyorized non-formaldehyde electroless copper at $0.40/ssf, and conveyorized graphite at $0.22/ssf).

**Table 7.6 Cost of MHC Technologies**

| Cost Category | Cost Components | Electroless Copper, non-conveyorized | Carbon, conveyorized | Conductive Polymer, conveyorized |
|---|---|---|---|---|
| Capital Cost | Primary Equipment | $64,000 | $7,470 | $5,560 |
| | Installation | $11,200 | $299 | $0 |
| | Facility | $8,690 | $2,690 | $2,250 |
| Material Cost | Chemicals | $22,500 | $32,900 | $10,400 |
| Utility Cost | Water | $6,540 | $725 | $410 |
| | Electricity | $2,780 | $836 | $460 |
| | Natural Gas | $0 | $418 | $0 |
| Wastewater Cost | Wastewater Discharge | $13,700 | $1,710 | $965 |
| Production Cost | Transportation of Material | $737 | $446 | $673 |
| | Labor for Line Operation | $36,100 | $10,200 | $5,830 |
| Maintenance Cost | Tank Cleanup | $5,430 | $3,280 | $4,960 |
| | Bath Setup | $1,220 | $740 | $1,120 |
| | Sampling and Testing | $4,260 | $405 | $436 |
| | Filter Replacement | $2,800 | $116 | $376 |
| **Total Cost** | | **$180,000** | **$62,200** | **$33,400** |
| **Unit Cost ($/ssf)** | | **$0.51** | **$0.18** | **$0.09** |

| Cost Category | Cost Components | Electroless Copper, conveyorized | Graphite, conveyorized | Non-Formaldehyde Electroless Copper, non-conveyorized |
|---|---|---|---|---|
| Capital Cost | Primary Equipment | $6,190 | $3,580 | $29,300 |
| | Installation | $212 | $131 | $5,120 |
| | Facility | $2,800 | $1,090 | $3,350 |
| Material Cost | Chemicals | $22,600 | $59,800 | $69,600 |
| Utility Cost | Water | $642 | $251 | $2,100 |
| | Electricity | $669 | $462 | $1,310 |
| | Natural Gas | $0 | $145 | $0 |
| Wastewater Cost | Wastewater Discharge | $1,450 | $612 | $4,520 |
| Production Cost | Transportation of Material | $883 | $319 | $682 |
| | Labor for Line Operation | $7,230 | $6,700 | $16,200 |
| Maintenance Cost | Tank Cleanup | $6,500 | $2,350 | $5,030 |
| | Bath Setup | $1,460 | $529 | $1,130 |
| | Sampling and Testing | $942 | $316 | $691 |
| | Filter Replacement | $612 | $901 | $214 |
| **Total Cost** | | **$52,200** | **$77,200** | **$139,200** |
| **Unit Cost ($/ssf)** | | **$0.15** | **$0.22** | **$0.40** |

**Table 7.6 Cost of MHC Technologies (cont.)**

| Cost Category | Cost Components | Organic-Palladium, conveyorized | Organic-Palladium, non-conveyorized |
|---|---|---|---|
| Capital Cost | Primary Equipment | $5,780 | $4,160 |
| | Installation | $356 | $256 |
| | Facility | $2,220 | $1,100 |
| Material Cost | Chemicals | $28,900 | $27,000 |
| Utility Cost | Water | $635 | $758 |
| | Electricity | $720 | $325 |
| | Natural Gas | $0 | $0 |
| Wastewater Cost | Wastewater Discharge | $1,510 | $1,670 |
| Production Cost | Transportation of Material | $1,260 | $1,050 |
| | Labor for Line Operation | $6,530 | $7,190 |
| Maintenance Cost | Tank Cleanup | $9,250 | $7,710 |
| | Bath Setup | $2,080 | $1,740 |
| | Sampling and Testing | $411 | $288 |
| | Filter Replacement | $271 | $385 |
| **Total Cost** | | **$59,900** | **$53,700** |
| **Unit Cost ($/ssf)** | | **$0.17** | **$0.15** |

| Cost Category | Cost Components | Tin-Palladium, conveyorized | Tin-Palladium, non-conveyorized |
|---|---|---|---|
| Capital Cost | Primary Equipment | $1,280 | $4,760 |
| | Installation | $205 | $381 |
| | Facility | $1,490 | $1,910 |
| Material Cost | Chemicals | $25,500 | $22,300 |
| Utility Cost | Water | $317 | $1,010 |
| | Electricity | $468 | $635 |
| | Natural Gas | $0 | $0 |
| Wastewater Cost | Wastewater Discharge | $754 | $2,340 |
| Production Cost | Transportation of Material | $537 | $455 |
| | Labor for Line Operation | $5,230 | $10,700 |
| Maintenance Cost | Tank Cleanup | $3,950 | $3,350 |
| | Bath Setup | $891 | $755 |
| | Sampling and Testing | $493 | $916 |
| | Filter Replacement | $332 | $616 |
| **Total Cost** | | **$41,400** | **$50,100** |
| **Unit Cost ($/ssf)** | | **$0.12** | **$0.14** |

Chemical cost was the single largest component cost for nine of the ten processes. Equipment cost was the largest cost for the non-conveyorized electroless copper process. Three separate sensitivity analyses of the results indicated that chemical cost, production labor cost, and equipment cost have the greatest effect on the overall cost results.

## Regulatory Status

Discharges of MHC chemicals may be restricted by federal, state or local air, water or solid waste regulations, and releases may be reportable under the federal Toxic Release Inventory program. Federal environmental regulations were reviewed to determine the federal regulatory status of MHC chemicals.[11] Table 7.7 lists the number of chemicals used in an MHC technology with federal environmental regulations restricting or requiring reporting of their discharges. Different chemical suppliers of a technology do not always use the same chemicals in their particular product lines. Thus, all of these chemicals may not be present in any one product line.

## International Information

The total world market for PWBs is approximately $21 billion (EPA, 1995). The U.S. and Japan are the leading suppliers of PWBs, but Hong Kong, Singapore, Taiwan, and Korea are increasing their market share. Information on the use of MHC technologies worldwide was collected to assess whether global trends affect the competitiveness of an alternative.

The alternatives to the traditional electroless copper MHC process are in use in many countries. Most of the suppliers of these alternatives have manufacturing facilities located in countries to which they sell. Several suppliers indicated the market shares of the alternatives are increasing internationally quicker than they are increasing in the U.S. The cost-effectiveness of an alternative has been the main driver causing PWB manufacturers abroad to switch from an electroless copper process to one of the newer alternatives. In addition to the increased capacity and decreased labor requirements of some of the MHC alternatives over the electroless copper process, environmental concerns also affected the process choice. For instance, the rate at which an alternative consumes water and the presence or absence of strictly regulated chemicals are two factors which have a substantial effect on the cost-effectiveness of MHC alternatives abroad. While environmental regulations do not seem to be the primary forces leading toward the adoption of the newer alternatives, it appears that the companies that supply these alternatives are taking environmental regulations and concerns into consideration when designing alternatives.

[11] In some cases, state or local requirements may be more restrictive than federal requirements. However, due to resource limitations, only federal regulations were reviewed.

## Table 7.7 Regulatory Status of MHC Technologies

| MHC Technology | Number of Chemicals Subject to Applicable Regulation | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CWA | | | | SDWA | | CAA | | | SARA 110 | EPCRA | | TSCA | | | RCRA Waste | |
| | 304b | 307a | 311 | Priority Pollutant | NPDWR | NSDWR | 111 | 112b | 112r | | 302a | 313 | 8d HSDR | MTL | 8a PAIR | P | U |
| Electroless Copper | 4 | 4 | 13 | 8 | 4 | 5 | 8 | 8 | 2 | 6 | 6 | 13 | 2 | 4 | 3 | 2 | 4 |
| Carbon | 1 | 1 | 3 | 2 | 1 | 1 | | | | 1 | | 1 | | | | | |
| Conductive Ink | 2 | 2 | | 2 | | 1 | 5 | 3 | | 1 | | 2 | 2 | | 3 | | 1 |
| Conductive Polymer | | | 3 | | | | 1 | | | | 1 | 2 | | | | | |
| Graphite | 2 | 1 | 3 | 1 | 1 | 1 | 1 | | 1 | 2 | 2 | 3 | | | | | |
| Non-Formaldehyde Electroless Copper | 1 | 1 | 5 | 1 | 1 | 1 | 1 | 1 | 1 | 3 | 3 | 4 | | 1 | 1 | | |
| Organic-Palladium | | | 2 | | | | | 1 | 1 | | 1 | 1 | | | | | |
| Tin-Palladium | 2 | 2 | 7 | 2 | 3 | 3 | 3 | 1 | 1 | 6 | 3 | 6 | | 3 | 3 | | 1 |

Abbreviations and definitions:

CAA - Clean Air Act
CAA 111 - Standards of Performance for New Stationary Sources of Air Pollutants-Equipment Leaks Chemical List
CAA 112b - Hazardous Air Pollutant
CAA 112r - Risk Management Program
CWA - Clean Water Act
CWA 304b - Effluent Limitations Guidelines
CWA 307a - Toxic Pollutants
CWA 311 - Hazardous Substances
CWA Priority Pollutants
EPCRA - Emergency Planning and Community Right-to-Know Act
EPCRA 302a - Extremely Hazardous Substances
EPCRA 313 - Toxic Chemical Release Inventory
RCRA - Resource Conservation and Recovery Act
RCRA P Waste - Listed acutely hazardous waste
RCRA U Waste - Listed hazardous waste
SARA - Superfund Amendments and Reauthorization Act
SARA 110 - Superfund Site Priority Contaminant
SDWA - Safe Drinking Water Act
SDWA NPDWR - National Primary Drinking Water Rules
SDWA NSDWR - National Secondary Drinking Water Rules
TSCA - Toxic Substances Control Act
TSCA 8d HSDR - Health & safety data reporting rules
TSCA MTL - Master Testing List
TSCA 8a PAIR - Preliminary Assessment Information Rule

### 7.1.3 Resource Conservation Summary

Resources typically consumed by the operation of the MHC process include water used for rinsing panels, process chemicals used on the process line, energy used to heat process baths and power equipment, and wastewater treatment chemicals. A quantitative analysis of the energy and water consumption rates of the MHC process alternatives was performed to determine if implementing an alternative to the baseline process would reduce consumption of these resources during the manufacturing process. A quantitative analysis of both process chemical and treatment chemical consumption could not be performed due to the variability of factors that affect the consumption of these resources. Section 5.1 discusses the role the MHC process has in the consumption of these resources and the factors affecting the consumption rates.

The relative water and energy consumption rates of the MHC process alternatives were determined as follows:

- The daily water consumption rate and hourly energy consumption rate of each alternative were determined based on data collected from the IPC Workplace Practices Questionnaire.
- The operating time required to produce 350,000 ssf of PWB was determined using computer simulations models of each of the alternatives.
- The water and energy consumption rates per ssf of PWB were calculated based on the consumption rates and operating times.

Table 7.8 presents the results of these analyses.

**Table 7.8 Energy and Water Consumption Rates of MHC Alternatives**

| Process Type | Water Consumption (gal/ssf) | Energy Consumption (Btu/ssf) |
|---|---|---|
| Electroless Copper, non-conveyorized (BASELINE) | 11.7 | 573 |
| Electroless Copper, conveyorized | 1.15 | 138 |
| Carbon, conveyorized | 1.29 | 514 |
| Conductive Polymer, conveyorized | 0.73 | 94.7 |
| Graphite, conveyorized | 0.45 | 213 |
| Non-Formaldehyde Electroless Copper, non-conveyorized | 3.74 | 270 |
| Organic-Palladium, non-conveyorized | 1.35 | 66.9 |
| Organic-Palladium, conveyorized | 1.13 | 148 |
| Tin-Palladium, non-conveyorized | 1.80 | 131 |
| Tin-Palladium, conveyorized | 0.57 | 96.4 |

The energy consumption rates ranged from 66.9 Btu/ssf for the non-conveyorized organic-palladium process to 573 Btu/ssf for the non-conveyorized electroless copper process. The results indicate that all of the MHC alternatives are more energy efficient than the baseline process. They also indicate that for alternatives with both types of automation, the conveyorized

version of the process is typically more energy efficient, with the notable exception of the organic-palladium process.

An analysis of the impacts directly resulting from the consumption of energy by the MHC process showed that the generation of the required energy has environmental impacts. Pollutants released to air, water, and soil can result in damage to both human health and the environment. The consumption of natural gas tends to result in releases to the air which contribute to odor, smog, and global warming, while the generation of electricity can result in pollutant releases to all media with a wide range of possible affects. Since all of the MHC alternatives consume less energy than the baseline, they all result in less pollutant releases to the environment.

Water consumption rates ranged from 0.45 gal/ssf for the graphite process to 11.7 gal/ssf for the non-conveyorized electroless copper process. In addition, results indicate that all of the alternatives consume significantly less water than the baseline process. Conveyorized processes were found to consume less water than non-conveyorized versions of the same process.

The rate of water consumption is directly related to the rate of wastewater generation. Most PWB facilities discharge process rinse water to an on-site wastewater treatment facility for pretreatment prior to discharge to a publicly-owned treatment works (POTW). A pollution prevention analysis identified a number of pollution prevention techniques that can be used to reduce rinse water consumption. These include use of more efficient rinse configurations, use of flow control technologies, and use of electronic sensors to monitor contaminant concentrations in rinse water. Further discussion of these and other pollution prevention techniques can be found in the Pollution Prevention section of this CTSA (Section 6.1) and in PWB Project Case Study 1 (EPA, 1995).

## 7.2 SOCIAL BENEFITS/COSTS ASSESSMENT

### 7.2.1 Introduction to Social Benefits/Costs Assessment

Social benefits/costs analysis[12] is a tool used by policy makers to systematically evaluate the impacts to all of *society* resulting from individual decisions. The decision evaluated in this analysis is the choice of an MHC technology. PWB manufacturers have a number of criteria they may use to assess which MHC technology they will use. For example, a PWB manufacturer might ask what impact their choice of an MHC alternative might have on operating costs, compliance costs, liability costs, and insurance premiums. This business planning process is unlike social benefit/cost analysis, however, because it approaches the comparison from the standpoint of the individual manufacturer and not from the standpoint of society as a whole.

A social benefits/costs analysis seeks to compare the benefits and costs of a given action, while considering both the private and external costs and benefits.[13] Therefore, the analysis will consider both the impact of the alternative MHC processes on the manufacturer itself (private costs and benefits) and the impact the choice of an alternative has on external costs and benefits, such as reductions in environmental damage and reductions in the risk of illness for the general public. External costs are not borne by the manufacturer, rather they are the true costs to society. Table 7.9 defines a number of terms used in benefit/cost assessment, including external costs and external benefits.

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[12] The term "analysis" is used here to refer to a more quantitative analysis of social benefits and costs, where a monetary value is placed on the benefits and costs to society of individual decisions. Examples of quantitative benefits/costs analyses are the regulatory impact analyses done by EPA when developing federal environmental regulations. The term "assessment" is used here to refer to a more qualitative examination of social benefits and costs. The evaluation performed in the CTSA process is more correctly termed an assessment because many of the social benefits and costs of MHC technologies are identified, but not monetized.

[13] Private costs typically include any direct costs incurred by the decision-maker and are generally reflected in the manufacturer's balance sheet. In contrast, external costs are incurred by parties other than the primary participants to the transaction. Economists distinguish between private and external costs because each will affect the decision-maker differently. Although external costs are real costs to some members of society, they are not incurred by the decision-maker and firms do not normally take them into account when making decisions. A common example of these "externalities" is the electric utility whose emissions are reducing crop yields for the farmer operating downwind. The external costs experienced by the farmer in the form of reduced crop yields are not considered by the utility when making decisions regarding electricity production. The farmer's losses do not appear on the utility's balance sheet.

**Table 7.9 Glossary of Benefits/Costs Analysis Terms**

| Term | Definition |
|---|---|
| Exposed Population | The estimated number of people from the general public or a specific population group who are exposed to a chemical through wide dispersion of a chemical in the environment (e.g., DDT). A specific population group could be exposed to a chemical due to its physical proximity to a manufacturing facility (e.g., residents who live near a facility using a chemical), use of the chemical or a product containing a chemical, or through other means. |
| Exposed Worker Population | The estimated number of employees in an industry exposed to the chemical, process, and/or technology under consideration. This number may be based on market share data as well as estimations of the number of facilities and the number of employees in each facility associated with the chemical, process, and/or technology under consideration. |
| Externality | A cost or benefit that involves a third party who is not a part of a market transaction; "a direct effect on another's profit or welfare arising as an incidental by-product of some other person's or firm's legitimate activity" (Mishan, 1976). The term "externality" is a general term which can refer to either external benefits or external costs. |
| External Benefits | A positive effect on a third party who is not a part of a market transaction. For example, if an educational program results in behavioral changes which reduce the exposure of a population group to a disease, then an external benefit is experienced by those members of the group who did not participate in the educational program. For the example of nonsmokers exposed to second-hand smoke, an external benefit can be said to result when smokers are removed from situations in which they expose nonsmokers to tobacco smoke. |
| External Costs | A negative effect on a third party who is not part of a market transaction. For example, if a steel mill emits waste into a river which poisons the fish in a nearby fishery, the fishery experiences an external cost as a consequence of the steel production. Another example of an external cost is the effect of second-hand smoke on nonsmokers. |
| Human Health Benefits | Reduced health risks to workers in an industry or business as well as to the general public as a result of switching to less toxic or less hazardous chemicals, processes, and/or technologies. An example would be switching to a less volatile organic compound, lessening worker inhalation exposures as well as decreasing the formation of photochemical smog in the ambient air. |
| Human Health Costs | The cost of adverse human health effects associated with production, consumption, and disposal of a firm's product. An example is respiratory effects from stack emissions, which can be quantified by analyzing the resulting costs of health care and the reduction in life expectancy, as well as the lost wages as a result of being unable to work. |
| Illness Costs | A financial term referring to the liability and health care insurance costs a company must pay to protect itself against injury or disability to its workers or other affected individuals. These costs are known as illness benefits to the affected individual. |
| Indirect Medical Costs | Indirect medical costs associated with a disease or medical condition resulting from exposure to a chemical or product. Examples would be the decreased productivity of patients suffering a disability or death and the value of pain and suffering borne by the afflicted individual and/or family and friends. |

| Term | Definition |
|---|---|
| Private (Internalized) Costs | The direct costs incurred by industry or consumers in the marketplace. Examples include a firm's cost of raw materials and labor, a firm's costs of complying with environmental regulations, or the cost to a consumer of purchasing a product. |
| Social Costs | The total cost of an activity that is imposed on society. Social costs are the sum of the private costs and the external costs. Therefore, in the example of the steel mill, social costs of steel production are the sum of all private costs (e.g., raw material and labor costs) and the sum of all external costs (e.g., the costs associated with the poisoned fish). |
| Social Benefits | The total benefit of an activity that society receives, i.e., the sum of the private benefits and the external benefits. For example, if a new product yields pollution prevention opportunities (e.g., reduced waste in production or consumption of the product), then the total benefit to society of the new product is the sum of the private benefit (value of the product that is reflected in the marketplace) and the external benefit (benefit society receives from reduced waste). |
| Willingness-to-Pay | Estimates used in benefits valuation are intended to encompass the full value of avoiding a health or environmental effect. For human health effects, the components of willingness-to-pay include the value of avoiding pain and suffering, impacts on the quality of life, costs of medical treatment, loss of income, and, in the case of mortality, the value of life. |

Private benefits of the alternative MHC processes may include increased profits resulting from improved worker productivity and company image, a reduction in energy use, or reduced property and health insurance costs due to the use of less hazardous chemicals. External benefits may include a reduction in pollutants emitted to the environment or reduced use of natural resources. Costs of the alternative MHC processes may include private costs such as changes in operating expenses and external costs such as an increase in human health risks and ecological damage. Several of the benefit categories considered in this assessment share elements of both private and external costs and benefits. For example, use of an alternative may result in natural resource savings. Such a benefit may result in private benefits in the form of reduced water usage and a resultant reduction in payments for water as well as external benefits in the form of reduced consumption of shared resources.

### 7.2.2 Benefits/Costs Methodology and Data Availability

The methodology for conducting a social benefits/costs assessment can be broken down into four general steps: 1) obtain information on the relative human and environmental risk, performance, cost, process safety hazards, and energy and natural resource requirements of the baseline and the alternatives; 2) construct matrices of the data collected; 3) when possible, monetize the values presented within the matrices; and 4) compare the data generated for the alternative and the baseline in order to produce an estimate of net social benefits. Section 7.1 presented the results of the first task by summarizing risk, competitiveness, and conservation information for the baseline and alternative MHC technologies. Section 7.2.3 presents matrices of private benefits and costs data, while Section 7.2.4 presents information relevant to external benefits and costs. Section 7.2.5 presents the private and external benefits and costs together to produce an estimate of net social benefits.

Ideally, the analysis would quantify the social benefits and costs of using the alternative and baseline MHC technologies, allowing identification of the technology whose use results in the largest net social benefit. This is particularly true for national estimates of net social benefits or costs. However, because of resource and data limitations and because individual users of this CTSA will need to apply results to their own particular situations, the analysis presents a qualitative description of the risks and other external effects associated with each substitute technology compared to the baseline. Benefits derived from a reduction in risk are described and discussed, but not quantified. Nonetheless, the information presented can be very useful in the decision-making process. A few examples are provided to qualitatively illustrate some of the benefit considerations. Personnel in each individual facility will need to examine the information presented, weigh each piece according to facility and community characteristics, and develop an independent choice.

### 7.2.3 Private Benefits and Costs

While it is difficult to obtain an overall number to express the private benefits and costs of alternative MHC processes, some data were quantifiable. For example, the cost analysis estimated the average manufacturing costs of the MHC technologies, including the average capital costs (primary equipment, installation, and facility cost), materials costs (limited to chemical costs), utility costs (water, electricity, and natural gas costs), wastewater costs (limited to wastewater discharge cost), production cost (production labor and chemical transport costs), and maintenance costs (tank cleanup, bath setup, sampling and analysis, and filter replacement costs). Other cost components may contribute significantly to overall manufacturing costs, but were not quantified because they could not be reliably estimated. These include wastewater treatment cost, sludge recycling and disposal cost, other solid waste disposal costs, and quality costs.

Differences in the manufacturing costs estimated in the cost analysis are summarized below. However, in order to determine the overall private benefit/cost comparison, a qualitative discussion of the data is also necessary. Following the discussion of manufacturing costs are discussions of private costs associated with occupational and population health risks and other private costs or benefits that could not be monetized but are important to the decision-making process.

**Manufacturing Costs**

Table 7.10 presents the percent change in manufacturing costs for the MHC alternatives as compared to the baseline. Only costs that were quantified in the cost analysis are presented. All of the alternatives result in cost savings in the form of lower total costs; most of the alternatives result in cost savings in almost every cost category. In addition, the Performance Demonstration determined that each alternative has the capability to achieve comparable levels of performance to electroless copper, thus quality costs are considered equal among the alternatives. This is important to consider in a benefits/costs analysis since changes in performance necessarily result in changed costs in the market. This is not the case in this assessment since all alternatives yield comparable performance results.

## Table 7.10 Differences in Private Costs[a]

| MHC Technology | Average Cost | | Capital Cost | | Chemical Cost | | Water Cost | | Electricity Cost | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $/ssf | % change | $/ssf | % change | $/ssf | % change | $/ssf | % change | $/ssf | % change |
| Electroless Copper, non-conveyorized (BASELINE) | $ 0.51 | | $ 0.24 | | $ 0.06 | | $ 0.02 | | $ 0.008 | |
| Electroless Copper, conveyorized | $ 0.15 | -71 | $ 0.03 | -88 | $ 0.06 | 0 | $ 0.002 | -90 | $ 0.002 | -75 |
| Carbon, conveyorized | $ 0.18 | -65 | $ 0.03 | -88 | $ 0.10 | +66 | $ 0.002 | -90 | $ 0.001 | -88 |
| Conductive Polymer, conveyorized | $ 0.09 | -82 | $ 0.02 | -92 | $ 0.03 | -50 | $ 0.001 | -95 | $ 0.001 | -88 |
| Graphite, conveyorized | $ 0.22 | -57 | $ 0.01 | -96 | $ 0.17 | +183 | $ 0.001 | -95 | $ 0.004 | -50 |
| Non-Formaldehyde Electroless Copper, non-conveyorized | $ 0.40 | -22 | $ 0.11 | -54 | $ 0.20 | +233 | $ 0.01 | -50 | $ 0.004 | -50 |
| Organic-Palladium, non-conveyorized | $ 0.15 | -71 | $ 0.02 | -92 | $ 0.08 | +33 | $ 0.002 | -90 | $ 0.001 | -88 |
| Organic-Palladium, conveyorized | $ 0.17 | -67 | $ 0.02 | -92 | $ 0.08 | +33 | $ 0.002 | -90 | $ 0.002 | -75 |
| Tin-Palladium, non-conveyorized | $ 0.14 | -73 | $ 0.02 | -92 | $ 0.06 | 0 | $ 0.003 | -85 | $ 0.002 | -75 |
| Tin-Palladium, conveyorized | $ 0.12 | -77 | $ 0.01 | -96 | $ 0.07 | +17 | $ 0.001 | -95 | $ 0.001 | -88 |

| MHC Technology | Natural Gas Cost | | Wastewater Cost | | Production Cost | | Maintenance Cost | |
|---|---|---|---|---|---|---|---|---|
| | $/ssf | % change | $/ssf | % change | $/ssf | % change | $/ssf | % change |
| Electroless Copper, non-conveyorized (BASELINE) | $ - | | $ 0.04 | | $ 0.11 | | $ 0.04 | |
| Electroless Copper, conveyorized | $ - | NA | $ 0.004 | -90 | $ 0.02 | -82 | $ 0.03 | -25 |
| Carbon, conveyorized | $ 0.001 | NA | $ 0.005 | -88 | $ 0.03 | -73 | $ 0.01 | -75 |
| Conductive Polymer, conveyorized | $ - | NA | $ 0.003 | -93 | $ 0.02 | -82 | $ 0.02 | -50 |
| Graphite, conveyorized | $ 0.0004 | NA | $ 0.002 | -95 | $ 0.02 | -82 | $ 0.01 | -75 |
| Non-Formaldehyde Electroless Copper, non-conveyorized | $ - | NA | $ 0.01 | -75 | $ 0.05 | -55 | $ 0.02 | -50 |
| Organic-Palladium, non-conveyorized | $ - | NA | $ 0.005 | -88 | $ 0.02 | -82 | $ 0.03 | -25 |
| Organic-Palladium, conveyorized | $ - | NA | $ 0.004 | -90 | $ 0.02 | -82 | $ 0.03 | -25 |
| Tin-Palladium, non-conveyorized | $ - | NA | $ 0.007 | -83 | $ 0.03 | -73 | $ 0.02 | -50 |
| Tin-Palladium, conveyorized | $ - | NA | $ 0.002 | -95 | $ 0.02 | -82 | $ 0.02 | -50 |

[a] Table lists costs and percent change in cost from the baseline.

NA: Not Applicable, % change cannot be calculated because baseline has zero cost in this cost category.

## Occupational Health Risks

Reduced risks to workers can be considered both a private and external benefit. Private worker benefits include reductions in worker sick days and reductions in health insurance costs to the PWB manufacturer. External worker benefits include reductions in medical costs to workers in addition to reductions in pain and suffering associated with work-related illness. External benefits from reduced risk to workers are discussed in more detail in Section 7.2.4.

Health risks to workers were estimated for inhalation exposure to vapors and aerosols from MHC baths and for dermal exposure to MHC bath chemicals. Inhalation exposure estimates are based on the assumptions that emissions to indoor air from conveyorized lines are negligible, that the air in the process room is completely mixed and chemical concentrations are constant over time, and that no vapor control devices (e.g., bath covers) are used in non-conveyorized lines. Dermal exposure estimates are based on the assumption that workers do not wear gloves and that all non-conveyorized lines are operated by manual hoist. Dermal exposure to workers on non-conveyorized lines could occur from routine line operation and maintenance (i.e., bath replacement, filter replacement, etc.). Dermal exposure to workers on conveyorized lines was assumed to occur from bath maintenance alone. Worker dermal exposure to all MHC technologies can be easily minimized by using proper protective equipment such as gloves during MHC line operation and maintenance. In addition, many PWB manufacturers report that their employees routinely wear gloves in the process area. Nonetheless, risk from dermal contact was estimated assuming workers do not wear gloves to account for those workers who do not wear proper personal protective equipment.

Because some parts of the exposure assessment for both inhalation and dermal exposures qualify as "what-if" descriptors,[14] the entire assessment should be considered "what-if." Table 7.11 summarizes the number of chemicals of concern for the exposure pathways evaluated and lists the number of suspected carcinogens in each technology.

Based on the results of the risk characterization, it appears that alternatives to the non-conveyorized electroless copper process have private benefits due to reduced occupational risks. However, there are also occupational inhalation risk concerns for some chemicals in the non-formaldehyde electroless copper and tin-palladium non-conveyorized processes. In addition, there are occupational dermal exposure risk concerns for some chemicals in the conveyorized electroless copper process, the non-conveyorized non-formaldehyde electroless copper, and the tin-palladium and organic palladium processes with conveyorized or non-conveyorized equipment. Finally, occupational health risks could not be quantified for one or more of the chemicals used in each of the MHC technologies. This is due to the fact that proprietary chemicals in the baths are not included[15] for chemical products submitted by Atotech (except one

[14] A "what-if" risk descriptor represents an exposure estimate based on postulated questions, making assumptions based on limited data where the distribution is unknown.

[15] Electrochemicals, LeaRonal, and Solution Technology Systems provided information on proprietary chemical ingredients to the project for evaluation in the risk characterization. Atotech provided information on one proprietary chemical ingredient. Risk results for proprietary chemicals in chemical products but not chemical identities or concentrations, are included in this CTSA.

proprietary chemical in one of Atotech's technologies), Enthone-OMI, MacDermid and Shipley, and to a lack of toxicity or chemical property data for some chemicals known to be present in the baths.

**Table 7.11 Summary of Occupational Hazards, Exposures, and Risks of Potential Concern**

| MHC Technology | No. of Chemicals of Concern by Pathway[a] | | No. of Suspected Carcinogens |
|---|---|---|---|
| | Inhalation | Dermal | |
| Electroless Copper, non-conveyorized (BASELINE) | 10 | 8 | 5[b] |
| Electroless Copper, conveyorized | 0 | 8 | 5[b] |
| Carbon, conveyorized | 0 | 0 | 1 |
| Conductive Polymer, conveyorized | 0 | 0 | 0 |
| Graphite, conveyorized | 0 | 0 | 2[c] |
| Non-Formaldehyde Electroless Copper, non-conveyorized | 1 | 2 | 0 |
| Organic-Palladium, non-conveyorized | 0 | 1 | 0 |
| Organic-Palladium, conveyorized | 0 | 1 | 0 |
| Tin-Palladium, non-conveyorized | 2 | 5 | 0 |
| Tin-Palladium, conveyorized | 0 | 5 | 0 |

[a] Number of chemicals of concern for an MHC line operator (the most exposed individual).
[b] Includes formaldehyde (EPA Group B1, probable human carcinogen) and dimethylformamide (IARC Group 2B, possible human carcinogen). Also included are the proprietary chemicals, cyclic ether, alkyl oxide, and trisodium acetate amine B.
[c] Includes the proprietary chemicals, cyclic ether and alkyl oxide.

Occupational cancer risks were estimated for inhalation exposure to formaldehyde and alkyl oxide in the non-conveyorized electroless copper process, and for dermal exposure to cyclic ether and alkyl oxide in the conveyorized graphite, conveyorized electroless copper, and non-conveyorized electroless copper processes. Formaldehyde has been classified by EPA as Group B1, a Probable Human Carcinogen. Results indicate clear concern for formaldehyde inhalation exposure; the upper bound excess individual cancer risk estimate for line operators in the non-conveyorized electroless copper process from formaldehyde inhalation may be as high as one in 1,000, but may be 50 times less, or one in 50,000.[16] Inhalation risks to other workers were assumed to be proportional to the amount of time spent in the process area, which ranged from three percent to 61 percent of the risk for a line operator. Occupational risks associated with dermal and inhalation exposure to cyclic ether and alkyl oxide were below $1 \times 10^{-6}$ (one in one million) for the graphite and electroless copper processes and are therefore considered to be of low concern. The occupational cancer risks associated with exposure to dimethylformamide, carbon black, and trisodium acetate amine B could not be quantified because cancer slope factors have not been determined for these chemicals.

[16] To provide further information on the possible variation of formaldehyde exposure and risk, an additional exposure estimate was provided in the Risk Characterization (Section 3.4) using average and median values (rather than high-end) as would be done for a central tendency exposure estimate. This results in approximately a 35-fold reduction in occupational formaldehyde exposure and risk from the estimates presented here.

## Public Health Risks

In addition to worker exposure, members of the general public may be exposed to MHC chemicals due to their close physical proximity to a PWB plant or due to the wide dispersion of chemicals. Reduced public health risks can also be considered both a private and external benefit. Private benefits include reductions in potential liability costs; external benefits include reductions in medical costs. External benefits from reduced public health risk are discussed in more detail in Section 7.2.4.

Public health risk was estimated for inhalation exposure only for the general populace living near a facility. Environmental releases and risk from exposure to contaminated surface water were not quantified due to a lack of data; chemical constituents and concentrations in wastewater could not be adequately characterized. Public health risk estimates are based on the assumption that emissions from both conveyorized and non-conveyorized process configurations are steady-state and vented to the outside. Risk was not characterized for short-term exposures to high levels of hazardous chemicals when there is a spill, fire, or other periodic release.

The risk indicators for ambient exposures to humans, although limited to airborne releases, indicate low concern from all MHC technologies for nearby residents. The estimated upper bound excess individual cancer risk for nearby residents exposed to emissions from the non-conveyorized electroless copper process ranged from values approaching zero to $1 \times 10^{-7}$ (one in ten million) for formaldehyde, and from approaching zero to $1 \times 10^{-11}$ (one in 100 billion) for the alkyl oxide. The estimated cancer risk values for the conveyorized electroless copper process ranged from values approaching zero to $3 \times 10^{-7}$ (one in three million) for formaldehyde, and from approaching zero to $3 \times 10^{-11}$ (one in 33 billion) for the alkyl oxide. The estimated cancer risk for nearby residents exposed to emissions from the conveyorized graphite process ranged from values approaching zero to $9 \times 10^{-11}$ (one in 11 billion) for the alkyl oxide. The risk characterization for ambient exposure to other MHC chemicals also indicated low concern from the estimated air concentrations for chronic non-cancer effects.

These results suggest little change in public health risks and, thus, private benefits or costs if a facility switched from the baseline to an MHC alternative. However, it is important to note that it was not within the scope of this comparison to assess all community health risks. The risk characterization did not address all types of exposures that could occur from MHC processes or the PWB industry, including short-term or long-term exposures from sudden releases due to spills, fires, or periodic releases.

## Ecological Risks

MHC chemicals are potentially damaging to terrestrial and aquatic ecosystems, resulting in both private costs borne by the manufacturers and external costs borne by society. Private costs could include increased liability costs while external costs could include loss of ecosystem diversity and reductions in the recreational value of streams and rivers. The CTSA evaluated the ecological risks of the baseline and alternatives in terms of aquatic toxicity hazards. Aquatic risk could not be estimated because chemical concentrations in MHC line effluents and streams were not available and could not be estimated. It is not possible to reliably estimate concentrations

only from the MHC process since most PWB manufacturers combine MHC effluents with effluents from other process lines.

Table 7.12 presents the number of chemicals in each technology with a high aquatic hazard concern level. There are well documented copper pollution problems associated with discharges to surface waters and many of the MHC alternatives contain copper compounds. The lowest CC for an MHC chemical is for copper sulfate, which is found in five of the MHC technology categories: electroless copper, carbon, graphite, non-formaldehyde electroless copper, and tin-palladium. Bath concentrations of copper sulfate vary, ranging from a high of 22 g/l for the non-formaldehyde electroless copper technology to a low of 0.2 g/l in one of the tin-palladium processes (and, based on MSDS data, not present in the conductive ink, conductive polymer, or organic-palladium processes). Because the concentration of copper sulfate in different MHC line effluents is not known, the benefits or costs of using one of these MHC alternatives cannot be assessed. For example, the non-formaldehyde electroless copper process has a higher bath concentration of copper sulfate than the baseline; however, because the non-formaldehyde electroless copper process does not contain the chelator EDTA, more copper may be removed during wastewater treatment.

**Table 7.12 Number of Chemicals with High Aquatic Hazard Concern Level**

| MHC Technology | No. of Chemicals |
|---|---|
| Electroless Copper | 9 |
| Carbon | 2 |
| Conductive Ink | 2 |
| Conductive Polymer | 0 |
| Graphite | 3 |
| Non-Formaldehyde Electroless Copper | 3 |
| Organic-Palladium | 2 |
| Tin-Palladium | 9 |

**Plant-Wide Benefits or Costs**

The CTSA did not determine the PWB plant-wide benefits or costs that could occur from implementing an alternative to the baseline MHC technology. However, a recent study of the Davila International PWB plant in Mountain View, California, identified a number of changes to the PWB manufacturing process that were only possible when an alternative to electroless copper was installed. These changes reduced copper pollution and water use, resulting in cost savings. A companion document to this publication, *Implementing Cleaner Technologies in the Printed Wiring Board Industry: Making Holes Conductive* (EPA, 1997), describes some of the systems benefits that can occur from implementing an MHC technology.

Improvements in the efficiency of the overall system not only provide private benefits, but also social benefits.

In addition, the baseline MHC process is a production bottleneck in many shops, but the alternative MHC technologies have substantially improved production rates. Thus, switching to

an alternative improves the competitiveness of a PWB manufacturer by enabling the same number of boards to be produced faster or even enabling an increase in overall production capacity. However, the increased productivity could have social costs if increased production rates cause increased pollution rates in other process steps. Greater production rates in all the processes should be coupled with pollution prevention measures.

Another cost could be incurred if increased production results in increased amounts of scrap board. The Performance Demonstration determined that all of the alternatives have the potential to perform as well as electroless copper if operated properly. However, vendors and manufacturers who have implemented the alternatives stress the importance of taking a "whole-process" view of new MHC technology installation. Process changes upstream or downstream may be necessary to optimize alternative MHC processes (EPA, 1997). This is also important from a societal perspective because an increase in scrap boards can increase pollution generation off-site. In particular, citizens groups are concerned about potential dioxin emissions from the off-site process of secondary metal smelting which recycles scrap boards (Smith and Karras, 1997).

**Other Private Benefits and Costs**

Table 7.13 gives additional examples of private costs and benefits that could not be quantified. These include wastewater treatment, solid waste disposal, compliance, liability, insurance and worker illness costs, and improvements in company image that accrue from implementing a substitute. Some of these were mentioned above, but are included in the table due to their importance to overall benefits and costs.

### 7.2.4 External Benefits and Costs

External costs are those costs that are not taken into account in the manufacturer's pricing and manufacturing decisions. These costs are commonly referred to as "externalities" and are costs that are borne by society and not by the individuals who are part of a market transaction. These costs can result from a number of different avenues in the manufacturing process. For example, if a manufacturer uses a large quantity of a non-renewable resource during the manufacturing process, society will eventually bear the costs for the depletion of this natural resource. Another example of an external cost is an increase in population health effects resulting from the emission of chemicals from a manufacturing facility. The manufacturer does not pay for any illnesses that occur outside the plant that result from air emissions. Society must bear these costs in the form of medical care payments or higher insurance premiums.

Conversely, external benefits are those that do not benefit the manufacturer directly. For example, an alternative that uses less water results in both private and external benefits. The manufacturer pays less for water; society in general benefits from less use of a scarce resource. This type of example is why particular aspects of the MHC process are discussed in terms of both private benefits and costs and external benefits and costs.

**Table 7.13 Examples of Private Costs and Benefits Not Quantified**

| Category | Description of Potential Costs or Benefits |
|---|---|
| Wastewater Treatment | Alternatives to the baseline MHC technology may provide cost savings by reducing the quantity and improving the treatability of process wastewaters. In turn, these cost savings can enable the implementation of other pollution prevention measures. Alternatives to the baseline process use less rinse water and, consequently, produce less wastewater. In addition, the elimination of the chelator EDTA found in electroless copper processes simplifies the removal of heavy metal ions by precipitation. However, other processes may contain complexing agents that form bonds with metal ions, also making them difficult to remove. For example, the graphite technology contains the complexing agent ammonia. All of these factors—reducing the quantity of wastewater, reducing the amount of chelated or complexed metals in wastewater effluents, and enabling pollution prevention measures—provide social benefits as well as private benefits. |
| Solid Waste Disposal | All of the alternatives result in the generation of sludge, off-specification PWBs, and other solid wastes, such as spent bath filters. These waste streams must be recycled or disposed of, some of them as hazardous waste. For example, many PWB manufacturers send sludges to a recycler to reclaim metals in the sludge. Sludges that cannot be effectively recycled will most likely have to be landfilled. It is likely that the manufacturer will incur costs in order to recycle or landfill these sludges and other solid wastes, however these costs were not quantified. Three categories of MHC technologies generate RCRA-listed wastes, including electroless copper, conductive ink, and tin-palladium. However, other technologies may generate wastes considered hazardous because they exhibit certain characteristics. In addition, most facilities combine wastewater from various process lines prior to on-site treatment, including wastewater from electroplating operations. Wastewater treatment sludge from copper electroplating operations is a RCRA F006 hazardous waste. Reducing the volume and toxicity of solid waste also provides social benefits. |
| Compliance Costs | The cost of complying with all environmental and safety regulations affecting the MHC process line was not quantified. However, chemicals and wastes from the MHC alternatives are subject to fewer overall federal environmental regulations than the baseline, suggesting that implementing an alternative could potentially reduce compliance costs. It is more difficult to assess the relative cost of complying with OSHA requirements, because the alternatives pose similar occupational safety hazards (although non-automated, non-conveyorized equipment may pose less overall process hazards than working with mechanized equipment). |
| Liability, Insurance, and Worker Illness Costs | Based on the results of the risk characterization, it appears that alternatives to the baseline process pose lower overall risk to human health and the environment. Implementing an alternative could cause private benefits in the form of lower liability and insurance cost and increased employee productivity from decreases in incidences of illness. Clearly, alternatives with reduced risk also provide social benefits (discussed in Section 7.2.4). |
| Company Image | Many businesses are finding that using cleaner technologies results in less tangible benefits, such as an improved company image and improved community relations. While it is difficult to put a monetary value on these benefits, they should be considered in the decision-making process. |

The potential external benefits associated with the use of an MHC alternative include: reduced health risk for workers and the general public, reduced ecological risk, and reduced use of energy and natural resources. Another potential externality is the influence a technology choice has on the number of PWB plant jobs in a community. Each of these is discussed in turn below.

## Occupational Health Risks

Section 7.2.3 discussed risk characterization results for occupational exposures. Based on the results of the risk characterization, it appears that alternatives to the non-conveyorized electroless copper process have private benefits due to reduced occupational risks. However, there are also occupational inhalation risk concerns for some chemicals in the non-formaldehyde electroless copper and tin-palladium non-conveyorized processes. In addition, there are occupational dermal exposure risk concerns for some chemicals in the conveyorized electroless copper, the non-conveyorized non-formaldehyde electroless copper, and organic-palladium and tin-palladium processes with conveyorized or non-conveyorized equipment. Finally, occupational health risks could not be quantified for one or more of the chemicals used in each of the MHC technologies. This is due to the fact that proprietary chemicals in the baths were not identified by some suppliers[17] and to missing toxicity or chemical property data for some chemicals known to occur in the baths.

Reduced occupational risks provide significant private as well as social benefits. Private benefits can include reduced insurance and liability costs, which may be readily quantifiable for an individual manufacturer. External benefits are not as easily quantifiable. They may result from the workers themselves having reduced costs such as decreased insurance premiums or medical payments or society having reduced costs based on the structure of the insurance industry.

Data exist on the cost of avoiding or mitigating certain illnesses that are linked to exposures to MHC chemicals. These cost estimates can serve as indicators of the potential benefits associated with switching to technologies using less toxic chemicals or with reduced exposures. Table 7.14 lists potential health effects associated with MHC chemicals of concern. It is important to note that, except for cancer risk from formaldehyde, the risk characterization did not link exposures of concern with particular adverse health outcomes or with the number of incidences of adverse health outcomes.[18] Thus, the net benefit of illnesses avoided by switching to an MHC alternative cannot be calculated.

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[17] Electrochemicals, LeaRonal, and Solution Technology Systems provided information on proprietary chemical ingredients to the project for evaluation in the risk characterization. Atotech provided information on one proprietary chemical used in the product line. Enthone-OMI, MacDermid, and Shipley declined to provide proprietary chemical information. Risk results for proprietary chemicals, as available, but not chemical identities or concentrations, are included in this CTSA.

[18] Cancer risk from formaldehyde exposure was expressed as a probability, but the exposure assessment did not determine the size of the potentially exposed population (e.g., number of MHC line operators and others working in the process area). This information would be necessary to estimate the number of illnesses avoided by switching to an alternative from the baseline.

**Table 7.14 Potential Health Effects Associated with MHC Chemicals of Concern**

| Chemical of Concern | Alternatives with Exposure Levels of Concern | Pathway of Concern[a] | Potential Health Effects |
|---|---|---|---|
| Alkene Diol | Electroless Copper | inhalation | Exposure to low levels may result in irritation of the throat and upper respiratory tract. |
| Copper Chloride | Electroless Copper | inhalation | Long-term exposure to copper dust can irritate nose, mouth, eyes and cause dizziness. Long-term exposure to high levels of copper may cause liver damage. Copper is not known to cause cancer. The seriousness of the effects of copper can be expected to increase with both level and length of exposure. |
| | | dermal | No data were located for health effects from dermal exposure in humans. |
| Ethanolamine | Electroless Copper, Tin-Palladium | inhalation | Ethanolamine is a strong irritant. Animal studies showed that the chemical is an irritant to the respiratory tract, eyes, and skin. No data were located for inhalation exposure in humans. |
| 2-Ethoxyethanol | Electroless Copper | inhalation | In animal studies 2-ethoxyethanol caused harmful blood effects, including destruction of red blood cells and releases of hemoglobin (hemolysis), and male reproductive effects at high exposure levels. The seriousness of the effects of the chemical can be expected to increase with both level and length of exposure. No data were located for inhalation exposure in humans. |
| Ethylene Glycol | Electroless Copper | inhalation | In humans, low levels of vapors produce throat and upper respiratory irritation. When ethylene glycol breaks down in the body, it forms chemicals that crystallize and that can collect in the body and prevent kidneys from working. The seriousness of the effects of the chemical can be expected to increase with both level and length of exposure. |
| Fluoroboric Acid | Electroless Copper, Tin-Palladium | dermal | Fluoroboric acid in humans produces strong caustic effects leading to structural damage to skin and eyes. |

| Chemical of Concern | Alternatives with Exposure Levels of Concern | Pathway of Concern[a] | Potential Health Effects |
|---|---|---|---|
| Formaldehyde | Electroless Copper | inhalation | EPA has classified formaldehyde as a probable human carcinogen (EPA Group B1). Inhalation exposure to formaldehyde in animals produces nasal cancer at low levels. In humans, exposure to formaldehyde at low levels in air produces skin irritation and throat and upper respiratory irritation. The seriousness of these effects can be expected to increase with both level and length of exposure. |
| | | dermal | In humans, exposure to formaldehyde at low levels in air produces skin irritation. The seriousness of these effects can be expected to increase with both level and length of exposure. |
| Methanol | Electroless Copper | inhalation | Long-term exposure to methanol vapors can cause headache, irritated eyes and dizziness at high levels. No harmful effects were seen when monkeys were exposed to highly concentrated vapors of methanol. When methanol breaks down in the tissues, it forms chemicals that can collect in the tissues or blood and lead to changes in the interior of the eye causing blindness. |
| Nitrogen Heterocycle | Electroless Copper | dermal | No data were located for health effects from dermal exposure in humans. |
| Palladium | Electroless Copper, Tin-Palladium | dermal | No specific information was located for dermal exposure of palladium in humans. |
| Palladium Chloride | Tin-Palladium | dermal | Long-term dermal exposure to palladium chloride in humans produces contact dermatitis. |
| Palladium Salt | Organic-Palladium | dermal | Exposure may result in skin irritation and sensitivity. |
| Sodium Carboxylate | Electroless Copper | dermal | No data were located for health effects from dermal exposure in humans. |
| Sodium Chlorite | Electroless Copper, Non-Formaldehyde Electroless Copper | dermal | No specific information was located for health effects from dermal exposure to sodium chlorite in humans. Animal studies showed that the chemical produces moderate irritation of skin and eyes. |
| Stannous Chloride | Electroless Copper, Non-Formaldehyde Electroless Copper, Tin-Palladium | dermal | Mild irritation of the skin and mucous membrane has been shown from inorganic tin salts. However, no specific information was located for dermal exposure to stannous chloride in humans. Stannous chloride is only expected to be harmful at high doses; it is poorly absorbed and enters and leaves the body rapidly. |

| Chemical of Concern | Alternatives with Exposure Levels of Concern | Pathway of Concern[a] | Potential Health Effects |
|---|---|---|---|
| Sulfuric Acid | Electroless Copper, Non-Formaldehyde Electroless Copper, Tin-Palladium | inhalation | Sulfuric acid is a very strong acid and can cause structural damage to skin and eyes. Humans exposed to sulfuric acid mist at low levels in air experience a choking sensation and irritation of lower respiratory passages. |
| Tin Salt | Electroless Copper | dermal | No data were located for health effects from dermal exposure in humans. Inorganic tin compounds may irritate the eyes, nose, throat, and skin. |

[a] Inhalation concerns only apply to non-conveyorized processes. Dermal concerns may apply to non-conveyorized and/or conveyorized processes (see Table 7.3).

Health endpoints potentially associated with MHC chemicals of concern include: nasal cancer (for formaldehyde), eye irritation, and headaches. The draft EPA publication, *The Medical Costs of Selected Illnesses Related to Pollutant Exposure* (EPA, 1996), evaluates the medical cost of some forms of cancer, but not nasal cancer. Other publications have estimated the economic costs associated with eye irritation and headaches. These data are discussed below.

**Benefits of Avoiding Illnesses Potentially Linked to MHC Chemical Exposure**

This section presents estimates of the economic costs of some of the illnesses or symptoms associated with exposure to MHC chemicals. To the extent that MHC chemicals are not the only factor contributing toward the illnesses described, individual costs may overestimate the potential benefits to society from substituting alternative MHC technologies for the baseline electroless copper process. For example, other PWB manufacturing process steps may also contribute toward adverse worker health effects. The following discussion focuses on the external benefits of reductions in illness. However, private benefits may be accrued by PWB manufacturers through increased worker productivity and a reduction in liability and health care insurance costs. While reductions in insurance premiums as a result of pollution prevention are not currently widespread, the opportunity exists for changes in the future.

Exposure to several of the chemicals of concern is associated with eye irritation. Other potential health effects include headaches and dizziness. The economic literature provides estimates of the costs associated with eye irritation and headaches. An analysis by Unsworth and Neumann summarizes the existing literature on the costs of illness based on estimates of how much an individual would be willing to pay to avoid certain acute effects for one symptom day (Unsworth and Neumann, 1993). These estimates are based upon a survey approach designed to elicit estimates of individual willingness-to-pay to avoid a single incidence and not the lifetime costs of treating a disease. Table 7.15 presents a summary of the low, mid-range, and high estimates of individual willingness-to-pay to avoid eye irritation and headaches. These estimates provide an indication of the benefit per affected individual that would accrue to society if switching to a substitute MHC technology reduced the incidence of these health endpoints.

**Table 7.15 Estimated Willingness-to-Pay to Avoid Morbidity Effects for One Symptom Day (1995 dollars)**

| Health Endpoint | Low | Mid-Range | High |
|---|---|---|---|
| Eye Irritation[a] | $21 | $21 | $46 |
| Headache[b] | $2 | $13 | $67 |

[a] Tolley, G.S., et al. January 1986. *Valuation of Reductions in Human Health Symptoms and Risks.* University of Chicago. Final Report for the U.S. EPA. As cited in Unsworth, Robert E. and James E. Neumann, Industrial Economics, Incorporated. Memorandum to Jim DeMocker, Office of Policy Analysis and Review. *Review of Existing Value of Morbidity Avoidance Estimates: Draft Valuation Document.* September 30, 1993.

[b] Dickie, M., et al. September 1987. *Improving Accuracy and Reducing Costs of Environmental Benefit Assessments.* U.S. EPA, Washington, DC. Tolley, G.S., et al. *Valuation of Reductions in Human Health Symptoms and Risks.* January 1986. University of Chicago. Final Report for the U.S. EPA. As cited in Unsworth, Robert E. and James E. Neumann, Industrial Economics, Incorporated. Memorandum to Jim DeMocker, Office of Policy Analysis and Review. *Review of Existing Value of Morbidity Avoidance Estimates: Draft Valuation Document.* September 30, 1993.

## Public Health Risk

Section 7.2.3 discussed public health risks from MHC chemical exposure. The risk characterization identified no concerns for the general public through ambient air exposure with the possible exception of formaldehyde exposure from electroless copper processes. While the study found little difference among the alternatives for those public health risks that were assessed, it was not within the scope of this comparison to assess all community health risks. Risk was not characterized for exposure via other pathways (e.g., drinking water, fish ingestion, etc.) or short-term exposures to high levels of hazardous chemicals when there is a spill, fire, or other periodic release.

## Ecological Hazards

The CTSA evaluated the ecological risks of the baseline and alternatives in terms of aquatic toxicity hazards. Aquatic risk could not be estimated because chemical concentrations in MHC line effluents and streams were not available and could not be estimated. Reduced aquatic hazards can provide significant external benefits, including improved ecosystem diversity, improved supplies for commercial fisheries, and improved recreational values of water resources. There are well documented aquatic toxicity problems associated with copper discharges to receiving waters, but this assessment was unable to determine the relative reduction in copper or other toxic discharges from the baseline to the alternatives. Five processes contain copper sulfate, the most toxic of the copper compounds found in MHC lines, and other processes contain copper chloride. In order to evaluate the private and external benefits or costs of implementing an alternative, PWB manufacturers should attempt to determine what the changes in their mass loading of copper or other toxic discharges would be.[19]

[19] Copper discharges are a particular problem because of the cumulative mass loadings of copper discharges from a number of different industry sectors, including the PWB industry.

**Energy and Natural Resources Consumption**

Table 7.16 summarizes the water and energy consumption rates and percent changes in consumption from the baseline to the MHC alternatives. All of the alternatives use substantially less energy and water per ssf of PWB produced, with the exception of the carbon technology which only has a slight decrease (< ten percent) in energy use from the baseline. While manufacturers face direct costs from the use of energy and water in the manufacturing process, society as a whole also experiences costs from this usage. For energy consumption, these types of externalities can come in the form of increased emissions to the air either during the initial manufacturing of the energy or the MHC processes themselves. These emissions include $CO_2$, $SO_x$, $NO_2$, CO, $H_2SO_4$, and particulate matter. Table 5.9 in the Energy Impacts section (Section 5.2) details the pollution resulting from the generation of energy consumed by MHC alternatives. Environmental and human health concerns associated with these pollutants include global warming, smog, acid rain, and health effects from toxic chemical exposure.

**Table 7.16 Energy and Water Consumption of MHC Technologies**

| MHC Technology | Water Consumption | | Energy Consumption | |
|---|---|---|---|---|
| | gal/ssf | % change | Btu/ssf | % change |
| Electroless Copper, non-conveyorized (BASELINE) | 11.7 | | 573 | |
| Electroless Copper, conveyorized | 1.15 | -90 | 138 | -76 |
| Carbon, conveyorized | 1.29 | -89 | 514 | -9.6 |
| Conductive Polymer, conveyorized | 0.73 | -94 | 94.7 | -83 |
| Graphite, conveyorized | 0.45 | -96 | 213 | -63 |
| Non-Formaldehyde Electroless Copper, non-conveyorized | 3.74 | -68 | 270 | -53 |
| Organic-Palladium, non-conveyorized | 1.35 | -88 | 66.9 | -88 |
| Organic-Palladium, conveyorized | 1.13 | -90 | 148 | -74 |
| Tin-Palladium, non-conveyorized | 1.80 | -85 | 131 | -77 |
| Tin-Palladium, conveyorized | 0.57 | -95 | 96.4 | -83 |

In addition to increased pollution, the higher energy usage of the baseline also results in external costs in the form of depletion of natural resources. Some form of raw resource is required to make electricity, whether it be coal, natural gas or oil, and these resources are non-renewable. While it is true that the price of the electricity to the manufacturer takes into account the actual raw materials costs, the price of electricity does not take into account the depletion of the natural resource base. As a result, eventually society will have to bear the costs for the depletion of these natural resources.

The use of water and consequent generation of wastewater also results in external costs to society. While the private costs of this water usage are included in the cost estimates in Table 7.10, the external costs are not. The private costs of water usage account for the actual quantities of water used in the MHC process by each different technology. However, clean water is quickly becoming a scarce resource, and activities that utilize water therefore impose external costs on society. These costs can come in the form of higher water costs for the surrounding area or for higher costs paid to treatment facilities to clean the water. These costs may also come in the

form of decreased water quality available to society. In fact, in Germany, PWB manufacturers are required to use their wastewater at least three times before disposing of it because of the scarcity of water.

**Effects on Jobs**

The results of the cost analysis suggest that alternative MHC technologies are generally more efficient than the baseline process due to decreased cycle times. In addition, labor costs are one of the biggest factors causing the alternatives to be cheaper. Neither the Cost Analysis nor the CTSA analyzed the potential for job losses resulting from implementing an alternative. However, if job losses were to occur, this could be a significant external cost to the community. For example, in Silicon Valley, community groups are striving to retain clean, safe jobs through directing cost savings to environmental improvements that create or retain jobs. While the effects on jobs of wide-scale adoption of an alternative were not analyzed, anecdotal evidence from facilities that have switched from the baseline suggests that jobs are not lost, but workers are freed to work on other tasks (Keenan, 1997). In addition, one incentive for PWB manufacturers to invest in the MHC alternatives is the increased production capacity of the alternatives. Some PWB manufacturers who choose to purchase new capital-intensive equipment are doing so because of growth, and would not be expected to lay off workers (Keenan, 1997).

**Other External Benefits or Costs**

In addition to the externalities discussed above, the baseline and MHC alternatives can have other external benefits and costs. Many of these were discussed in Table 7.13 because many factors share elements of both private and external benefits and costs. For example, regulated chemicals result in a compliance cost to industry, but they also result in an enforcement cost to society whose governments are responsible for ensuring environmental requirements are met.

### 7.2.5 Summary of Benefits and Costs

The objective of a social benefits/costs assessment is to identify those technologies or decisions that maximize net benefits. Ideally, the analysis would quantify the social benefits and costs of using the alternative and baseline MHC technologies in terms of a single unit (e.g., dollars) and calculate the net benefits of using an alternative instead of the baseline technology. Due to data limitations, however, this assessment presents a qualitative description of the benefits and costs associated with each technology compared to the baseline. Table 7.17 compares some of the relative benefits and costs of each technology to the baseline, including production costs, worker health risks, public health risks, aquatic toxicity concerns, water consumption, and energy consumption. The effects on jobs of wide-scale adoption of an alternative are not included in the table because the potential for job losses was not evaluated in the CTSA. However, the results of the Cost Analysis suggest there are significantly reduced labor requirements for the alternatives. Clearly, the loss of manufacturing jobs would be a significant external cost to the community and should be considered by PWB manufacturers when choosing an MHC technology.

## Table 7.17 Relative Benefits and Costs of MHC Alternatives Versus Baseline

| MHC Technology | Production Costs ($/ssf) | Number of Chemicals of Concern[a] | | | | Water Consumption (gal/ssf) | Energy Consumption (Btu/ssf) |
|---|---|---|---|---|---|---|---|
| | | Worker Health Risks[b,c,d] | | Public Health Risks[e] | High Aquatic Toxicity Concern[b,f] | | |
| | | Inhalation | Dermal | Inhalation | | | |
| Electroless Copper, non-conveyorized (BASELINE) | $0.51 | 10 | 8 | 0[g] | 9 | 11.7 | 573 |
| Electroless Copper, conveyorized | ↗↗ | ↗↗ | ↔ | ↔[h] | ↔ | ↗↗ | ↗↗ |
| Carbon, conveyorized | ↗↗ | ↗↗ | ↗↗ | ↗ | ↔ | ↗↗ | ↔ |
| Conductive Polymer, conveyorized | ↗↗ | ↗↗ | ↗↗ | ↗ | ↗ | ↗↗ | ↗↗ |
| Graphite, conveyorized | ↗↗ | ↗↗ | ↗↗[i] | ↗[j] | ↔ | ↗↗ | ↗↗ |
| Non-Formaldehyde Electroless Copper, non-conveyorized | ↗ | ↗ | ↗ | ↗ | ↔ | ↗↗ | ↗↗ |
| Organic-Palladium, non-conveyorized | ↗↗ | ↗↗ | ↗ | ↗ | ↗ | ↗↗ | ↗↗ |
| Organic-Palladium, conveyorized | ↗↗ | ↗↗ | ↗ | ↗ | ↗ | ↗↗ | ↗↗ |
| Tin-Palladium, non-conveyorized | ↗↗ | ↗ | ↗ | ↗ | ↔ | ↗↗ | ↗↗ |
| Tin-Palladium, conveyorized | ↗↗ | ↗↗ | ↗ | ↗ | ↔ | ↗↗ | ↗↗ |

[a] Includes proprietary chemicals that were identified.

[b] For technologies with more than one chemical supplier (i.e., electroless copper, graphite, and tin-palladium) all chemicals may not be present in any one product line.

[c] For the most exposed individual (i.e., an MHC line operator).

[d] Because the risk characterization did not estimate the number of incidences of adverse health outcomes, the amount of reduced risk benefit cannot be quantifed. However, based on the level of formaldehyde risk and the number of chemicals of concern for the baseline, it appears all of the alternatives have at least some reduced risk benefits from the baseline.

[e] Because the risk characterization did not estimate the number of incidences of adverse health outcomes, the amount of reduced risk benefit cannot be quantifed. However, based on the level of formaldehyde risk for the baseline, it appears all of the alternatives except the conveyorized electroless copper process have at least some reduced risk benefits from the baseline.

[f] Technologies using copper sulfate were assigned a neutral benefit or cost; other technologies were assigned "some benefit" because none of their chemicals are as toxic to aquatic organisms as copper sulfate. This assessment is based on hazard, not risk.

[g] No chemical risks above concern levels. However, it should be noted that formaldehyde cancer risks as high as $1 \times 10^{-7}$ were estimated.

[h] No chemical risks above concern levels. However, it should be noted that formaldehyde cancer risks as high as $3 \times 10^{-7}$ were estimated.

[i] No chemical risks above concern levels. However, it should be noted that proprietary chemical cancer risks as high as $1 \times 10^{-7}$ were estimated.

[j] No chemical risks above concern levels. However, it should be noted that proprietary chemical cancer risks as high as $9 \times 10^{-11}$ were estimated.

Key:

↔ - Neutral, less than 20 percent increase or decrease from baseline.

↗ - Some benefit, 20 to <50 percent decrease from baseline.

↗↗ - Greater benefit, 50 percent or greater decrease from baseline.

While each alternative presents a mixture of private and external benefits and costs, it appears that each of the alternatives have social benefits as compared to the baseline. In addition, at least three of the alternatives appear to have social benefits over the baseline in every category, but public health risk. These are the conveyorized conductive polymer process and both conveyorized and non-conveyorized organic-palladium processes. However, the supplier of these technologies has declined to provide complete information on proprietary chemical ingredients for evaluation in the risk characterization, meaning health risks could not be fully assessed. Little or no improvement is seen in public health risks because concern levels were very low for all technologies, although formaldehyde cancer risks as high as from $1 \times 10^{-7}$ to $3 \times 10^{-7}$ were estimated for non-conveyorized and conveyorized electroless copper processes, respectively.

In terms of worker health risks, conveyorized processes have the greatest benefits for reduced worker inhalation exposure to bath chemicals; they are enclosed and vented to the atmosphere. However, dermal contact from bath maintenance activities can be of concern regardless of the equipment configuration for electroless copper, organic palladium, and tin-palladium processes. No data were available for conveyorized non-formaldehyde electroless copper processes (the same chemical formulations were assumed), but the non-conveyorized version of this technology also has chemicals with dermal contact concerns.

The relative benefits and costs of technologies from changes in aquatic toxicity concerns were more difficult to assess because only aquatic hazards were evaluated and not risk. Several of the technologies contain copper sulfate, which has a very low aquatic toxicity concern concentration (0.00002 mg/l). However, all of the technologies contain other chemicals with high aquatic toxicity concern levels, although these chemicals are not as toxic as copper sulfate.

All of the alternatives provide significant social benefits in terms of energy and water consumption, with the exception of energy consumption for the carbon technology. The drying ovens used with this technology cause this technology to consume nearly as much energy per ssf as the baseline.

## 7.3 TECHNOLOGY SUMMARY PROFILES

This section of the CTSA presents summary profiles of each of the MHC technologies. The profiles summarize key information from various sections of the CTSA, including the following:

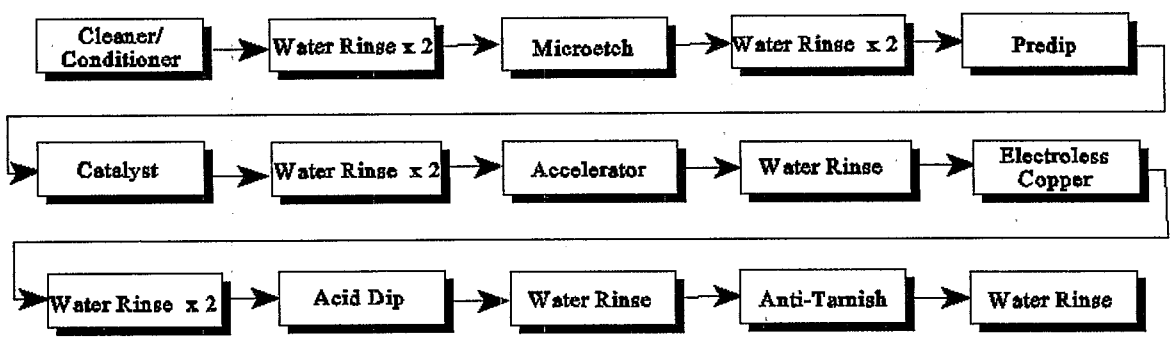
- Generic process steps, typical bath sequences and equipment configurations evaluated in the CTSA.
- Human health and environmental hazards data and risk concerns for non-proprietary chemicals.
- Production costs and resource (water and energy) consumption data.
- Federal environmental regulations affecting chemicals in each of the technologies.
- The conclusions of the social benefits/costs assessment.

The first summary profile (Section 7.3.1) presents data for both the baseline process and the conveyorized electroless copper process. Sections 7.3.2 through 7.3.7 present data for the carbon, conductive polymer, graphite, non-formaldehyde electroless copper, organic-palladium, and tin-palladium technologies, respectively.

As discussed in Section 7.2, each of the alternatives appear to provide private as well as external benefits compared to the non-conveyorized electroless copper process (the baseline process), though net benefits could not be assessed without a more thorough assessment of effects on jobs and wages. However, the actual decision of whether or not to implement an alternative occurs outside of the CTSA process. Individual decision-makers may consider a number of additional factors, such as their individual business circumstances and community characteristics, together with the information presented in this CTSA.

### 7.3.1 Electroless Copper Technology

**Generic Process Steps and Typical Bath Sequence**




**Equipment Configurations Evaluated**: Non-conveyorized (the baseline process) and conveyorized.

## Risk Characterization

Table 7.18 summarizes human and environmental hazards and risk concerns for non-proprietary chemicals in the electroless copper technology. The risk characterization identified occupational inhalation risk concerns for ten chemicals in non-conveyorized electroless copper processes and dermal risk concerns for eight chemicals for either equipment configuration. No public health risk concerns were identified for the pathways evaluated, although formaldehyde cancer risks as high as $1 \times 10^{-7}$ and $3 \times 10^{-7}$ were estimated for non-conveyorized and conveyorized electroless copper processes, respectively.

**Table 7.18 Summary of Human Health and Environmental Hazard Data and Risk Concerns for the Electroless Copper Technology**

| Chemical[a] | Human Health Hazard and Occupational Risks[b] | | | | Carcinogenicity Weight-of-Evidence Classification | Aquatic Toxicity CC (mg/l) |
|---|---|---|---|---|---|---|
| | Inhalation[c] | | Dermal[d] | | | |
| | Toxicity[e] ($mg/m^3$) | Risk Concerns | Toxicity[e] (mg/kg-d) | Risk Concerns | | |
| Alkene Diol | NR[f] | no | NR | no | Probable human carcinogen[g] | NR |
| Alkyl Oxide | NR[f] | no | NR | no | Possible/probable human carcinogen[g] | NR |
| Ammonium Chloride | ND | NA | 1691(NOAEL) | no | none | 0.05 |
| Benzotriazole | ND | NE | 109 (LOAEL) | no | none | 0.023[h] |
| Boric Acid | ND | NE | 62.5 (LOAEL) | no | none | 0.022 |
| **Copper (I) Chloride[l]** | 0.6 (LOAEL) | yes | 0.07 (LOAEL) | yes | EPA Class D | 0.0004 |
| **Copper Sulfate[l]** | ND | NE | ND | NE | none | 0.00002 |
| Cyclic Ether | ND | NA | NR | yes | none | NR |
| Dimethylaminoborane | ND | NE | ND | NE | none | 0.007[j] |
| Dimethylformamide | 0.03 (RfC) | no | 125 (LOAEL) | no | IARC Group 2B[k] | 0.12 |
| Ethanolamine | 12.7 (LOAEL) | yes | 320 (NOAEL) | no | none | 0.075 |
| 2-Ethoxyethanol | 0.2 (RfC) | yes | 0.4 (RfD) | no | none | 5.0 |
| Ethylenediaminetetraacetic Acid (EDTA) | ND | NA | ND | NE | none | 0.41 |
| Ethylene Glycol | 31 | yes | 2 (RfD) | no | none | 3.3 |
| Fluoroboric Acid | ND | NE | 0.77 | yes | none | 0.125 |
| **Formaldehyde** | 0.1 ppm (LOAEL) | yes | 0.2 (RfD) | yes | EPA Class B1 IARC Group 2A | 0.0067 |
| Formic Acid | 59.2 (NOAEL) | yes | ND | NE | none | 0.08 |
| **Hydrochloric Acid[l]** | 0.007 (RfC) | no | ND | NE[m] | IARC Group 3 | 0.1 |
| Hydrogen Peroxide | 79 | no | 630 (NOAEL) | no | IARC Group 3 | 1.2 |
| Hydroxyacetic Acid | ND | NE | 250 (NOAEL) | no | none | 1[h] |

| Chemical[a] | Human Health Hazard and Occupational Risks[b] | | | | Carcinogenicity Weight-of-Evidence Classification | Aquatic Toxicity CC (mg/l) |
|---|---|---|---|---|---|---|
| | Inhalation[c] | | Dermal[d] | | | |
| | Toxicity[c] ($mg/m^3$) | Risk Concerns | Toxicity[e] (mg/kg-d) | Risk Concerns | | |
| Isopropyl Alcohol; or 2-Propanol | 980 (NOAEL) | no | 100 (NOAEL) | no | none | 9.0 |
| m-Nitrobenzene Sulfonic Acid | ND | NE | ND | NE | none | 5.0 |
| Magnesium Carbonate | Generally regarded as safe (U.S. FDA as cited in HSDB, 1995) | | | | none | 1.0[j] |
| **Methanol** | 1,596 - 10,640 | yes | 0.5 (RfD) | no | none | 17 |
| Nitrogen Heterocycle | ND | NA | NR | yes | none | NR |
| Palladium | ND | NA | 0.95 (LOAEL) | yes | none | 0.00014 |
| Peroxymonosulfuric Acid | ND | NA | ND | NE | none | 0.030[j] |
| Potassium Bisulfate | ND | NE | ND | NE | none | >1.0[j] |
| Potassium Cyanide | ND | NE | 0.05 (RfD) | no | none | 0.79 |
| Potassium Hydroxide | 7.1 | no | ND | NE | none | 0.08 |
| Potassium Persulfate | ND | NE | ND | NE | none | 0.92 |
| Potassium Sodium Tartrate | Generally regarded as safe (U.S. FDA as cited in HSDB, 1996) | | | | none | ND |
| Potassium Sulfate | 15 ($TC_{LO}$) | no | ND | NE | none | 0.11 |
| Sodium Bisulfate | ND | NA | ND | NE | none | 0.058 |
| Sodium Carbonate | 10 (NOAEL) | no | ND | NE | none | 2.4 |
| Sodium Carboxylate | ND | NA | NR | yes | none | NR |
| Sodium Chlorite | ND | NA | 10 (NOAEL) | yes | none | 0.00016 |
| Sodium Cyanide | ND | NE | 0.04 (RfD) | no | none | 0.79 |
| **Sodium Hydroxide** | 2 (LOAEL) | yes | ND | NE | none | 2.5 |
| Sodium Hypophosphite | ND | NA | ND | NE | none | 0.006[j] |
| Sodium Sulfate | ND | NA | 420 (NOAEL) | no | none | 0.81 |
| Stannous Chloride | ND | NA | 0.62 (RfD) | yes | none | 0.0009 |
| **Sulfuric Acid** | 0.066 (NOAEL) | yes | ND | NE[m] | none | 2.0 |
| Tartaric Acid | ND | NE | 8.7 | no | none | 1.0 |
| Tin Salt | ND | NA | NR | no | none | NR |
| p-Toluene Sulfonic Acid | ND | NA | ND | ND | none | 1.0[j] |
| Triethanolamine | ND | NA | 32 (LOAEL) | no | none | 0.18 |

[a] Chemicals in bold were in all electroless copper technologies evaluated, unless otherwise noted.

[b] Risk concerns are for MHC line operators (the most exposed individual).

[c] Inhalation risk concerns for non-conveyorized process only. Inhalation risk from fully enclosed, conveyorized process is assumed to be negligible.

[d] Dermal risk concerns apply to both conveyorized and non-conveyorized equipment.

[e] Toxicity measure is RfC, RfD, NOAEL, or LOAEL as indicated. If not indicated, the type of toxicity measure was not specified in the available information, but assumed to be LOAEL in risk calculations.
[f] Toxicity data are available but not reported in order to protect proprietary chemical identities.
[g] Specific EPA and/or IARC groups not reported in order to protect proprietary chemical identities.
[h] Estimated using ECOSAR computer software, based on structure-activity relationship.
[i] Either copper (I) chloride or copper sulfate was in all electroless copper lines evaluated.
[j] Estimated by EPA's Structure-Activity Team.
[k] Cancer risk was not evaluated because no slope (unit risk) factor is available.
[l] Hydrochloric acid was listed on the MSDSs for five of six electroless copper lines.
[m] Chronic dermal toxicity data are not typically developed for strong acids.
ND: No Data. No toxicity measure available for this pathway.
NE: Not Evaluated; due to lack of toxicity measure.
NA: Not Applicable. Inhalation exposure level was not calculated because the chemical is not volatile (vapor pressure below $1 \times 10^{-3}$ torr) and is not used in any air-sparged bath.
NR: Not Reported.

## Performance

The performance of the electroless copper technology was demonstrated at seven test facilities, including six sites using non-conveyorized equipment and one site using conveyorized equipment. Performance test results were not differentiated by the type of equipment configuration used. The Performance Demonstration determined that each of the alternative technologies has the capability of achieving comparable levels of performance to electroless copper.

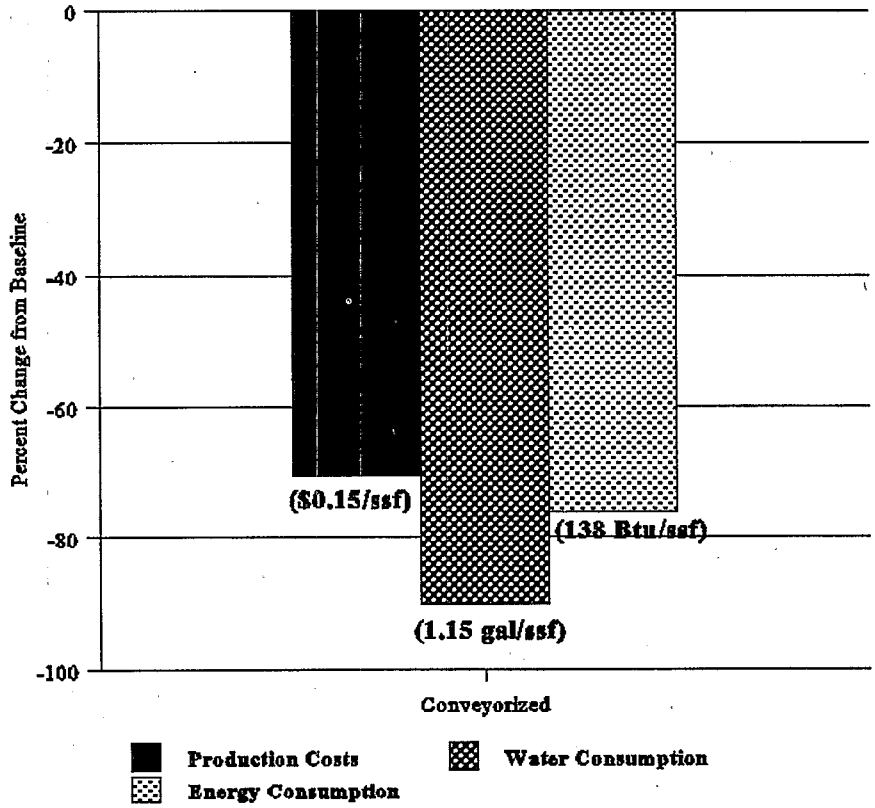
## Production Costs and Resource Consumption

Computer simulation was used to model key operating parameters, including the time required to process a job consisting of 350,000 ssf and the amount of resources (water and energy) consumed. This information was used with a hybrid cost model of traditional cost (i.e., capital costs, etc.) and activity-based costs to determine average manufacturing costs per ssf and water and energy consumption per ssf. Average manufacturing costs for the baseline process (the non-conveyorized electroless copper process) were $0.51/ssf, while water and energy consumption were 11.7 gal/ssf and 573 Btu/ssf, respectively. However, the conveyorized electroless copper process consumed less water and energy and was more cost-effective than the baseline process (non-conveyorized electroless copper). Figure 7.1 lists the results of the production costs and resource consumption analyses for the conveyorized electroless copper process and illustrates the percent changes in costs and resource consumption from the baseline. Manufacturing costs, water consumption, and energy consumption are less than the baseline by 71 percent, 90 percent, and 76 percent, respectively.

## Regulatory Concerns

Chemicals contained in the electroless copper technology are regulated by the Clean Water Act, the Safe Drinking Water Act, the Clean Air Act, the Superfund Amendments and Reauthorization Act, the Emergency Planning and Community Right-to-Know Act, and the Toxic Substances Control Act. In addition, the technology generates wastes listed as hazardous (P or U wastes) under RCRA.

**Figure 7.1 Production Costs and Resource Consumption of Conveyorized Electroless Copper Technology**
**(Percent Change from Baseline with Actual Values in Parentheses)**

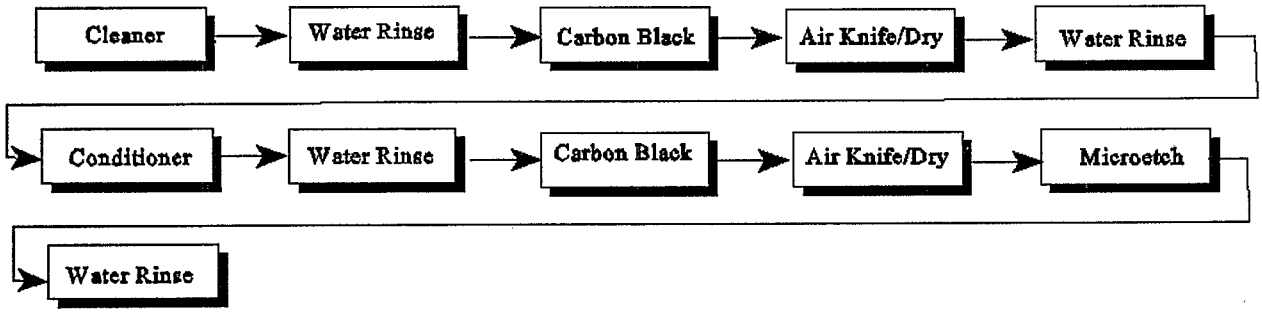



## Social Benefits and Costs

A qualitative assessment of the private and external (e.g., social) benefits and costs of the baseline and alternative technologies was performed to determine if there would be net benefits to society if PWB manufacturers switched to alternative technologies from the baseline. It was concluded that all of the alternatives, including the conveyorized electroless copper process, appear to have net societal benefits, though net benefits could not be completely assessed without a more thorough assessment of effects on jobs and wages. For the conveyorized electroless copper process this is due to reduced occupational inhalation risk as well as to lower production costs and to reduced consumption of limited resources (water and energy).

### 7.3.2 Carbon Technology

**Generic Process Steps and Typical Bath Sequence**




**Equipment Configurations Evaluated**: Conveyorized.

**Risk Characterization**

Table 7.19 summarizes human and environmental hazards and risk concerns for non-proprietary chemicals in the carbon technology. The risk characterization identified no human health risk concerns for the pathways evaluated. However, proprietary chemicals are not included in this assessment and toxicity data were not available for some chemicals in carbon technology baths.

**Performance**

The performance of the carbon technology was demonstrated at two test facilities. The Performance Demonstration determined that this technology has the capability of achieving comparable levels of performance to electroless copper.

**Production Costs and Resource Consumption**

Computer simulation was used to model key operating parameters, including the time required to process a job consisting of 350,000 ssf and the amount of resource (water and energy) consumed. This information was used with a hybrid cost model of traditional costs (i.e., capital costs, etc.) and activity-based costs to determine average manufacturing costs per ssf and water and energy consumption per ssf. The conveyorized carbon technology consumed less water and energy and was more cost-effective than the baseline process (non-conveyorized electroless copper). Figure 7.2 lists the results of these analyses and illustrates the percent changes in costs and resources consumption from the baseline. Manufacturing costs, water consumption, and energy consumption are less than the baseline by 65 percent, 89 percent, and 9.6 percent, respectively.

**Table 7.19 Summary of Human Health and Environmental Hazard Data and Risk Concerns for the Carbon Technology**

| Chemical[a] | Human Health Hazard and Occupational Risks[b] | | | Carcinogenicity Weight-of-Evidence Classification | Aquatic Toxicity CC (mg/l) |
|---|---|---|---|---|---|
| | Inhalation[c] | Dermal | | | |
| | Toxicity[d] ($mg/m^3$) | Toxicity[d] (mg/kg-d) | Risk Concerns | | |
| **Carbon Black** | 7.2 (LOAEL) | ND | NE | IARC 2B | ND |
| **Copper Sulfate** | ND | ND | NE | none | 0.00002 |
| **Ethanolamine** | 12.7 (LOAEL) | 320 (NOAEL) | no | none | 0.075 |
| **Ethylene Glycol** | 31 | 2 (RfD) | no | none | 3.3 |
| **Potassium Carbonate** | ND | ND | NE[e] | none | >3.0 |
| **Potassium Hydroxide** | 7.1 | ND | NE | none | 0.08 |
| **Sodium Persulfate** | ND | ND | NE | none | 0.065 |
| **Sulfuric Acid** | 0.066 (NOAEL) | ND | NE[f] | none | 2.0 |

[a] Only one carbon technology was evaluated. All chemicals listed were present in that product line.
[b] Risk evaluated for conveyorized process only. Risk concerns are for line operator (the most exposed individual).
[c] Exposure and risk not calculated. Inhalation exposure and risk from fully enclosed, conveyorized process is assumed to be negligible.
[d] Toxicity measure is RfC, RfD, NOAEL, or LOAEL, as indicated. If not indicated, the type of toxicity measure was not specified in the available information, but assumed to be a LOAEL in risk calculations.
[e] Chemical has very low skin absorption (based on EPA's Structure-Activity Team evaluation); risk from dermal exposure not expected to be of concern.
[f] Chronic dermal toxicity data are not typically developed for strong acids.
ND: No Data. No toxicity measure available for this pathway.
NE: Not Evaluated; due to lack of toxicity measure.

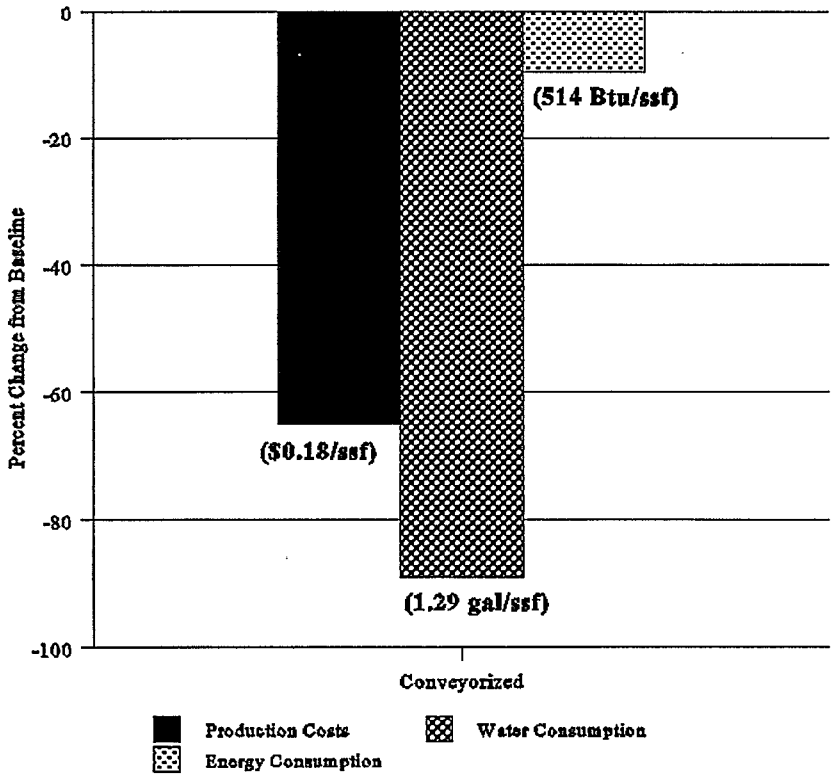
## Regulatory Concerns

Chemicals contained in the carbon technology are regulated by the Clean Water Act, the Safe Drinking Water Act, the Clean Air Act, the Superfund Amendments and Reauthorization Act, and the Emergency Planning and Community Right-to-Know Act. The technology does not generate wastes listed as hazardous (P or U waste) under RCRA, but some wastes may have RCRA hazardous characteristics.

## Social Benefits and Costs

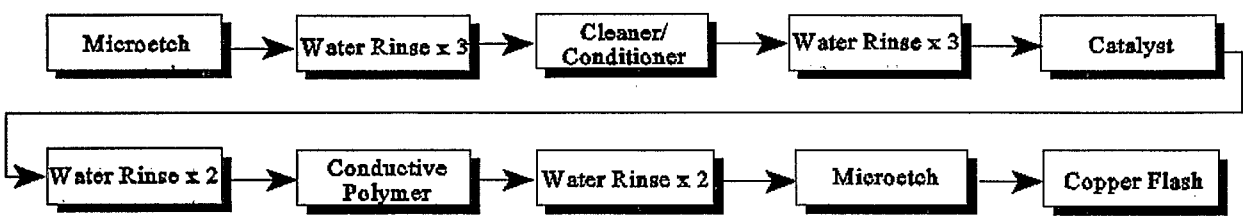
A qualitative assessment of the private and external benefits and costs of this technology suggests there would be net benefits to society if PWB manufacturers switched to the carbon technology from the baseline. Among other factors, this is due to lower occupational risks to workers and to reduced consumption of limited resources (water and, to a lesser degree, energy).

**Figure 7.2 Production Costs and Resource Consumption of Carbon Technology**
**(Percent Change from Baseline with Actual Values in Parentheses)**




### 7.3.3 Conductive Polymer Technology

**Generic Process Steps and Typical Bath Sequence**




**Equipment Configurations Evaluated**: Conveyorized.

**Risk Characterization**

Table 7.20 summarizes human and environmental hazards and risk concerns for non-proprietary chemicals in the conductive polymer technology. The risk characterization identified no human health risk concerns for the pathways evaluated. However, proprietary chemicals are not included in this assessment and no toxicity data are available for some chemicals in conductive polymer technology baths.

**Table 7.20 Summary of Human Health and Environmental Hazard Data and Risk Concerns for the Conductive Polymer Technology**

| Chemical[a] | Human Health Hazard and Occupational Risks[b] | | | Carcinogenicity Weight-of-Evidence Classification | Aquatic Toxicity CC (mg/l) |
|---|---|---|---|---|---|
| | Inhalation[c] | Dermal | | | |
| | Toxocity[d] ($mg/m^3$) | Toxicity[d] (mg/kg-d) | Risk Concerns | | |
| 1H-Pyrrole | ND | ND | NE | none | 0.21 |
| Peroxymonosulfuric Acid | ND | ND[e] | ND | none | 0.030 |
| Phosphoric Acid | ND | ND | NE[f] | none | 0.138 |
| Sodium Carbonate | 10 (NOAEL) | ND | NE | none | 2.4 |
| Sodium Hydroxide | 2 (LOAEL) | ND | NE | none | 2.5 |
| Sulfuric Acid | 0.066 (NOAEL) | ND | NE[f] | none | 2.0 |

[a] Only one conductive polymer technology was evaluated. All chemicals were present in that product line.
[b] Risk evaluated for conveyorized process only. Risk concerns are for line operator (the most exposed individual).
[c] Exposure and risk not calculated. Inhalation exposure and risk from fully enclosed, conveyorized process is assumed to be negligible.
[d] Toxicity measure is RfC, RfD, NOAEL, or LOAEL, as indicated. If not indicated, the type of toxicity measure was not specified in the available information, but assumed to be a LOAEL in risk calculations.
[e] Chemical has very low skin absorption (based on EPA's Structure-Activity Team evaluation); risk from dermal exposure not expected to be of concern.
[f] Chronic dermal toxicity data are not typically developed for strong acids.
ND: No Data. No toxicity measure available for this pathway.
NE: Not Evaluated; due to lack of toxicity measure.

## Performance

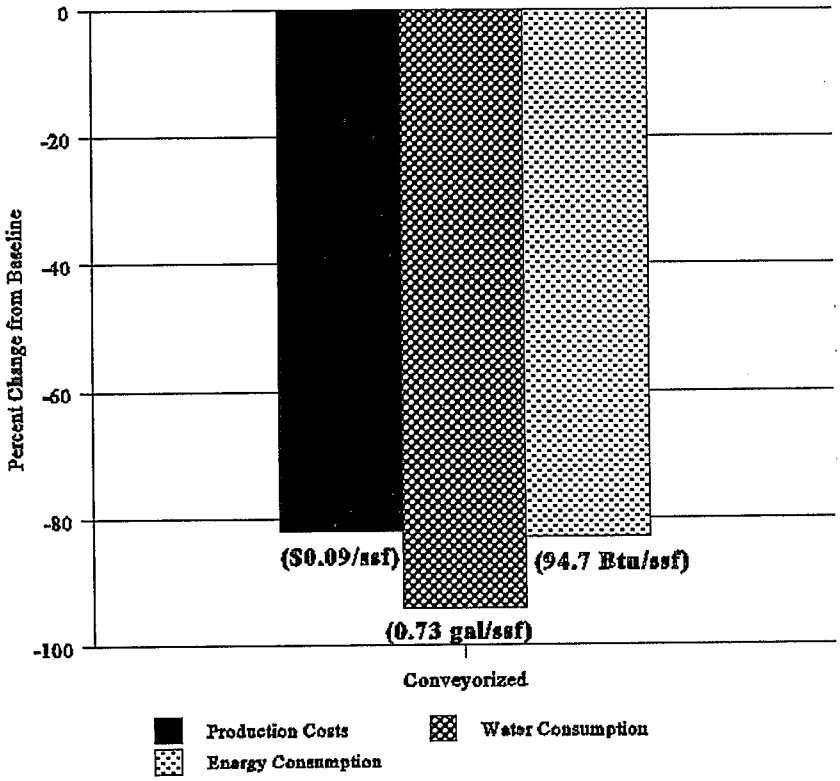
The performance of the conductive polymer technology was demonstrated at one test facility. The Performance Demonstration determined that this technology has the capability of achieving comparable levels of performance to electroless copper.

## Production Costs and Resource Consumption

Computer simulation was used to model key operating parameters, including the time required to process a job consisting of 350,000 ssf and the amount of resources (water and energy) consumed. This information was used with a hybrid cost model of traditional costs (i.e., capital costs, etc.) and activity-based costs to determine average manufacturing costs per ssf and water and energy consumption per ssf.

The conveyorized conductive polymer technology consumed less water and energy than the baseline process (non-conveyorized electroless copper). Figure 7.3 lists the results of these analyses and illustrates the percent changes in resources consumption from the baseline. Manufacturing costs, water consumption, and energy consumption are less than the baseline by 82 percent, 94 percent, and 83 percent, respectively.

**Figure 7.3 Production Costs and Resource Consumption of Conductive Polymer Technology**
**(Percent Change from Baseline with Actual Values in Parentheses)**




## Regulatory Concerns

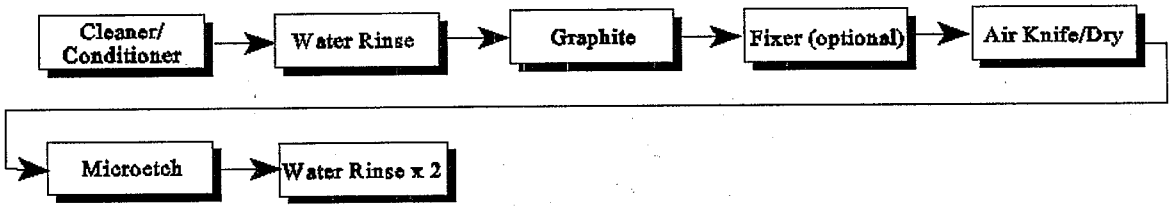
Chemicals contained in the conductive polymer technology are regulated by the Clean Water Act, the Clean Air Act, and the Emergency Planning and Community Right-to-Know Act. The technology does not generate wastes listed as hazardous (P or U waste) under RCRA, but some wastes may have RCRA hazardous characteristics.

## Social Benefits and Costs

A qualitative assessment of the private and external benefits and costs of this technology suggests there would be net benefits to society if PWB manufacturers switched to the conductive polymer technology from the baseline. Among other factors, this is due to lower occupational risks to workers and to reduced consumption of limited resources (water and energy).

## 7.3.4 Graphite Technology

**Generic Process Steps and Typical Bath Sequence**




**Equipment Configurations Evaluated**: Conveyorized.

**Risk Characterization**

Table 7.21 summarizes human and environmental hazards and risk concerns for chemicals in the graphite technology. The risk characterization identified no human health risk concerns for the pathways evaluated. However, the identification of proprietary chemicals was only provided by one of the two companies that submitted information concerning the graphite process. In addition, toxicity data was not available from some chemicals in the graphite technology baths.

**Performance**

The performance of the graphite technology was demonstrated at three test facilities. The Performance Demonstration determined that this technology has the capability of achieving comparable levels of performance to electroless copper.

**Production Costs and Resource Consumption**

Computer simulation was used to model key operating parameters, including the time required to process a job consisting of 350,000 ssf and the amount of resources (water and energy) consumed. This information was used with a hybrid cost model of traditional costs (i.e., capital costs, etc.) and activity-based costs to determine average manufacturing costs per ssf and water and energy consumption per ssf. The conveyorized graphite technology consumed less water and energy and was more cost-effective than the baseline process (non-conveyorized electroless copper). Figure 7.4 lists the results of these analyses and illustrates the percent changes in costs and resource consumption from the baseline. Manufacturing costs, water consumption, and energy consumption are less than the baseline by 57 percent, 96 percent, and 63 percent, respectively.

**Regulatory Concerns**

Chemicals contained in the graphite technology are regulated by the Clean Water Act, the Safe Drinking Water Act, the Clean Air Act, the Superfund Amendments and Reauthorization Act, and the Emergency Planning and Community Right-to-Know Act. The technology does not generate wastes listed as hazardous (P or U waste) under RCRA, but some wastes may have RCRA hazardous characteristics.

**Table 7.21 Summary of Human Health and Environmental Hazard Data and Risk Concerns for the Graphite Technology**

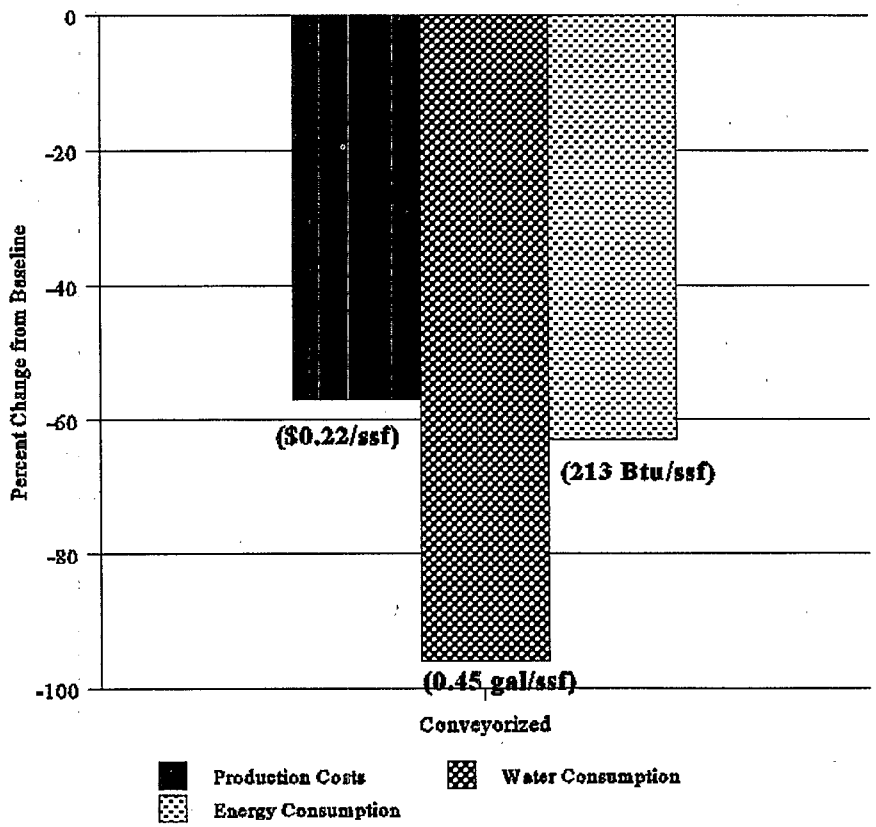
| Chemical[a] | Human Health Hazard and Occupational Risks[b] | | | Carcinogenicity Weight-of Evidence Classification | Aquatic Toxicity CC (mg/l) |
|---|---|---|---|---|---|
| | Inhalation[c] | Dermal | | | |
| | Toxicity[d] ($mg/m^3$) | Toxicity[d] (mg/kg-d) | Risk Concerns | | |
| Alkyl Oxide | ND | NR[e] | no | Probable human carcinogen[f] | NR |
| Ammonia | 0.1 (RfC) | ND | NE | none | 0.0042 |
| Copper Sulfate; or Cupric Sulfate | ND | ND | NE | none | 0.00002 |
| Cyclic Ether | ND | NR[e] | no | Possible/ probable human carcinogen[f] | NR |
| Ethanolamine | 12.7 (LOAEL) | 320 (NOAEL) | no | none | 0.075 |
| **Graphite** | 56 (LOAEL) | ND | NE | none | ND[g] |
| Peroxymonosulfuric Acid | ND | ND[h] | NE | none | 0.030[i] |
| Potassium Carbonate | ND | ND[h] | NE | none | >3.0 |
| **Sodium Persulfate** | ND | ND | NE | none | 0.065 |
| **Sulfuric Acid** | 0.066 (NOAEL) | ND | NE[j] | none | 2.0 |

[a] Chemicals in bold were in both graphite technologies evaluated.
[b] Risk evaluated for conveyorized process only. Risk concerns are for line operator (the most exposed individual).
[c] Exposure and risk not calculated. Inhalation exposure and risk from fully enclosed, conveyorized process is assumed to be negligible.
[d] Toxicity measure is RfC, RfD, NOAEL, or LOAEL, as indicated.
[e] Toxicity data are available but not reported in order to protect proprietary chemical identities.
[f] Specific EPA and/or IARC groups not reported in order to protect proprietary chemical identities.
[g] Not expected to be toxic at saturation levels (based on EPA Structure-Activity Team evaluation).
[h] Chemical has very low skin absorption (based on EPA's Structure-Activity Team evaluation); risk from dermal exposure not expected to be of concern.
[i] Estimated by EPA's Structure-Activity Team.
[j] Chronic toxicity data are not typically developed for strong acids.
ND: No Data. No toxicity measure available for this pathway.
NE: Not Evaluated; due to lack of toxicity measure.
NR: Not Reported.

## Social Benefits and Costs

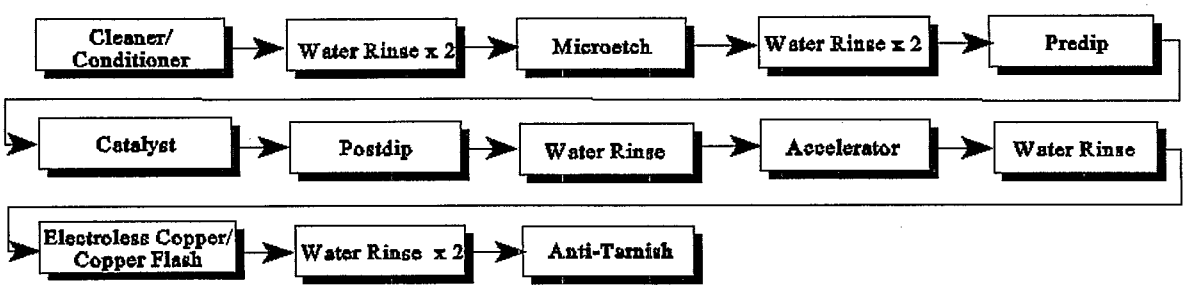
A qualitative assessment of the private and external benefits and costs of this technology suggests there would be net benefits to society if PWB manufacturers switched to the carbon technology from the baseline. Among other factors, this is due to lower occupational risks to workers and to reduced consumption of limited resources (water and energy).

**Figure 7.4 Production Costs and Resource Consumption of Graphite Technology**
**(Percent Change from Baseline with Actual Values in Parentheses)**




## 7.3.5 Non-Formaldehyde Electroless Copper Technology

**Generic Process Steps and Typical Bath Sequence**




**Equipment Configurations Evaluated**: Non-conveyorized.

## Risk Characterization

Table 7.22 summarizes human and environmental hazards and risk concerns for non-proprietary chemicals in the non-formaldehyde electroless copper technology. The risk characterization identified occupational inhalation risk concerns for one chemical and dermal risk concerns for two chemicals. No public health risk concerns were identified for the pathways evaluated. However, proprietary chemicals are not included in this assessment and toxicity values were not available for some chemicals.

**Table 7.22 Summary of Human Health and Environmental Hazard Data and Risk Concerns for the Non-Formaldehyde Electroless Copper Technology**

| Chemical[a] | Human Health Hazard and Occupational Risks[b] | | | | Carcinogenicity Weight-of-Evidence Classification | Aquatic Toxicity CC (mg/l) |
|---|---|---|---|---|---|---|
| | Inhalation | | Dermal | | | |
| | Toxicity[c] ($mg/m^3$) | Risk Concerns | Toxicity[c] (mg/kg-d) | Risk Concerns | | |
| Copper Sulfate | ND | NE | ND | NE | none | 0.00002 |
| Hydrochloric Acid | 0.007 (RfC) | NA | ND[d] | NE | IARC Group 3 | 0.1 |
| Hydrogen Peroxide | 79 | no | 630 (NOAEL) | no | IARC Group 3 | 1.2 |
| Isopropyl Alcohol; or 2-Propanol | 980 (NOAEL) | no | 100 (NOAEL) | no | none | 9.0 |
| Potassium Hydroxide | 7.1 | no | ND | NE | none | 0.08 |
| Potassium Persulfate | ND | NE | ND | NE | none | 0.92 |
| Sodium Chlorite | ND | NA | 10 (NOAEL) | yes | none | 0.00016 |
| Sodium Hydroxide | 2 (LOAEL) | no | ND | ND | none | 2.5 |
| Stannous Chloride | ND | NA | 0.62 (RfD) | yes | none | 0.0009 |
| Sulfuric Acid | 0.066 (NOAEL) | yes | ND[d] | NE | none | 2.0 |

[a] Only one non-formaldehyde electroless copper technology was evaluated. All chemicals listed were present in that product line.

[b] Risk evaluated for non-conveyorized process only. Inhalation risk from fully enclosed, conveyorized process is assumed to be low. Risk concerns are for line operator (the most exposed individual).

[c] Toxicity measure is RfC, RfD, NOAEL, or LOAEL, as indicated. If not indicated, the type of toxicity measure was not specified in the available information, but assumed to be a LOAEL in risk calculations.

[d] Chronic toxicity data are not typically available for strong acids.

ND: No Data. No toxicity measure developed for this pathway.

NE: Not Evaluated; due to lack of toxicity measure.

NA: Not Applicable. Inhalation exposure level was not calculated because the chemical is not volatile (vapor pressure below $1 \times 10^{-3}$ torr) and is not used in any air-sparged bath.

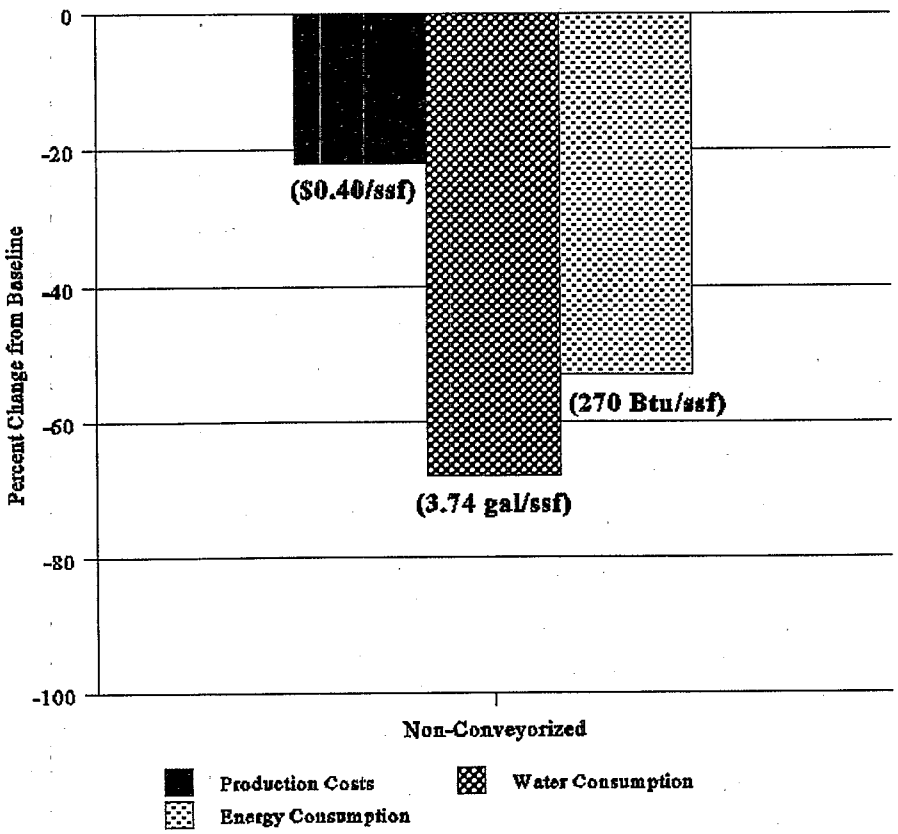
## Performance

The performance of the non-formaldehyde electroless copper technology was demonstrated at two test facilities. The Performance Demonstration determined that this technology has the capability of achieving comparable levels of performance to electroless copper.

## Production Costs and Resource Consumption

Computer simulation was used to model key operating parameters, including the time required to process a job consisting of 350,000 ssf and the amount of resources (water and energy) consumed. This information was used with a hybrid cost model of traditional costs (i.e., capital costs, etc.) and activity-based costs to determine average manufacturing costs per ssf and water and energy consumption per ssf. The non-conveyorized non-formaldehyde electroless copper process consumed less water and energy and was more cost-effective than the baseline process (non-conveyorized electroless copper). Figure 7.5 lists the results of these analyses and illustrates the percent changes in costs and resource consumption from the baseline. Manufacturing costs, water consumption, and energy consumption are less than the baseline by 22 percent, 68 percent, and 53 percent, respectively.

**Figure 7.5 Production Costs and Resource Consumption of Non-Formaldehyde Electroless Copper Technology**
**(Percent Change from Baseline with Actual Values in Parentheses)**



## Regulatory Concerns

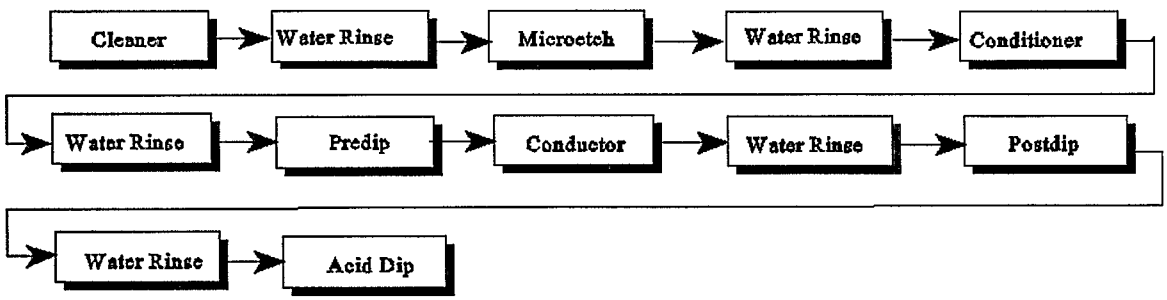
Chemicals contained in the non-formaldehyde electroless copper technology are regulated by the Clean Water Act, the Safe Drinking Water Act, the Clean air Act, the Superfund Amendments and Reauthorization Act, the Emergency Planning and Community Right-to-Know Act, and the Toxic Substances Control Act. The technology does not generate wastes listed as hazardous (P or U waste) under RCRA, but some wastes may have RCRA hazardous characteristics.

## Social Benefits and Costs

A qualitative assessment of the private and external benefits and costs of this technology suggests there would be net benefits to society if PWB manufacturers switched to the non-formaldehyde electroless copper technology from the baseline. Among other factors, this is due to lower occupational risks to workers and to reduced consumption of limited resources (water and energy).

### 7.3.6 Organic-Palladium Technology

## Generic Process Steps and Typical Bath Sequence




**Equipment Configurations Evaluated**: Non-conveyorized and conveyorized.

## Risk Characterization

Table 7.23 summarizes human and environmental hazards and risk concerns for non-proprietary chemicals in the organic-palladium technology. The risk characterization identified occupational dermal risk concerns for one chemical, palladium salt. No occupational inhalation risk concerns were identified. The risk characterization identified public health risk concerns for the pathways evaluated. However, proprietary chemicals are not included in this table and toxicity data were not available for some chemicals.

**Table 7.23 Summary of Human Health and Environmental Hazard Data and Risk Concerns for the Organic-Palladium Technology**

| Chemical[a] | Human Health Hazard and Occupational Risks[b] | | | | Carcinogenicity Weight-of-Evidence Classification | Aquatic Toxicity CC (mg/l) |
|---|---|---|---|---|---|---|
| | Inhalation[c] | | Dermal[d] | | | |
| | Toxicity[e] ($mg/m^3$) | Risk Concerns | Toxicity[e] (mg/kg-d) | Risk Concerns | | |
| **Hydrochloric Acid** | 0.007 (RfC) | NA | ND[f] | NE | IARC Group 3 | 0.1 |
| **Palladium Salt** | ND | NA | NR[g] | yes | none | NR |
| **Sodium Bisulfate** | ND | NA | ND[h] | NE | none | 0.058 |
| **Sodium Carbonate** | 10 (NOAEL) | NA | ND | NE | none | 2.4 |
| **Sodium Bicarbonate** | 10 (NOAEL)[i] | NA | ND | NE | none | 2.4[i] |
| **Sodium Hypophosphite** | ND | NA | ND | NE | none | 0.006 |
| **Sodium Persulfate** | ND | NA | ND[h] | NE | none | 0.065 |
| **Trisodium Citrate 5,5-Hydrate or Sodium Citrate** | ND | NA | ND | NE | none | 3.3 |

[a] Only one organic-palladium technology was evaluated. All chemicals listed were present in that product line.
[b] Risk concerns are for MHC line operators (the most exposed individual).
[c] Inhalation risk concerns for non-conveyorized process only. Inhalation risk from fully enclosed, conveyorized process is assumed to be negligible.
[d] Dermal risk concerns apply to both conveyorized and non-conveyorized equipment.
[e] Toxicity measure is RfC, RfD, NOAEL, or LOAEL as indicated.
[f] Chronic dermal toxicity data are not typically developed for strong acids.
[g] Toxicity data are available but not reported in order to protect proprietary chemical identities.
[h] Chemical has very low skin absorption (based on EPA's Structure-Activity Team evaluation); risk from dermal exposure not expected to be of concern.
[i] Chemical properties and toxicity measures for sodium carbonate used in exposure assessment and risk characterization since these compounds form the same ions in water and are used in aqueous baths.
ND: No Data. No toxicity measure available for this pathway.
NE: Not Evaluated; due to lack of toxicity measure.
NA: Not Applicable. Inhalation exposure level was not calculated because the chemical is not volatile (vapor pressure below $1 \times 10^{-3}$ torr) and is not used in any air-sparged bath.
NR: Not Reported.

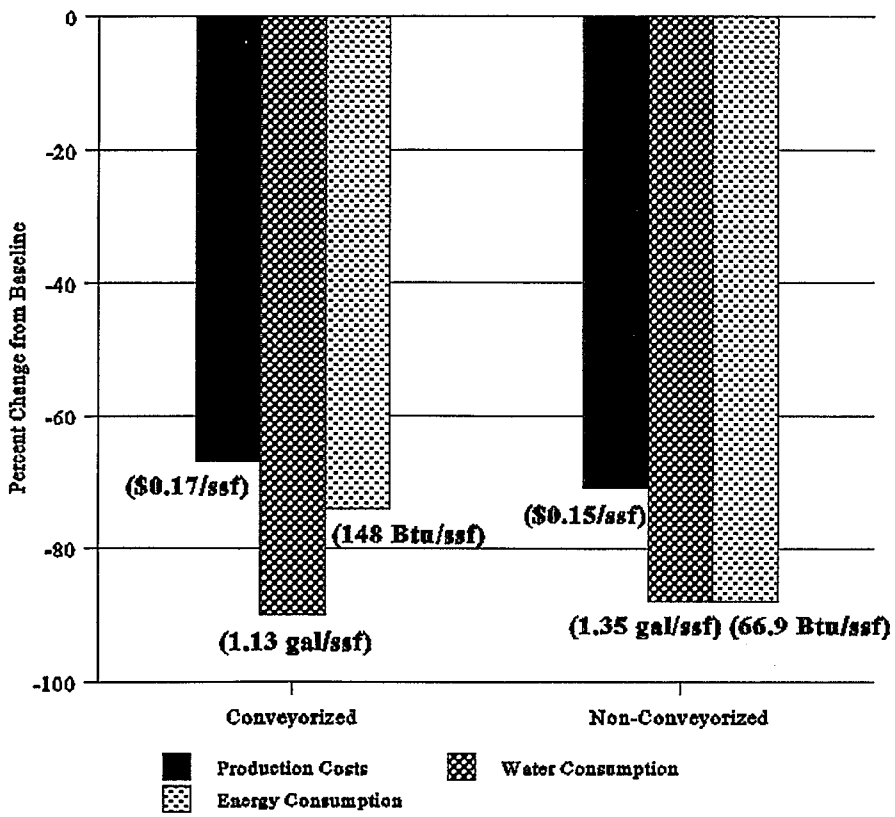
## Performance

For the purposes of the Performance Demonstration project, the organic-palladium and tin-palladium technologies were grouped together into a single palladium technology category. The performance of the palladium technology was demonstrated at ten test facilities. The Performance Demonstration determined that this technology has the capability of achieving comparable levels of performance to electroless copper.

## Production Costs and Resource Consumption

Computer simulation was used to model key operating parameters, including the time required to process a job consisting of 350,000 ssf and the amount of resources (water and energy) consumed. This information was used with a hybrid cost model of traditional cost (i.e., capital costs, etc.) and activity-based costs to determine average manufacturing costs per ssf and water and energy consumption per ssf. With either equipment configuration, the organic-palladium technology consumed less water and energy and was more cost-effective than the baseline process (non-conveyorized electroless copper). In addition, the conveyorized organic-palladium process consumed less water than the non-conveyorized process ($1.13 gal/ssf vs. $1.35 gal/ssf, respectively), but consumed more energy (148 Btu/ssf vs. 66.9 Btu/ssf). However, the conveyorized organic-palladium is not as cost effective as the non-conveyorized process ($0.17/ssf vs. $0.15/ssf, respectively). Figure 7.6 lists the results of these analyses and illustrates the percent changes in costs and resource consumption for either equipment configuration from the baseline.

**Figure 7.6 Production Costs and Resource Consumption of Organic-Palladium Technology**
**(Percent Change from Baseline with Actual Values in Parentheses)**



## Regulatory Concerns

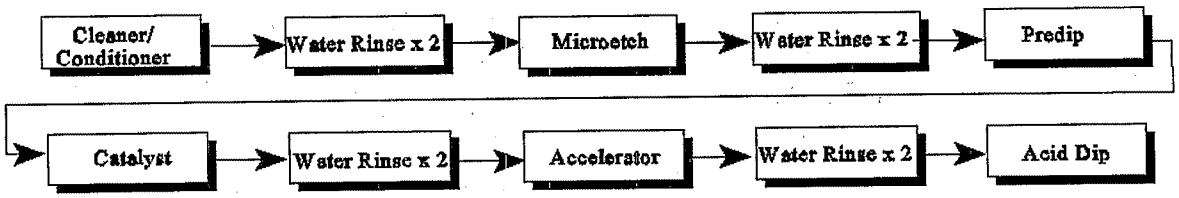
Chemicals contained in the organic-palladium technology are regulated by the Clean Water Act, the Clean Air Act, and the Emergency Planning and Community Right-to-Know Act. The technology does not generate wastes listed as hazardous (P or U waste) under RCRA, but some wastes may have RCRA hazardous characteristics.

## Social Benefits and Costs

A qualitative assessment of the private and external (e.g., social) benefits and costs of this technology suggests there would be net benefits to society if PWB manufacturers switched to the organic-palladium technology from the baseline. Among other factors, this is due to lower occupational risks to workers and to reduced consumption of limited resources (water and energy).

### 7.3.7 Tin-Palladium Technology

## Generic Process Steps and Typical Bath Sequence




**Equipment Configurations Evaluated**: Non-conveyorized and conveyorized.

## Risk Characterization

Table 7.24 summarizes human and environmental hazards and risk concerns for non-proprietary chemicals in the tin-palladium technology. The risk characterization identified occupational inhalation risk concerns for two chemicals and dermal risk concerns for five chemicals. No public health risk concerns were identified for the pathways evaluated. However, five proprietary chemicals are not included in this table and toxicity values were not available for some chemicals. At least two of these chemicals (potassium carbonate and sodium bisulfate) have very low skin absorption, indicating risk from dermal exposure is not expected to be of concern.

## Performance

For the purposes of the Performance Demonstration project, the organic-palladium and tin-palladium technologies were grouped together into a single palladium technology category. The performance of the palladium technology was demonstrated at ten test facilities. The Performance Demonstration determined that this technology has the capability of achieving comparable levels of performance to electroless copper.

## Table 7.24 Summary of Human Health and Environmental Hazard Data and Risk Concerns for the Tin-Palladium Technology

| Chemical[a] | Human Health Hazard and Occupational Risks[b] | | | | Carcinogenicity Weight-of Evidence Classification | Aquatic Toxicity CC (mg/l) |
|---|---|---|---|---|---|---|
| | Inhalation[c] | | Dermal[d] | | | |
| | Toxicity[e] ($mg/m^3$) | Risk Concerns | Toxicity[e] (mg/kg-d) | Risk Concerns | | |
| 1,3-Benzenediol | ND | NA | 100 (NOAEL) | no | IARC Group 3 | 0.0025 |
| **Copper (I) Chloride[f]** | 0.6 (LOAEL) | no | 0.07 (LOAEL) | yes | EPA Class D | 0.0004 |
| **Copper Sulfate[f]** | ND | NE | ND | NE | none | 0.00002 |
| Dimethylaminoborane | ND | NA | ND | NE | none | 0.007[g] |
| Ethanolamine | 12.7 (LOAEL) | yes | 320 (NOAEL) | no | none | 0.075 |
| Fluoroboric Acid | ND | NE | 0.77 | yes | none | 0.125 |
| **Hydrochloric Acid[h]** | 0.007 (RfC) | NA | ND | NE[i] | IARC Group 3 | 0.1 |
| Hydrogen Peroxide | 79 | no | 630 (NOAEL) | no | IARC Group 3 | 1.2 |
| Isopropyl Alcohol; or 2-Propanol | 980 (NOAEL) | no | 100 (NOAEL) | no | none | 9.0 |
| Lithium Hydroxide | ND | NA | ND | NE | none | ND |
| **Palladium[j]** | ND | NA | 0.95 (LOAEL) | yes | none | 0.00014 |
| **Palladium Chloride[j]** | ND | NA | 0.95 (LOAEL) | yes | none | 0.00014 |
| Phosphoric Acid | ND | NE | ND | ND | none | 0.138 |
| Potassium Carbonate | ND | NA | ND[k] | NE[l] | none | >3.0 |
| Sodium Bisulfate | ND | NA | ND[k] | NE | none | 0.058 |
| Sodium Chloride | ND | NA | ND | NE[l] | none | 2.8 |
| Sodium Hydroxide | 2 (LOAEL) | NA | ND | NE | none | 2.5 |
| Sodium Persulfate | ND | NE | ND | NE[l] | none | 0.065 |
| **Stannous Chloride[m]** | ND | NA | 0.62 (RfD) | yes | none | 0.0009 |
| **Sulfuric Acid[h]** | 0.066 (NOAEL) | yes | ND | NE[l] | none | 2.0 |
| Triethanolamine | ND | NA | 32 (LOAEL) | no | none | 0.18 |
| Vanillin | ND | NE | 64 (LOAEL) | no | none | 0.057 |

[a] Chemicals in bold were in all tin-palladium technologies evaluated, unless otherwise noted.

[b] Risk concerns are for MHC line operators (the most exposed individual).

[c] Inhalation risk concerns for non-conveyorized process only. Inhalation risk from fully enclosed, conveyorized process is assumed to be negligible.

[d] Dermal risk concerns apply to both conveyorized and non-conveyorized equipment.

[e] Toxicity measure is RfC, RfD, NOAEL, or LOAEL as indicated. If not indicated, the type of toxicity measure was not specified in the available information, but assumed to be a LOAEL in risk calculations.

[f] Either copper (I) chloride or copper sulfate was listed on the MSDSs for four of five tin-palladium lines evaluated.

[g] Estimated by EPA's Structure-Activity Team.

[h] Hydrochloric and sulfuric acid were listed on the MSDSs for four of five tin-palladium lines evaluated.

[i] Chronic dermal toxicity data are not typically developed for strong acids.

[j] Palladium or palladium chloride was listed on the MSDSs for three of five tin-palladium lines evaluated. The MSDSs for the two other lines did not list a source of palladium.

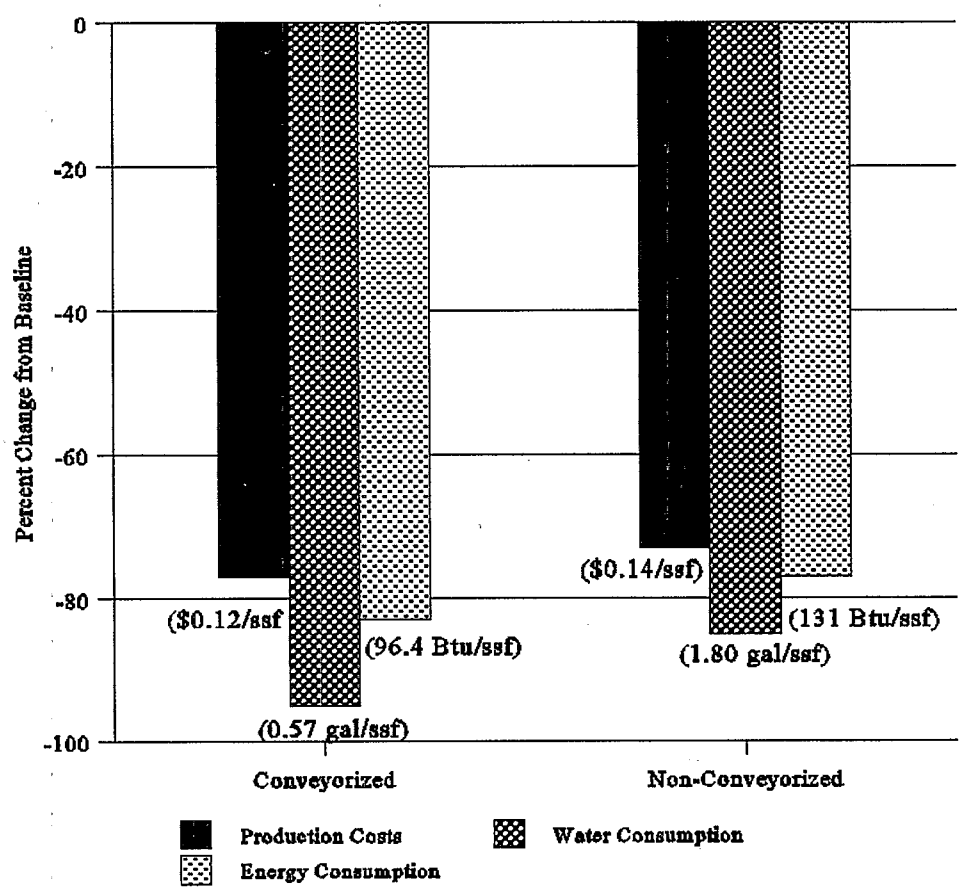
[k] Chemical has very low skin absorption (based on EPA's Structure-Activity Team evaluation); risk from dermal exposure not expected to be of concern.

[l] Dermal exposure level for line operator of conveyorized equipment was in top ten percent of dermal exposures for all MHC chemicals.
[m] Stannous chloride was listed on the MSDSs for four of the five tin-palladium lines evaluated. The MSDSs for the remaining tin-palladium product line did not list a source of tin.
ND: No Data. No toxicity measure available for this pathway.
NE: Not Evaluated; due to lack of toxicity measure.
NA: Not Applicable. Inhalation exposure level was not calculated because the chemical is not volatile (vapor pressure below 1 x $10^{-3}$ torr) and is not used in any air-sparged bath.

## Production Costs and Resource Consumption

Computer simulation was used to model key operating parameters, including the time required to process a job consisting of 350,000 ssf and the amount of resources (water and energy) consumed. This information was used with a hybrid cost model of traditional cost (i.e., capital costs, etc.) and activity-based costs to determine average manufacturing costs per ssf and water and energy consumption per ssf. With either equipment configuration, the tin-palladium technology consumed less water and energy and was more cost-effective than the baseline process (non-conveyorized electroless copper). In addition, the conveyorized tin-palladium process consumed less water and energy and was more cost-effective than the non-conveyorized process ($0.12/ssf vs. $0.14/ssf, respectively). Figure 7.7 lists the results of these analyses and illustrates the percent changes in costs and resource consumption for either equipment configuration from the baseline.

**Figure 7.7 Production Costs and Resource Consumption of Tin-Palladium Technology**
**(Percent Change from Baseline with Actual Values in Parentheses)**



## Regulatory Concerns

Chemicals contained in the tin-palladium technology are regulated by the Clean Water Act, the Safe Drinking Water Act, the Clean Air Act, the Superfund Amendments and Reauthorization Act, the Emergency Planning and Community Right-to-Know Act, and the Toxic Substances Control Act. In addition, the technology generates a waste listed as hazardous (U waste) under RCRA.

## Social Benefits and Costs

A qualitative assessment of the private and external (e.g., social) benefits and costs of this technology suggests there would be net benefits to society if PWB manufacturers switched to the tin-palladium technology from the baseline. However, this alternative contains chemicals of concern for occupational inhalation risk (for non-conveyorized equipment configurations) and occupational dermal contact risks (for either equipment configuration). Among other factors, net social benefits would be due primarily to lower production costs and to reduced consumption of limited resources (water and energy).

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