



# **SOURCE REDUCTION TECHNOLOGIES IN CALIFORNIA PRINTED CIRCUIT BOARD MANUFACTURE**

**Gray Davis, Governor  
State of California**

**Peter M. Rooney, Secretary  
California Environmental Protection Agency**

**Jesse R. Huff, Director  
Department of Toxic Substances Control**

**California Environmental Protection Agency**

**Department of Toxic Substances Control**

**Office of Pollution Prevention  
and Technology Development**

**January 1999**



**SOURCE REDUCTION TECHNOLOGIES  
IN  
CALIFORNIA PRINTED CIRCUIT BOARD MANUFACTURE**

**Prepared by Benjamin Fries**

**State of California Department of Toxic Substances Control  
Office of Pollution Prevention and Technology Development**

**January 1999**

This report was prepared by Benjamin Fries under the direction of Alan Ingham and Kim Wilhelm, Source Reduction Unit, Office of Pollution Prevention and Technology Development

## **DISCLAIMER**

The mention of any products, companies or source reduction technologies, their source or their use in connection with materials reported herein is not to be construed as either an actual or implied endorsement of such products, companies or technologies.

Cover image courtesy of *Environmental Protection*, August 1997

# SOURCE REDUCTION TECHNOLOGIES in California Printed Circuit Board Manufacture

1. SUMMARY .....	1
2. INTRODUCTION .....	2
2.1 Information Limitations .....	2
2.2 Proprietary Information. ....	2
3. PRINTED CIRCUIT BOARD MANUFACTURE .....	3
3.1 Wastestreams .....	3
3.2 Source Reduction .....	3
3.3 Recycling .....	3
4. SOURCE REDUCTION OF PROCESS CHEMICALS .....	4
5. SOURCE REDUCTION OF DRY FILM PHOTORESIST DEVELOPER .....	4
5.1 Aqueous Dry Film Developer .....	4
6. SOURCE REDUCTION OF DRY FILM PHOTORESIST STRIPPER .....	5
6.1 Source Reduction by Bath Operation and Maintenance .....	5
6.2 Source Reduction by Chemical Substitution. ....	5
6.3 Source Reduction by Process Substitution .....	5
6.4 Onsite Recovery .....	5
7. COPPER ETCHANTS .....	6
7.1 Ammoniacal Etchant .....	6
7.2 Cupric Chloride Etchant. ....	6
8. RECOVERY OF AMMONIACAL COPPER ETCHANT .....	8
8.1 Ion Exchange Recovery .....	8
8.2 Electrolytic Recovery. ....	8
8.3 Electrolytic Recovery Bleedstream .....	8
8.4 MECER Onsite Regeneration System .....	9
9. SOURCE REDUCTION AND RECOVERY OF CUPRIC CHLORIDE ETCHANT .....	10
9.1 Source Reduction of Hydrochloric Acid - Sodium Chlorate Etchant .....	10
9.2 Onsite Recovery .....	10
9.3 Onsite Recovery Limitations .....	10
10. OFFSITE ETCHANT RECOVERY .....	11

11. MICROETCHANTS AND MICROETCHANT RECOVERY .....	12
11.1 Hydrogen Peroxide CobraEtch. ....	12
11.2 Microetch “D” .....	12
12. ONSITE TREATMENT WITH COPPER RECOVERY .....	13
12.1 Carbamate Precipitation of Copper. ....	13
12.2 Onsite Recovery of Etchant Rinse .....	13
13. TIN OR TIN/LEAD SOLDER PLATE .....	14
13.1 Fluoroboric Acid Anti-Oxidant. ....	14
13.2 Material Substitution using Methanesulfonic Acid Anti-Oxidant .....	14
13.3 Product Modification using Tin Plate .....	14
14. SOURCE REDUCTION OF SOLDER OR TIN STRIPPER .....	15
14.1 Chemical Substitution of Fluoride Formulations .....	15
14.2 Chemical Substitution using Nitric Acid. ....	15
14.3 Chemical Substitution using Ferric Nitrate .....	16
14.4 Process Modification with Material Substitution .....	16
15. ONSITE RECYCLING OF SOLDER STRIPPER .....	17
15.1 Electrodialysis .....	17
16. OXIDE PROCESS .....	17
16.1 Material Substitution using a Textured Copper Surface .....	17
16.2 Product Modification using a Waterblasted Surface .....	17
17. SOURCE REDUCTION OF PERMANGANATE BATH .....	18
18. SPENT SULFURIC ACID REUSE.....	18
19. SHADOW PROCESS .....	19
19.1 Innovative Shadow Process .....	19
19.2 Shadow Process Applications .....	19
19.3 Shadow Process Limitations .....	19
20. ELECTROLESS RINSEWATER RECOVERY .....	20
21. CONTINUOUS FEED AND BLEED .....	21
21.1 Feed and Bleed Operation .....	21
21.2 Feed and Bleed Advantages .....	21
21.3 Quality Control and Source Reduction .....	21
21.4 Copper Etchant .....	21
21.5 Photoresist Stripper Bath .....	22
21.6 Electroless Copper and Sodium Borohydrate .....	22
21.7 Rinsewater Tank .....	22
21.8 Feed and Bleed Recirculation and Recovery .....	22
21.9 Spray Stream Recirculation with Feed And Bleed .....	23
21.10 Rinsewater Spray Stream .....	23

22. MATERIAL SUBSTITUTION .....	24
22.1 Finishing Solution for Etchant Residues .....	24
22.2 Plating Tape Residue Cleaning .....	24
23. PROCESS MODIFICATION .....	24
23.1 Plastic Plating Racks .....	24
23.2 Baking Procedure .....	24
24. PROCESS SUBSTITUTION .....	25
24.1 Additive Process for Printed Circuit Board Manufacture .....	25
24.2 Aluminum Oxide Abrasive Cleaning .....	25
25. PRODUCT SUBSTITUTION .....	25
26. HEAVY METALS WASTE TREATMENT .....	26
26.1 Electroplating Wastewater .....	26
26.2 Process Substitution and Waste Treatment .....	26
26.3 Heavy Metals Precipitation by Ferrous Sulfate .....	26
26.4 Heavy Metals Precipitation with Dithiocarbamate Acid .....	26
26.5 Heavy Metals Precipitation with Calcium Polysulfide .....	27
26.6 Heavy Metals Precipitation with Sodium Hydroxide .....	27
26.7 Copper Precipitation with Sodium Borohydrate .....	27
26.8 ElectroStrip Recovery Systems .....	27
27. WATER CONSERVATION .....	28
28. ADMINISTRATIVE IMPROVEMENTS .....	28
28.1 Cost Control .....	28
28.2 Inventory Control .....	28
29. CLOSING COMMENTS .....	29
29.1 Information Sources .....	29
29.2 Shared Information .....	29
PUBLICATIONS .....	30



# SOURCE REDUCTION TECHNOLOGIES IN CALIFORNIA PRINTED CIRCUIT BOARD MANUFACTURE

## 1. SUMMARY

A detailed technical review was made of hazardous waste source reduction technology used by California printed circuit board manufacturers. The purpose of the review was to assess the implementation of hazardous waste source reduction technology available for the printed circuit board manufacturing industry.

At the request of the Department of Toxic Substances Control (DTSC), 33 printed circuit board manufacturers submitted SB 14 Hazardous Waste Source Reduction Evaluation Review and Plan (Plan) documents for review by DTSC. The documents were prepared by September 1, 1991, by each of the firms, as required under the Hazardous Waste Source Reduction And Management Review Act of 1989 (SB 14). SB 14 requires DTSC review the documents of at least two industries every two years.

Technical review was conducted of the 19 submitted plans that had evaluated or implemented source reduction technologies for use in their operations. The process engineer or scientist of each of the manufacturers was contacted by DTSC, to discuss detailed technical information not included in their documents. The information indicated that innovative source reduction technologies were being used at 13 of the manufacturers. Depending upon the process, many of the innovative technologies reviewed have general applications throughout the printed circuit board manufacturing industry.

The innovative technologies found in the review are discussed in this report. Most are commercially available, yet innovative in that they are new or improved technologies that offer economic and/or environmental advantages over conventional technologies.

## 2. INTRODUCTION

This document is intended to stimulate the implementation of source reduction measures across California's printed circuit board industry. Advancing technology can bring benefits including improved products, improved process operations, reduced environmental impact, and better economics. This corresponds favorably to the rapidly changing technology in the printed circuit board industry. For that reason printed circuit board manufacturers should include source reduction in their ongoing investigation to improve their products and processes. This report describes some product and process changes that are underway, or currently under investigation by circuit board makers.

### 2.1 Information Limitations

While this document is intended to provide sufficient detail to encourage further investigation, it is not meant to answer questions that arise when investigating source reduction applications. Nor is this document intended as a technical information source or bibliography for manufacturing technology. Due to rapidly changing technology in the electronics industry, such comprehensive information would rapidly become outdated. To pursue further information, the reader is encouraged to pursue common information sources suggested herein.

### 2.2 Proprietary Information

This report does provide many examples of source reduction measures pursued by circuit board manufacturers, some are notably innovative. However much of the information is limited as proprietary or confidential. Often only the proprietary name is provided, and the detailed chemical formulation is not available. Also, the technology is often unique to a given operation, process, or product. For these reasons, this document does not provide detailed information about the technology discussed nor about its source. Rather, this report provides examples of innovative source reduction technologies that have been implemented or investigated. The printed circuit board manufacturer can use the examples provided in this document as a source of ideas to investigate and develop specific source reduction technology to fit higher specific needs and limitations.

The manufacturing process for a printed circuit board varies according to the process and product. The following process is used at many circuit board manufacturing operations.

### 3. PRINTED CIRCUIT BOARD MANUFACTURE

The manufacture of a multi-layer circuit board typically starts with preparing the board laminates. Each laminate has a core of fiberglass-reinforced polymer resin, with both sides of the core laminated over with copper foil surfaces. The resulting laminate is then baked, to cure and stabilize the polymer core. Subsequent processing etches the copper surfaces, so that the copper circuit patterns are formed on each surface. After additional processing, the laminates are layered onto each other using isolation sheets, and fabricated into the multi-layer printed circuit board. Holes are then drilled through the board, according to the intended circuit design. After etching and deburring the drillholes, the board is electroless-plated with copper to deposit a conductive copper coating onto the wall of each drillhole. This conductive surface is then electroplated with copper, to strengthen and build up the copper surfaces on the drillhole walls. The purpose of the copper-coated drillhole walls is to connect the circuit pattern on each board laminate into a continuous circuit design among the laminated layers of the completed printed circuit board.

The copper-coated, multi-layered board then undergoes additional processing to complete the circuitry. Initially in this process, a dry film mask is applied onto the exposed copper surfaces on both sides of the board. The mask is applied as a pattern so that a circuit design is traced onto the copper surface. Subsequent processing exposes the copper tracings by removing the dry film mask according to the circuit design. The exposed copper tracings are plated with solder to protect the copper circuit. The mask is then stripped from the unplated copper areas, which are then etched to remove any unsoldered copper strips. The ammoniacal etchant removes the unmasked copper, but does not remove the tin/lead solder plating

that protects the copper circuit tracings. Then the panel is rinsed, and processed in 10% sulfuric acid as an oxidation inhibitor.

#### 3.1 Wastestreams

For circuit board manufacture, the most prevalent hazardous wastestreams are spent aqueous process solutions, spent rinsewater, other metal-laden wastewaters, and the metal-laden sludge that is precipitated by the treatment of the spent solutions, rinsewater, and other wastewaters. Many of the innovative source reduction measures listed here would reduce or eliminate sludge generation. Some of the measures would reduce the volume of aqueous wastestreams.

#### 3.2 Source Reduction

Hazardous waste source reduction reduces or eliminates the quantity of hazardous waste generated at the source generating the waste. Source reduction can simplify and economize hazardous waste management.

Source reduction of process solutions includes several process substitution measures that reduce or eliminate the use of some process baths that generate hazardous waste. Some of the substitutions still do generate spent process solutions, but often at reduced volume, or as spent solutions that can be easily regenerated for reuse.

#### 3.3 Recycling

Onsite and offsite recycling are a complement to source reduction. While source reduction avoids generation of waste at the source, recycling manages the waste to derive further benefit. Like source reduction, recycling is a preferable alternative to treatment or disposal of the waste. Recycling can recover spent

process chemicals or rinsewaters. Recycling can also recover contaminants like copper and other etched metals. Like source reduction, recycling can reduce the risk and impact to

human health and the environment. Recycling can reduce or delay the need for storage, handling, transport, and disposal of spent process chemicals.

## 4. SOURCE REDUCTION OF PROCESS CHEMICALS

Spent process chemicals often become hazardous waste due to their original chemical properties. Chemical substitution is a commonly used source reduction method, whereby a hazardous process chemical is replaced by a less-hazardous or nonhazardous chemical.

Various alternative process solutions are often available from chemical suppliers. Some may

provide source reduction opportunities that eliminate the use of hazardous chemicals. Successful waste reduction improvements also reduce waste management costs. Specific examples are discussed below. Detailed technical information on substitute chemicals and their application can be obtained from vendors, trade journals, and industry exhibitions.

## 5. SOURCE REDUCTION OF DRY FILM PHOTORESIST DEVELOPER

To establish the copper-coated laminate circuit design, a dry film mask is applied to the exposed copper surface. The dry film is exposed to an image according to the desired circuitry. The dry film is then developed and processed into the image pattern. The image guides the plating, etching, and other operations to produce the final circuitry. The dry film is subsequently removed from the copper surface as part of the process. Technical details of this process and its operational sequence vary according to the process and product.

### 5.1 Aqueous Dry Film Developer

The chemical bath used as the dry film developer often uses an alkaline solution to develop the photoimage on the dry film surface of each laminate. One circuit board company recently changed its operation to fully aqueous dry film developer, precluding need for the ethylene glycol monobutyl ether component of dry film developer. The bath is now 99% water and 1-2% potassium carbonate. The spent bath is no longer a hazardous waste, because it does not contain hazardous chemical components.

## 6. SOURCE REDUCTION OF DRY FILM PHOTORESIST STRIPPER

Processes that use a photoresist procedure, produce the circuitry from a photo image on the circuit board surfaces. The photoresist controls the formation of circuitry on the copper surface of the laminate.

As part of the processing, unexposed photoresist is stripped from the board surface. Stripper solutions are used to selectively remove dry film mask and copper laminate during the processing that forms the copper circuit patterns on the laminate surfaces.

Dry film stripper is usually an alkaline solution that removes dry film from copper laminate surfaces, as part of the processing. A stripper solution in common use is 80-95% water, containing potassium hydroxide, monoethanolamine, ethylene glycol monobutyl ether, and other ingredients.

Once spent, the solution is typically shipped offsite to a solvent treatment/recycle/disposal facility, or treated onsite.

### 6.1 Source Reduction by Bath Operation and Maintenance

One operation changed the criteria for adding replenishment chemicals to the dry film stripper bath. Formerly, chemicals were routinely added based on the passage of time alone. Now, bath parameters are continuously monitored, with replenishment chemicals added as necessary to maintain bath performance.

### 6.2 Source Reduction by Chemical Substitution

To supplement vendor information, one manufacturer's approach did its own source

reduction research on process chemical alternatives. The firm has tested 4 alternative dry film stripper solutions over a six-month period, to replace a stripper solution having hazardous components. While the tests provided no immediate benefits to apply operationally, the firm is hopeful that continued testing of alternative chemistries will result in an acceptable alternative.

### 6.3 Source Reduction by Process Substitution

One operation has implemented a fully aqueous chemistry for photoresist stripper that does not remove as much copper as it removes the photoresist. One source reduction benefit of this new stripper is that less copper removal results in less toxicity in the spent stripper solution.

### 6.4 Onsite Recovery

Other considerations that affect source reduction decisions include reliability and economics. As alternatives to offsite management of spent stripper, some firms routinely treat the solution for discharge to the publicly owned treatment works (POTW).

One firm investigated onsite management of spent dry film stripper solution. Available technology could recycle the solution to the process. However the alternative technologies that were found to be available, are not proven. Also, considering the modest amount of stripper solution recycled, the equipment cost recovery for onsite treatment was found to be prohibitively expensive.

## 7. COPPER ETCHANTS

In the process that produces the circuit on the circuit board, copper etchant is used to remove copper from the copper foil surfaces of the circuit board. The copper that is removed, is etched away according to the circuit pattern on the film mask. The copper that is removed with etchant, is that which is not to be part of the circuitry. The copper which is not removed, is the copper that forms the circuitry of the circuit board. Details of the etching process vary according to the process technology and product. A number of copper etchant processes are discussed below, along with source reduction highlights and waste management practices.

### 7.1 Ammoniacal Etchant

Alkaline (ammoniacal etch) ammonia-based etchant and cupric chloride ( $\text{CuCl}_2$  etch) acid-based etchant are both well established copper etch process technologies. The ammoniacal etchants, either ammonium chloride or ammonium sulfate, are most commonly used.

The ammoniacal etch and the  $\text{CuCl}_2$  etch function differently, each having unique advantages and limitations. The choice between the two processes is also affected by personal preference, according to the familiarity of the operating personnel with each technology. Due to the unique advantages of each process, some operations use both ammoniacal etch and  $\text{CuCl}_2$  etch.

The ammoniacal etch has been in common use for 20 to 30 years. It has the advantage of being able to etch exposed copper from the surface of the circuit board, while not removing the tin/lead solder plating that covers the protected portions of the copper circuit.

However ammoniacal etch cannot achieve the fine-line etching that  $\text{CuCl}_2$  etch can provide.

Regarding hazardous waste generation, an advantage of ammoniacal etch is that  $\text{CuCl}_2$  etch onsite recovery often involves use of chlorine gas, a significant health and environmental concern. However  $\text{CuCl}_2$  etch has a longer solution service life than ammoniacal etch.

### 7.2 Cupric Chloride Etchant

The formulations for  $\text{CuCl}_2$  etch vary, according to the needs of the operation.  $\text{CuCl}_2$  etch is basically a solution of hydrochloric acid and  $\text{CuCl}_2$ . The hydrochloric acid etches the copper from the laminate, producing  $\text{CuCl}_2$  as a reaction product. However  $\text{CuCl}_2$  is also an active ingredient in the solution. It is needed in the solution to have a proper etch reaction, because the  $\text{CuCl}_2$  controls the rate and quality of etching. Some  $\text{CuCl}_2$  etch solutions consist of hydrochloric acid and sodium chlorate. The sodium chlorate is an oxidizing agent.

For etching, the  $\text{CuCl}_2$  etch solution is sprayed onto the PC board, where the etchant removes copper. The  $\text{CuCl}_2$  accumulates in the etch solution as a reaction product, as a result of etching the copper from the copper laminate. For that reason the etch solution eventually becomes spent by becoming laden with cupric ion, and must be replaced with fresh  $\text{CuCl}_2$  etch.

$\text{CuCl}_2$  etch solution is better than ammoniacal etch, for some product types. For a board having close traces,  $\text{CuCl}_2$  etch is better by not over-etching or undercutting the traces.  $\text{CuCl}_2$  etch achieves the fine-line etching that some products require.

$\text{CuCl}_2$  etch also has some process advantages.  $\text{CuCl}_2$  etch is not a chelator<sup>1</sup>, while ammoniacal etch is. Chelation can be a useful property for controlling metal ions in solution. However a chelator has the disadvantage of inhibiting sodium hydroxide precipitation of metals during waste treatment.

$\text{CuCl}_2$  etch has a longer solution service life than does ammoniacal etch, since  $\text{CuCl}_2$  etch can retain much more copper in solution before it becomes spent.  $\text{CuCl}_2$  etch will hold up to 26 ounces copper per gallon, compared to 18 to 22 ounces/gallon for the ammoniacal etch. Also, when the  $\text{CuCl}_2$  etch solution becomes

spent, the higher copper content is of benefit to the offsite metal recovery vendor. For a company that generates large volumes of spent  $\text{CuCl}_2$  that can be sold to a recovery vendor, some vendors will pay a higher price for the higher copper content.

One disadvantage is that  $\text{CuCl}_2$  etch cannot be used to etch copper in the outer layer processing. This is because it will strip from the outer layer surface, the tin/lead solder plating that protects the copper circuit. For this reason ammoniacal etchant is used for the outer circuit layer.

---

<sup>1</sup>A chelator (kee-lay-tor) keeps metals in solution. A chelator is also used when manufacturing with the electroless copper process. Because a chelator will hold metals in the wastestream, a spent ammoniacal etchant wastestream will inhibit sodium hydroxide precipitation of metals during waste treatment.

## 8. RECOVERY OF AMMONIACAL COPPER ETCHANT

Some spent etchants can be recovered onsite using electrowinning, ion exchange, or precipitation, to remove copper from spent etchant solution. Spent ammoniacal etch can also use solvent extraction to remove copper and recycle the etch solution. The recovered etchant can be recycled to the process. Often the copper-laden recovery residue can be sold to an offsite metal reclaimer.

Regeneration of spent ammoniacal etch is much less hazardous than  $\text{CuCl}_2$  etch regeneration. Spent ammoniacal etch can be regenerated onsite as a closed loop with minimal personnel exposure, making it safer to handle. Alternatively, spent ammoniacal etch, like  $\text{CuCl}_2$  etch, is often sent to an offsite waste management service, for copper recovery and etchant regeneration.

### 8.1 Ion Exchange Recovery

Onsite ion exchange recovery of spent ammoniacal etch often uses a liquid-liquid ion exchange system employing kerosene or other immiscible organic solvent. The extraction system sprays the solvent upward into the spent etchant as fine droplets in liquid-liquid extraction. The solvent holds an ionic charge, and works like resin beads to draw the copper cations from the spent ammoniacal etch. The copper-laden solvent rises to the surface, then is processed with dilute sulfuric acid in a cone-shaped process vessel. The sulfuric acid reacts with the copper to precipitate copper sulfate. The copper sulfate precipitate can be sold to an offsite metals reclaimer for its copper content. The recovery system returns the ion exchange effluent back to the etch process as recovered ammoniacal etchant.

### 8.2 Electrolytic Recovery

Electrolytic recovery uses an electrolytic cell to remove the copper from the spent ammoniacal etch. The recovered etch is recycled directly back to the process. The copper deposits at the cathode as metallic sludge, metallic flakes, or solid copper, and can be sold to an offsite metals reclaimer. This process, also called “electrowinning,” can readily be operated onsite.

Often, the best economic and operational approach to onsite electrolytic recovery does not attempt to remove all the copper. It removes enough copper to reactivate the etchant for recirculation back to the process. An electrowinning unit might remove only a portion of the ionic copper, by lowering copper content of the etchant solution from 1500 parts per million to 1000 ppm. The process parameters are determined by consultation between the equipment vendor and the plant technical personnel.

### 8.3 Electrolytic Recovery Bleedstream

For electrolytic recovery, some of the spent etchant must be periodically, or continually, bled off from the recycle loop and discharged from the process as wastewater. The bleed-off prevents excessive impurity accumulation in the etchant solution recycle loop. This bleed-off is necessary for an electrolytic recovery unit, because the unit selectively removes only copper or other metal. The unit does not remove contaminants such as the trace impurities that enter the process with the fresh etchant replenishment chemicals and makeup water. The bleed-off waste can be treated and discharged to the sewer, or managed offsite to recover the copper.

## 8.4 MECER Onsite Regeneration System

Offsite recovery of spent ammoniacal etch can be replaced by the MECER™ onsite recovery system. The MECER system uses solvent extraction and electrowinning to recover etchant, recover rinsewater, and reclaim high purity copper.

Several operations in this review have evaluated onsite ammoniacal etch regeneration, including the MECER. The MECER is often not cost effective, because the maintenance and installation costs are high. Some operations find better economics with offsite etchant recovery services that return the regenerated ammoniacal etch.

The MECER process is from Sweden. Reportedly, one operation has the MECER system in California. Another company located in southern California, is interested in installing the MECER system. It has been installed in two other US locations; in Oregon, and in Nashua, NH. The MECER system has also been installed outside the continental US. In Puerto Rico, it was installed to overcome the difficulty of obtaining the fresh process solution.

The MECER system is not a proprietary process:

- The MECER system has three stages. An extraction stage extracts copper from the etchant; another extraction stage extracts copper from rinsewater; and an electrolytic stage removes copper from the extractant.
- The MECER system removes copper from spent etchant and spent rinsewater by solvent extraction. After copper removal, the etchant is regenerated by adding makeup solvent and ammonia. Makeup ammonia is added automatically during processing. Ammonia content is monitored by pH measurement.
- The MECER system can recover 95% of the ammoniacal etch. The regenerated ammoniacal etch is usually recirculated directly back to the process.
- The MECER system can also be used to remove copper from spent rinsewater in electrolytic recovery units. The recovered rinsewater is likewise recirculated to the process.
- The MECER system reclaims copper from the solvent in electrolytic cells. The copper is peeled off the cell electrode as copper foil. The copper foil has a 99% purity. The released copper foil can be sold to an offsite copper reclaimer.
- The MECER system has its greatest cost advantage in its elimination of the need to transport spent etchant for offsite recovery.

## 9. SOURCE REDUCTION AND RECOVERY OF CUPRIC CHLORIDE ETCHANT

### 9.1 Source Reduction of Hydrochloric Acid - Sodium Chlorate Etchant

One operation that uses an etchant of hydrochloric acid with sodium chlorate, has improved its blending of the acid and sodium chlorate. The blending proportions are now monitored by a Reduction-Oxidation Potential (ROP) instrument. The ROP monitor is a much more accurate control of the correct proportions than the former colorimetric Visuetch instrument.

### 9.2 Onsite Recovery

Some operations replenish the spent  $\text{CuCl}_2$  etchant onsite with hydrochloric acid. Some operations replenish the spent  $\text{CuCl}_2$  with  $\text{Cl}_2$  gas. Spent etchant that is not replenished

onsite, can be manifested for offsite management, where the copper can be recovered.

### 9.3 Onsite Recovery Limitations

Chemical replenishment is difficult for  $\text{CuCl}_2$  etch recovered onsite. One onsite replenishment method uses chlorine. This entails onsite hazardous materials storage and handling of chlorine, either in  $\text{Cl}_2$  gas cylinders or as  $\text{HOCl}$  crystals. The risks related to onsite chlorine storage and handling is one reason why some operations do not use  $\text{CuCl}_2$  etch.

Hydrogen peroxide can also replenish spent  $\text{CuCl}_2$  etch. This can provide onsite recovery of  $\text{CuCl}_2$  etch. However, concentrated hydrogen peroxide is a strong oxidizer, which requires special onsite hazardous material storage and handling procedures.

## 10. OFFSITE ETCHANT RECOVERY

Offsite waste management services for spent etchant are commonly used by circuit board manufacturers. The offsite services are available for spent etchant pickup and recycling, with copper recovery.

For spent ammoniacal etch, one offsite service can process the spent etchant as well as the copper-laden sludge generated from onsite treatment of spent etchant. The vendor also processes other copper wastes.

The vendor can recover the etchant as well as the copper when treating ammoniacal etch. Thus, the offsite recovery of spent etchant can be contracted to the vendor as a completely closed-loop service. The vendor service brings fresh etchant to the circuit board manufacturing site, and takes the spent etchant to its offsite facility for recovery of both the etchant and copper. The vendor is paid a package price per gallon, which includes vendor pick

up of the spent etchant, return of fresh etchant, transportation, and processing costs.

The offsite recovery process distills off the ammonia as vapor, and then condenses the ammonia vapor to make fresh etchant. The still bottoms are processed to remove copper, as either copper oxide or copper sulfate. The copper compound is often sold to pesticide formulators, as an ingredient in agricultural fungicides and wood preservatives. The residual water is also recovered and used to make fresh etchant.

Spent  $\text{CuCl}_2$  etch is processed using electrolytic recovery of copper. Often, the residual solution can be neutralized and discharged to the POTW under a permit. For some wastes, the copper is precipitated from the spent solution. The sludge is sent to a vendor where the copper is recovered. There are several vendors available to receive the sludge and recover the copper.

## 11. MICROETCHANTS AND MICROETCHANT RECOVERY

Microetchants are used where precision etching is needed. Like  $\text{CuCl}_2$ , microetchants are acid-based to achieve fine-line etching. Some source reduction approaches for proprietary microetchant processes are discussed below.

### 11.1 Hydrogen Peroxide CobraEtch

CobraEtch™ has been installed at one operation, to replace Microetch “D.” The active ingredient in CobraEtch is hydrogen peroxide. Spent CobraEtch can be recycled onsite by adding  $\text{H}_2\text{SO}_4$  to precipitate copper sulfate crystals. The precipitated copper sulfate residue is recyclable offsite. The supernate is decanted off and recycled back to the process, after replenishing the hydrogen peroxide concentration.

### 11.2 Microetch “D”

Microetch “D” is still used in some processes. Microetch “D” is an acidic etch solution, using potassium persulfate or sodium persulfate as the active etchant. Microetch “D” becomes spent at a copper content of 3 ounces/gallon. Unlike peroxide sulfuric etchant, Spent Microetch “D” doesn’t crystallize its excess copper.

Spent Microetch “D” is usually retained in an onsite waste treatment tank. In the tank, an electrolytic recovery process plates the copper out of solution and onto the cathodes. The recovered copper can be peeled from the electrode as a foil, and sold as high purity copper scrap. The electrolytic recovery effluent solution then goes to an ion exchange process, so that it can then be discharged to the sewer according to permit conditions.

## 12. ONSITE TREATMENT WITH COPPER RECOVERY

Onsite treatment of aqueous wastestreams is often needed to meet regulatory requirements. This can occur if the copper content exceeds permit limits for discharge to the municipal sewer. Wastewater needing onsite treatment can include spent etchant, as well as spent rinsewater. Onsite treatment can include copper recovery.

Water conservation often results in the copper content of spent rinsewater exceeding the permit limits for discharge to the municipal sewer. The spent rinsewater can be treated onsite so that the treatment effluent meets the discharge limits.

### 12.1 Carbamate Precipitation of Copper

One operation uses carbamate to precipitate copper from spent etchant. Following treatment, the wastewater is discharged to the publicly owned treatment works (POTW). The recovered sludge is sent offsite for copper recovery, which is easier on sludge precipitated from carbamate.

### 12.2 Onsite Recovery of Etchant Rinse

The etch process is followed by a rinse step. Electrolytic recovery of spent rinsewater can recover the copper. One operation reported that fifty percent of their spent rinsewater can be recycled using electrolytic recovery to remove the metal content.

For efficient electrolytic recovery, rinsewater usage must be minimized to keep the copper concentration as high as possible. Water conservation can help minimize the dilution of spent rinsewater. Rinsewaters that are too dilute for electrolytic recovery, might be recoverable with a fixed bed ion exchange unit. Alternatively, reverse osmosis or dialysis could be used to concentrate the copper and recycle the rinsewater. The copper in the concentrate could then be recovered using electrolytic recovery.

In some manufacturing operations, an electroplate of solder or tin is applied to the copper surfaces, to protect the copper surface and facilitate the fabrication of the circuit board.

## 13. TIN OR TIN/LEAD SOLDER PLATE

### 13.1 Fluoroboric Acid Anti-Oxidant

Fluoroboric acid is commonly used as a preparation to prevent electroplated copper from oxidizing or tarnishing before the solder plate is applied.

### 13.2 Material Substitution using Methanesulfonic Acid Anti-Oxidant

One operation changed its tin/lead anti-oxidant treatment from the electrolytic fluoroboric acid dip, to a methanesulfonic acid dip. The purpose of the change is to reduce toxicity, and to reduce the number of process steps. Other advantages of using methanesulfonic acid instead of fluoroboric acid, is that methanesulfonic acid is less corrosive to pumps and motors, it won't etch the concrete floor if it spills from the process, and it is less toxic to human health.

### 13.3 Product Modification using Tin Plate

Due to the hazards associated with metallic lead, most operations are phasing out the tin/

lead solder plating process, in favor of a tin plating process. The modification involves installing a bright tin acid bath to plate solder-mask-over-bare-copper (SMOBC) boards. The plate contains tin, and no lead. By eliminating lead from the solder, the modification would eliminate lead from spent solder stripper. The result is that solder related wastes will be lead-free and therefore of less toxicity.

However, the tin/lead plate provides a surface that is more resistant to oxidation, compared to tin plate. The tin/lead plate has better storage properties for work-in-process inventory, because its surface does not oxidize as readily as that of tin. The tin/lead plate does not need a protective coating to prevent oxidation of its exposed surfaces. The tin plate would need a protective surface coating for oxide prevention.

Some customers are slow to accept the tin plate as a substitute for tin/lead plate. This is partly due to reluctance to change from an established process, when that change might affect the product that presently works well for the customer. The circuit board manufacturer must work with its assembly plant customers to implement product modifications of this kind, because the circuit board assembly plants must meet the end customer expectations.

## 14. SOURCE REDUCTION OF SOLDER OR TIN STRIPPER

Solder stripper is not to be confused with etchant. Etchant removes copper from the circuit board laminate for the purpose of defining the circuit traces. Solder stripper removes the solder that was applied to the circuit board to protect the circuit traces from being etched during processing.

Solder stripper is also used to remove the solder from inside the plated-through drillholes. The result is a laminate with circuit traces and plated-through drillholes of only copper, so that the final circuitry is free of the etch resist solder that was used to protect the circuitry during processing. Nitric and sulfuric acid formulations are used to strip off etch resist solder, tin or tin/lead. Some formulations include a fluoride base. The solder stripper attacks only the tin/lead solder, and not the copper. There are three established solder stripper technologies.

### 14.1 Chemical Substitution of Fluoride Formulations

By changing to a more efficient solder stripper with a higher loading capacity, less volume of spent solder stripper is generated and the stripper is more economically treated for metal recovery.

One operation formerly used C-Strip. Now it uses RSS-1 by Cherokee Chemical. RSS-1 can hold more dissolved solder per gallon, resulting in longer bath life and a more concentrated waste. The solder loading content increases from 12 to 14 ounces solder per gallon of spent stripper.

Both C-Strip and RSS-1 are fluoride-based formulations. Fluoride based strippers are extremely hazardous. The fluoride-based spent stripper cannot be treated onsite under a Permit By Rule.

### 14.2 Chemical Substitution using Nitric Acid

One operation explored the use of a non-fluoride, nitric acid based solder stripper, to eliminate the classification of the spent stripper as an extremely hazardous waste. This nitric acid based material can strip solder more rapidly, and hold more stripped solder in solution. However, early efforts with the non-fluoride stripper did not work well, with resulting product quality problems. As a result, the operation continued its use of a fluoride-based solder stripper.

The previous decision to continue using a fluoride based solder stripper was based on an inability to find a nitric acid based stripper that would meet quality control needs. As a result of additional research since that time, such a stripper was found, and the operation has thereby switched from the fluoride based Cherokee Chemical RSS-1 to the nitric acid based Florida Cirtech EZ-5001.

The operation also upgraded the solder stripping line from a manual dip tank to a conveyerized spray unit. Their main purpose was to improve quality, but source reduction benefits have resulted as well. The nitric acid based solder stripper in conjunction with the conveyerized line now removes 18-20 ounces solder per gallon of stripper. This is a significant improvement over the earlier fluoride-based chemistry, thus reducing raw material consumption as well as waste generation.

Another improvement was to convert one tin-lead plating bath to a tin plating bath. With this elimination of lead usage, the spent solder stripper loses its D008 (lead-bearing) hazardous waste characteristic, although it does retain a D002 (corrosive) hazardous waste

classification. Furthermore, the operation has reduced the thickness of the plated tin deposit that will be stripped off from 0.3 mils to 0.2 mils. In so doing, the number of panels processed per gallon of solder stripper has increased by about 50%.

### **14.3 Chemical Substitution using Ferric Nitrate**

One operation now uses Ardrex PC 1115 in lieu of nitric/fluoroboric solder stripper, Tinstrip TLS-120, by Duratech. Ardrex PC1115 contains no fluoroboric acid. It contains nitric acid plus ferric nitrate as key ingredients. The new chemistry was found to be more efficient, and it works more completely than the nitric/fluoroboric stripper. The substitution reduces spent acid from 55 gallons/day to 55 gallons/week. Savings are estimated at \$35,000/year.

### **14.4 Process Modification with Material Substitution**

At one operation, a two-step solder stripper was replaced with a vendor-supplied one-step stripper. The two-step dip tank was replaced by a one-step conveyORIZED process. As the board passes through the process on the conveyor, the stripper is sprayed onto both sides of the board. Then the work passes through a spray rinse. The machinery is enclosed, with a recirculating pump.

The conveyORIZED system improved stripping quality. The former system generated 100 gallons of spent solution per week that needed waste treatment. This was reduced to 100 gallons in six weeks.

The one-step process uses a chemistry similar to the two-step process, with the exception that the one-step stripper uses a nitric acid base.

## 15. ONSITE RECYCLING OF SOLDER STRIPPER

Onsite recycling of spent solder stripper could complement source reduction and benefit a company's waste management program. Onsite recycling could replace either onsite treatment or offsite management of spent stripper.

Onsite recycling can save money by reducing the cost of purchased chemicals. Additionally, it can also reduce the cost of fees and services for waste management, by reducing the need for offsite waste management. However onsite recycling may require a hazardous waste facilities permit, depending on the technology.

### 15.1 Electrodialysis

One operation proposes to recycle nitric acid onsite using a membrane electrodialysis system to remove metals from the spent solder stripper. The electrodialysis purifies the nitric acid. Other stripper chemicals are replenished as needed, and the reconstituted nitric acid stripper is returned to the process bath. This system

removes the copper, the tin/lead solder metals, and other contaminants as filter sludge. The filter sludge can be sold to an offsite metals reclaimer. The installed cost is \$30,000. One barrier to onsite electro dialysis is the classification of the spent stripper or filter sludge residue as a toxic substance, which may require a permit for onsite treatment or storage. Another barrier is the 50 to 60% water content in the sludge. Metal recovery smelters need the sludge to be below 10 to 15% water content. Filter presses are available, that can achieve lower water content by circulating hot water through the filter unit to evaporate water from the filtercake.

After the mask, etch, plate, and strip processing completed, a brown oxide layer is formed on the laminate copper surfaces. This provides a roughened surface so that the laminates can be bonded together with epoxy, when fabricating a multi-layer circuit board. Without the rough oxide layer, the copper surface is normally too slick to properly adhere to the epoxy bond.

## 16. OXIDE PROCESS

### 16.1 Material Substitution using a Textured Copper Surface

The brown oxide process line can be eliminated by material substitution. This option requires the purchase of copper-clad blank laminates that have a textured surface pre-rolled into the copper foil surfaces. After the desired circuitry has been etched into the copper surfaces, the epoxy adhesive can be directly applied to the textured copper surface for bonding the laminates without use of the brown oxide process.

The raw material cost is somewhat higher for the copper-clad blank laminate having the textured copper surface, when compared to copper-clad blank laminates that have a slick

surface. However, the textured-surface option eliminates the entire oxide process line. That, in turn, eliminates hazardous waste generation from the oxide line, as well as the associated equipment and operating costs for the line.

### 16.2 Product Modification using a Waterblasted Surface

The brown oxide process can also be eliminated by using aluminum oxide particles applied as a waterblast slurry. The waterblast slurry impacts upon the copper surface, causing a textured surface of micro-indentations. The aluminum oxide does not impact as an abrasive, so that no copper is removed from the copper surface when making the indentations with the waterblast slurry.

## 17. SOURCE REDUCTION OF PERMANGANATE BATH

During the fabrication process, holes are drilled through the laminates to provide interconnecting circuitry between the circuitry that is in each of the laminates. Because the laminate core is fiberglass-reinforced polymer resin, the drillhole wall must be copper plated to make it electrically conductive. Prior to copper plating, the drillhole wall must first be resin-etched, to clean and prepare it copper plating.

Preceding the resin-etch, the process typically uses a MLB-496 bath. MLB-496 is a strong alkaline solution which swells and exposes the loose fibers left in the hole after drilling, making them more prominent and removable.

Then the drillhole walls that were sensitized using MLB-496 are cleaned with MLB-497 solution. The MLB-497 bath is a very strong oxidizing alkaline solution containing potassium permanganate and sodium hypochlorite. The potassium permanganate and sodium hypochlorite etches the drillhole wall by dissolving the fiberglass resin. Following the MLB-497 operation, the board is cleaned and neutralized. The board is now ready to enter the electroless copper plating line.

A chemical replenisher is available, MLB-497C, containing the sodium hypochlorite component of the bath. Using the replenisher extends the bath service life to six months.

## 18. SPENT SULFURIC ACID REUSE

Spent sulfuric acid is sometimes reused onsite for fume scrubbing. The reuse occurs in the ammonia fume scrubber. When used as scrubbing solution, the spent acid pH of 1 rises to about 4 or 5 pH. Using the spent acid to scrub ammonia fumes results in less quantity of sodium hydroxide needed to neutralize

the spent acid to pH of 7, prior to discharging the spent acid to the municipal sewer.

The arrangement works well. The spent sulfuric acid reuse also conserves the use of virgin sulfuric acid, so that virgin sulfuric acid is not needed in the ammonia fume scrubber.

## 19. SHADOW PROCESS

The "Shadow" brand process is an innovation that can replace the electroless process that is used to deposit copper onto the drillhole walls. The Shadow process reduces the number of process steps and replaces the hazardous chemicals commonly used in the electroless process with nonhazardous chemicals.

### 19.1 Innovative Shadow Process

The Shadow process is a direct metallization system. The process uses carbon-graphite to bond the copper electroplate onto the polymer surface of the drillhole walls. This process has 4 chemical formulations, with 10 process steps. By comparison, conventional electroless plating uses 9 chemical formulations and 20 steps.

Hazardous waste constituents in the electroless process include chelated copper, formaldehyde, and trace cyanide. Additionally, the electroless line consumes large amounts of water for processing and rinsing. Hazardous waste management is costly and difficult with the electroless process. The Shadow process uses no toxic chemicals.

### 19.2 Shadow Process Applications

One circuit board manufacturer that was contacted, had successfully converted from their electroless copper process to the Shadow process in 1995. They reported quality

problems that included sporadic voids in hole coverage. This occurred primarily on thick boards in the 0.093" to 0.125" panels. Thinner laminates were successfully processed. The firm expects that the quality problems could be overcome with operational adjustments. As of December 1995, the firm felt that the overall performance of the Shadow process was satisfactory. The increased throughput and lower waste generation justifies the conversion.

Another board maker that was contacted, reports having considered the Shadow system over electroless copper plating, along with several other source reduction technologies. The firm has postponed their installation of the Shadow system. It is too costly for now, requiring a \$140,000 investment with a payback of eight years. Another board maker expressed lack of confidence in the Shadow process.

### 19.3 Shadow Process Limitations

The Shadow process is innovative and not widely proven in application. Some applications have had problems with its reliability. For that reason no recommendation should be made for installing this process. Yet the Shadow process is successful in some operations. The process offers hope for dramatic cost reduction and waste reduction in the manufacture of printed circuit boards. Technologically aggressive companies could find the Shadow process worthwhile to investigate as a source reduction opportunity.

## 20. ELECTROLESS RINSEWATER RECOVERY

One circuit board manufacturer achieves wastewater source reduction with the Kinetico water system. The system uses ion exchange and carbon filters to purify spent rinsewater from the electroless plating line. The system recycles purified water back to the process in a closed loop. The system had recycled over 250,000 gallons of water during the first six weeks of operation.

The ion exchange process uses a solid phase resin, with beads that ionically pull copper from solution and onto the beads. The carbon filters remove organic impurities and turbidity.

The recycled water can be used for rinsewaters, and also for makeup water for bath preparation. The system is not used for recycling a spent process bath, because the metal concentrations in the bath would overload the ion exchange units.

## 21. CONTINUOUS FEED AND BLEED

Many process baths are used in printed circuit board manufacture. Uses include plating, etching, stripping, and rinsing. During its operation, a process bath solution gradually becomes spent and must be replaced or replenished. The solution becomes spent because it accumulates unwanted materials such as copper ions etched from the copper-clad laminate, film or solder mask stripped from the laminate surface, or other impurities. Another cause is the depletion of the active chemical ingredients in the bath solution. Another cause is rinsewater carryover into the bath that dilutes the bath solution, which dilutes the effectiveness of the bath chemicals. The accumulation, depletion, and dilution in the bath compels periodic replacement of the bath solution to maintain process performance.

A source reduction alternative to periodic, batchwise replacement of the bath solution is the continuous feed and bleed replacement. Like batchwise replacement, feed and bleed removes accumulated materials and maintains chemical ingredients of the bath solution within process parameters.

### 21.1 Feed and Bleed Operation

The feed and bleed system continuously feeds fresh makeup solution to the bath, while continuously bleeding an equal flow of solution from the bath as spent solution. The flow rate of feed and bleed is controlled by monitoring the quality of the bath contents, and so that fresh solution is added to keep the bath contents within specified process parameter limits. The system operates at steady state, so that the feed adds ingredients at the rate which they are being depleted by the bath process, while the bleed depletes the unwanted materials at the rate they accumulate.

### 21.2 Feed and Bleed Advantages

The feed and bleed bath has advantages over the batch bath. Instead of changing the bath nightly in a batchwise replacement with fresh solution, feed and bleed allows the bath to be changed bi-weekly or beyond. In that way, the bath is changed only when a system purge is needed to clean out the tank surfaces, the tank bottom sludges, and other contamination. The longer bath life minimizes process downtime and saves money. A bath change is costly because it means process downtime to clean out the system, prepare the new bath solution, and heat up the bath, with all this occurring while the operating crew stands by idle.

### 21.3 Quality Control and Source Reduction

Another advantage of a continuous feed and bleed bath is that it maintains steady state process operating conditions; instead of the swings in concentrations, impurities, and dilution that occur in a batch bath operation. The steady state operation provides consistent conditions for product quality control.

Steady state operation also allows optimum process operation. Optimum operation often minimizes the feed and bleed flow rate. The minimum flow rate is that which maintains the bath at or near the highest impurity concentration at which the bath can properly operate, while still maintaining effectiveness and product quality.

### 21.4 Copper Etchant

One operation minimizes the feed and bleed flow rate for copper etchant solution. Minimized flow rate means savings in operating

costs, as well as source reduction from minimized waste generation.

Flow rate is minimized by maintaining copper loading for the solution, as close as possible to the upper load capacity of the solution, without causing operating problems and product quality impairment. The copper content of the solution is maintained at 90% of the copper load capacity of the solution. This leaves a residual 10% copper loading capacity to maintain solution effectiveness. Another benefit of maintaining the copper loading near the upper limit for the solution, is improved recovery of copper from the spent solution when the bath is changed out.

## 21.5 Photoresist Stripper Bath

One operation uses feed and bleed to maintain the photoresist stripper bath. The bath is used to remove the polymer photoresist film from the surface of the circuit board. The photoresist film is removed as polymer particles, which become suspended in the bath solution. To remove the polymer particles from the bath, the bath solution is continually withdrawn, circulated through a filter, and returned to the bath.

The fine particles and other impurities that pass through the filter, can be removed to an acceptably low level. The bleed is discharged from the process as spent stripper solution. The filter extends the bath life by removing particles from the bath solution. Fresh make-up solution is added as feed, to replace the spent solution discharge.

The filter, along with the feed and bleed, improves the process operation and provides source reduction. The continuous feed and bleed keeps a consistent bath quality, so the process operating parameters can be more closely adjusted to optimum conditions. The continuous spent solution discharge allows the bath to operate on a longer, more consistent time period. All shifts can operate with the same bath composition, instead of the first

shift with fresh bath having rapid stripping, and the late shift with the near-spent bath being very slow to strip. The extended bath life saves chemical costs, reduces process downtime, and reduces waste generation.

## 21.6 Electroless Copper and Sodium Borohydrate

Feed and bleed can be used to maintain the electroless copper bath. Raw materials are pumped into the bath to maintain bath parameters. The displaced solution flows out as spent solution. At one operation, the bath is never changed, except for unusual conditions.

At another installation, the spent electroless bath solution goes into a drum. The copper is chemically precipitated as metallic copper, using sodium borohydrate (Section 26.7).

Alternatively, onsite treatment can use an electrowinning system to recover copper from the spent solutions.

## 21.7 Rinsewater Tank

Rinsewater becomes spent due to carryover of a chemical bath solution into the rinsewater tank, similar to a chemical bath solution becoming spent due to carryover of rinsewater into the chemical bath. Similarly, continuous feed and bleed can be applied to the rinsewater tank, to remove spent rinsewater. Feed and bleed can minimize chemical accumulation in the rinsewater.

## 21.8 Feed and Bleed Recirculation and Recovery

Some feed and bleed systems recover the bleedstream, and recirculate it back into the bath, as part of the feed. Rinsewater recirculation and recovery is a common example.

Recirculation can also be used for chemical baths including etchant, stripper, or plating.

In the recirculation loop, unwanted materials in the bleed, like plastic particles, copper, or carryover, are removed by the recovery unit. If needed, fresh chemical ingredients are added to maintain specifications.

The recirculation loop often needs a secondary bleed stream. The secondary bleed stream is needed to bleed off impurities which are not removed by the recovery unit, like trace impurities that enter with the fresh makeup chemicals. Without the secondary bleed, the trace impurities would gradually accumulate in the recirculation loop to a level that could impair bath performance. Usually such a secondary bleed undergoes treatment as a hazardous waste, and is then discharged to a POTW. The water leaving with the secondary bleed is replaced by adding fresh water with the makeup chemicals, as needed.

An alternative to the secondary bleed is periodic changing of the bath or rinse tank as wastewater, to purge out the accumulated trace impurities. However, periodic changing usually means non-steady, cycling operating parameters; process downtime; and waste generation; all of which often increase operating costs as discussed above.

## **21.9 Spray Stream Recirculation with Feed And Bleed**

Some operations have process steps that use a spray to apply an etchant or rinse to the

laminates, instead of immersing the laminates into an etchant bath or rinse tank. The spray stream can include a recirculation loop with a recovery unit, so that the spray stream is reused. The loop can include a feed and bleed to help maintain the spray stream at suitable concentrations. The recovery unit would remove etched copper or other unwanted materials. A continuous feed stream enables the addition of fresh chemicals into the recovered etchant, as needed to maintain bath effectiveness. A bleed stream would remove an equal volume from the loop, to remove accumulated trace impurities.

## **21.10 Rinsewater Spray Stream**

Often the rinse step is a spray system. The rinsewater spray is often applied countercurrently to the movement of the laminates being processed through the operation, often as a vertical cascade rinse. In such applications, the spent rinsewater at the bottom of the cascade has a high contaminant level, and the spent rinsewater is continually discharged from the process as wastewater. Often a spray rinse can save water compared to a rinse tank.

Instead of discharging the spent rinse as wastewater, the spent rinsewater can be treated in an ion exchange unit to remove metals, filtered to remove other contaminants, and recycled to the process as part of the fresh water supply.

More water savings and reduction of waste generation can be provided by including a feed and bleed in the spray rinsewater system. Similar to spent etchant, the feed and bleed can minimize spent rinse waste generation.

## 22. MATERIAL SUBSTITUTION

Several material substitution chemicals are discussed below. Some show promise for source reduction in circuit board manufacture, yet have not been fully investigated. Some substitution chemicals were found unsuitable for operations involved.

### 22.1 Finishing Solution for Etchant Residues

High speed finishing solution is used to neutralize etchant residues and remove stannic tin residues. The process leaves a clean solder surface. Finishing solutions free of thiourea have not been found satisfactory to date. The solution still contains hydrochloric acid. When the hydrochloric acid becomes spent, it is hazardous waste due to corrosivity.

## 23. PROCESS MODIFICATION

Process modification involves production process changes. These can include equipment modifications, changes in production methods or techniques, changes in process operating conditions, process automation; or recycling, if hard-plumbed within the process.

### 23.1 Plastic Plating Racks

A nitric acid stripping bath is sometimes used to remove copper deposits from electroplating racks and tanks. The copper deposits accumulate on stainless steel racks and tanks during plating service.

One operation installed plastic plating racks to replace its stainless steel racks. Because copper will not readily plate onto the plastic, the substitution eliminates the need for the nitric acid stripping bath. By eliminating the stripping bath, the substitution also reduces the need

### 22.2 Plating Tape Residue Cleaning

Plating tape is used to mask areas prior to gold plating, to avoid plating gold onto surfaces where it is not wanted. A substitute cleaner, EC-1, can be used to replace 1,1,1 trichloroethane to remove tape residues following the nickel-gold plating steps. EC-1 is non-toxic, biodegradable, and can be discharged to the POTW.

Alternatively, the tape can be replaced by a non-residue tape. This eliminates the need to use either of the cleaners, 1,1,1 trichloroethane or EC-1. The product name of the non-residue tape is 9190, and is made by Ideal.

to manifest the spent stripping solution as hazardous waste for offsite management.

The operation had invested \$8748 into the substitution, including laboratory tests, equipment purchase and installation, and operator training. The installation resulted in a savings of \$31,000/year, mostly from reduced waste management costs. The investment provided a three month payback.

### 23.2 Baking Procedure

One operation uses a lubricant release agent (Sprayway) on the baking plates used to form thermoset plastic laminated boards. The Sprayway precludes the use of chlorofluorocarbon (CFC) solvents to clean residual thermoset plastic (prepreg contact residue) from the sheet-forming baking plates. The release agent contains non-toxic, organic-based, biodegradable ingredients.

## 24. PROCESS SUBSTITUTION

Process substitution includes replacing an existing process with a different process to produce the same product, but generating less waste toxicity or quantity. Process substitution might include input changes in raw material or feedstock.

### 24.1 Additive Process for Printed Circuit Board Manufacture

Some operations are conducting research to change from the current subtractive process to an additive process, to form the conductive printed circuits. An image of the desired circuit pattern is printed onto the etch resist film in the subtractive process. The etch resist film covers the entire copper-clad surface of the laminate. The film is then developed, followed by the non-image areas of etch resist film being stripped off. This exposes the copper surface areas that are not to be part of the circuit. The exposed copper is then etched away, leaving the desired copper circuit on the laminate surface. Therefore with the subtractive process, most of the copper surface that was originally on the laminate is etched off.

Conversely, an additive process would print or screen the circuitry image directly onto the

polymer laminate base. The copper would then be deposited onto the printed image using a process similar to an electroless deposit. Copper electroplating would follow. The additive process negates the need for extensive etching of copper with its attendant costs and waste generation.

A couple of additive processes are in operation, and continuing research is underway at other operations. However the additive process technology has not yet been proven for extensive use in all applications. Technical trade journals and conferences are possible sources for obtaining the most recent information regarding this process.

### 24.2 Aluminum Oxide Abrasive Cleaning

Aluminum oxide abrasive cleaning can eliminate the chemical cleaning process and its generated waste. The abrasive cleaner eliminates six chemical process steps, including alkaline cleaning, hydrochloric acid cleaning, microetching, and the final rinse step. Under routine service, the abrasive material lasts four months, at which time it is changed. One company made a capital investment of \$120,000 with only a 2 year payback.

## 25. PRODUCT SUBSTITUTION

Product substitution involves producing a different product that meets the same purpose as the product that was replaced, but the replacement would not possess the same level of environmental risks during production, use,

or disposal as the previous product. This report did not include a review of product substitution measures as alternatives to printed circuit boards.

## 26. HEAVY METALS WASTE TREATMENT

Several vendor-supplied waste treatment systems can reduce the generation of hazardous waste sludge in the precipitation of metals from wastewater. Trade journals and expositions are sources of vendors who can provide performance information on treatment chemicals and equipment. Often the chemical formulations are proprietary, and are identified by their trade names.

### 26.1 Electroplating Wastewater

Title 40, Code of Federal Regulations, lists wastewater treatment sludges from electroplating operations as F006 hazardous waste. Proper selection of precipitation chemicals for treating electroplating wastewaters, can provide source reduction opportunities.

Several operations have improved the precipitation and flocculation of metals from electroplating wastewaters. Results include reduced volume and improved recyclability of the treatment residue sludge.

### 26.2 Process Substitution and Waste Treatment

One operation had very good results by using process substitution. Like the former chemistry, the new process chemistry included removal of the heavy metals. The new chemistry, however, greatly reduced the use of sulfuric acid and bleach. Formerly, the wastewater treatment system generated much sludge. It had to be cleaned weekly, including the waste treatment system and the membrane filtration system. Now, the treatment system uses new process chemistry which extended the time between weekly cleanings to 6 to 8 weeks. The change to the new chemistry has had little impact on amount of sludge generated; the sludge generation remained the same.

### 26.3 Heavy Metals Precipitation by Ferrous Sulfate

Heavy metals precipitation using ferrous sulfate is a long-standing process. This process required a large proportion of ferrous sulfate to be added for adequate metals precipitation, resulting in a large volume of generated sludge.

Less sludge is generated by using other chemicals instead of ferrous sulfate. Successful examples are discussed below. It is important to perform a cost/benefit analysis to determine the possible savings from this substitution.

### 26.4 Heavy Metals Precipitation with Dithiocarbamate Acid

Replacing ferrous sulfate with precipitation using dithiocarbamate acid (DTC) has reduced sludge volume and increased the copper sludge concentration. DTC breaks the chelator effect, resulting in less sludge generation. The higher cost of DTC can be offset by the savings in the sludge transportation and waste management costs.

At one operation, the reduced sludge volume provided by DTC precipitation was an essential part of operational changes. This is because increased heavy metals precipitation was needed to meet more stringent POTW discharge limits, while also accommodating a 50% increase in production.

The sludge precipitated by DTC is managed as a hazardous waste. However the effect of dithiocarbamate on mobility of the toxic sludge components would need evaluation, if the sludge were sent to land disposal.

## **26.5 Heavy Metals Precipitation with Calcium Polysulfide**

Following two years of operating with a DTC based precipitation system, one operation switched to a calcium polysulfide (CaPS) precipitation system. This generates even less sludge than the DTC system, as well as consuming a lower volume of chemicals overall. After about fifteen months on the CaPS system, the weight of sludge generated is 40% less than that generated by the DTC system. This source reduction occurred despite a slight increase in square footage of circuit boards manufactured.

The sludges generated by CaPS and DTC are hazardous waste, characterized as F006 under the federal guidelines. As such, they are subject to the Land Disposal Restrictions (LDR) for hazardous wastes, and are not suitable for land disposal. However, the Institute for Interconnecting and Packaging Electronic Circuits (IPC), a circuit board industry trade association, is working with the USEPA Project XL to exempt this sludge from classification as hazardous waste. It would then be classified as hazardous solely on its ability to meet the Extraction Procedure (EP) toxicity test. This is significant because CaPS chemically bonds to heavy metals more tightly than does DTC; thus CaPS sludge will have a higher likelihood of meeting the EP toxicity test for the purposes of LDR classification.

There are some reasons why this exemption may not translate into immediate benefits for the printed circuit board manufacturing in California. First, California's waste extraction test (WET) is used in place of the USEPA EP toxicity test, and is similar but not identical to the EP toxicity test. Therefore meeting the EP toxicity test does not guarantee meeting the WET. Secondly, California regulates copper, while the USEPA normally does not. The generator intends to closely monitor this proposed exemption in pursuing source reduction efforts.

## **26.6 Heavy Metals Precipitation with Sodium Hydroxide**

One operation used sodium hydroxide (NaOH) to precipitate metals from spent rinsewater and spent process baths. However for wastewater containing chelator, NaOH will not pull metals from the chelator. The result is that the metals would pass through the NaOH precipitation step with the chelator. This problem can be solved by the use of DTC to precipitate the heavy metals, mostly copper and some lead and nickel, from the chelator.

## **26.7 Copper Precipitation with Sodium Borohydrate**

At one system, a feed and bleed system discharges spent electroless plating solution from the electroless copper bath (Section 21.6). The spent bath solution goes into a drum. The copper is chemically precipitated as metallic copper, using sodium borohydrate. The borohydrate also consumes accumulated formaldehyde. Following precipitation of the copper from solution, there is no detectable copper and no formaldehyde remaining in the solution. The treated effluent solution contains sodium salts and some sodium hydroxide, and is managed as treatment residue which can be discharged to the POTW. The precipitated copper is shipped to an offsite recycling facility, with other metal-laden wastes. If this precipitation is done onsite, it might require an onsite treatment permit.

## **26.8 ElectroStrip Recovery Systems**

RC Chemical Ultima ElectroStrip is a possible substitution for onsite waste management of spent process solutions containing copper. This process deposits the etched copper onto a cathode, for recovery as nonhazardous metallic copper tank bottoms sludge.

## 27. WATER CONSERVATION

Water conservation is becoming increasingly important as water and energy resources become more limited and costly. The cost of water and sewer services, and the treatment cost of spent rinsewater, are major cost impacts.

New equipment often includes cascade rinses, counterflow rinsing, and other water saving technology. In one operation, new systems which use about 6 gallons/minute replaced 6 year old systems which used much more water at about 18 gallons/minute. This is a major savings over an 18 hour daily operation. Savings are \$35,000 year.

## 28. ADMINISTRATIVE IMPROVEMENTS

Publications available from regulatory agencies and environmental outreach programs can provide source reduction ideas for administrative procedures. Industry newsletters are another source of ideas and information. Vendor literature and equipment bid proposals often include operating cost information that can be a source of information for administrative costs, for process equipment procured from the vendor or being considered for procurement.

### 28.1 Cost Control

Improved cost accounting can be highly effective for reducing waste generation and improving process economics. The process engineer or staff scientist should work with the accounting department to identify and account for all of the costs and benefits of source reduction. The company should establish a cost center for the company's waste management and source reduction program, as separate from its other environmental and industrial health and safety programs.

Manufacturing costs should include water supply costs and waste management costs.

Costs and waste generation quantities should be unitized according to the number of panels produced or other units of production. Cost and waste generation then should be assigned to the specific processes producing those unit costs. This information will enable specific source reduction activities to be compared on the actual cost savings provided. This would normalize cost information based on production. The cost information can be compared from budget year to year. Through careful cost accounting, one operation found that waste management costs were among its top five operating expenses.

### 28.2 Inventory Control

Inventory control can be a simple and valuable source reduction opportunity. Chemical supplies can be purchased on a "just-in-time" basis. This can minimize the inventory of supplies kept onsite. The result is savings in inventory overhead; and less waste generation from obsolete, outdated, and surplus chemical supplies. Vendor recommendations can help establish the timing of delivery. The generator can choose from available vendors to get improved service and reduced costs.

## **29. CLOSING COMMENTS**

Information provided in this document is limited to that which the source chose to release. The reader is encouraged to pursue readily available information sources for investigating source reduction opportunities. Good sources are available for comprehensive, state-of-the-art technical knowledge in source reduction and recycling for printed circuit board manufacture.

### **29.1 Information Sources**

Detailed technical information can be obtained from vendors, process chemicals and equipment suppliers, equipment expositions, conferences, industry association newsletters, and trade journals. Such professional information sources can help the circuit board manufacturer select economical and effective

substitute chemicals and process systems that are compatible with its processes, products, and customer needs.

### **29.2 Shared Information**

Professional acquaintances in the industry are often willing to share their environmental technology with plant visits and other information. Such information sharing helps the industry to minimize its overall environmental impact. Shared knowledge of advancing technology can provide the generator and the industry with cost-effective source reduction alternatives that can lead to improved operations, less waste generation, and more cost-efficient operations.

## PUBLICATIONS

The following publications are available from the Department of Toxic Substances Control. The publications can assist the printed circuit board manufacturer in organizing an active source reduction and pollution prevention program. To obtain pollution prevention publications from the Department of Toxic Substances Control, please call (916) 322-3670.

Hazardous Waste Minimization Checklist and Assessment Manual for the Electronics Industry (1996, 76 pp.), Document #405

Assessment of the Semiconductor Industry Source Reduction Planning Efforts (1994, 85pp.), Document #530

Waste Minimization Fact Sheet on Printed Circuit Board Manufacturers (1992, 4 pp.), Document #209

Publications are also available from the U. S. Environmental Protection Agency, regional and local governmental authorities, and industry organizations. New publications are continually being released by these and other sources, which can be a valuable source of technical and regulatory information.



