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ENVIRONMENTAL RESEARCH BRIEF

Waste Minimization Assessment for Multilayered Printed Circuit Board Manufacturing

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Abstract

The U.S. Environmental Protection Agency (EPA) has funded a pilot project to assist small- and medium- size manufacturers who want to minimize their generation of hazardous waste but lack the expertise to do so. Waste Minimization Assessment Centers (WMACs) were established at selected universities and procedures were adapted from the EPA *Waste Minimization Opportunity Assessment Manual* (EPA/625/7-88/003, July 1988). The WMAC team at Colorado State University inspected a plant manufacturing multilayered circuit boards. This complex operation has seven key elements: preparing individual layers of boards; transferring circuit patterns to these layers and forming copper oxide castings; bonding to form multiple layers; applying copper (electroless plating) to ensure electrical contact; applying photoresist to define the area on which copper circuits are to be plated; applying copper electrolytically to establish circuit patterns on outer board surfaces followed by tin or tin/lead plating to protect the circuits; and applying solder and final cleanup after selectively removing protective tin layers. All these elements of the manufacturing process generate hazardous waste, e.g., electrolytic application of copper generates sulfuric acid; propylene glycol methyl ether; copper-laden deionized water and rinse water; ethoxylated octylphenol; copper-free drag-out-laden water; and copper sulfate. The plant had already instituted waste minimization techniques; the team's report, detailing findings and recommendations, indicated that additional reductions and savings, although not as great, were still possible. The greatest reduction would come from separating liquid wastes into four streams containing differing amounts of waste. Copper-containing streams could be further treated and reused in process rinses and baths. Spent process solutions could be stored for recycling and reclaiming.

This Research Brief was developed by the principal investigators and EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of an ongoing research project that is fully documented in a separate report of the same title available from the authors.

Introduction

The amount of hazardous waste generated by industrial plants has become an increasingly costly problem for manufacturers and an additional stress on the environment. One solution to the problem of hazardous waste is to reduce or eliminate the waste at its source.

University City Science Center (Philadelphia, PA) has begun a pilot project to assist small- and medium- size manufacturers who want to minimize their formation of hazardous waste but lack the inhouse expertise to do so. Under agreement with EPA's Risk Reduction Engineering Laboratory, the Science Center has established three WMACs. This assessment was done by engineering faculty and students at Colorado State University's (Fort Collins) WMAC. The assessment teams have considerable direct experience with process operations in manufacturing plants and also have the knowledge and skills needed to minimize hazardous waste generation.

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The waste minimization assessments are done for small- and medium-size manufacturers at no out-of-pocket cost to the client. To qualify for the assessment, each client must fall within Standard Industrial Classification Code 20-39, have gross annual sales not exceeding $50 million, employ no more than 500 persons, and lack inhouse expertise in waste minimization.

The potential benefits of the pilot project include minimization of the amount of waste generated by manufacturers, reduced waste treatment and disposal costs for participating plants, valuable experience for graduate and undergraduate students who participate in the program, and a cleaner environment without more regulations and higher costs for manufacturers.

Methodology of Assessments

The waste minimization assessments require several site visits to each client served. In general, the WMACs follow the procedures outlined in the EPA *Waste Minimization Opportunity Assessment Manual* (EPA/625/7-88/003, July 1988). The WMAC staff locates the sources of hazardous waste in the plant and identifies the current disposal or treatment methods and their associated costs. They then identify and analyze a variety of ways to reduce or eliminate the waste. Specific measures to achieve that goal are recommended and the essential supporting technological and economic information is developed. Finally, a confidential report that details the WMAC's findings and recommendations (including cost savings, implementation costs, and payback times) is prepared for each client.

Plant Background

This plant manufactures multilayered circuit boards from thin, flat sheets of combined epoxy resin and fiber glass upon which thin layers of copper have been laminated on both sides. After the circuit has been developed on each sheet, the multilayered board is produced by stocking the sheets through a bonding process using heat and pressure. Then the external circuits must also be created.

As in all circuit board manufacture, the processes in this plant are complex, but certain key elements must be described to make the results of a WMAC assessment understandable when they are being summarized. These are the key elements in this plant's operations:

- preparing boards of individual layers, including the drilling of tooling holes,
- transferring circuit patterns to layers and forming copper oxide castings,
- bonding to form multiple layers,
- applying copper by electroless plating to provide a continuous electrical path covering the entire external surface and drilled holes,
- applying photoresist techniques to define the area on which copper circuits are to be electrolytically plated,
- applying copper electrolytically to establish external circuit patterns of multiple layers, followed by tin or tin/lead plating to protect the circuits when extraneous copper's removed, and
- applying solder and final cleanup after selectively removing protective tin layers.

This plant had already established several waste minimization techniques:

- using dry-film photoresist to eliminate the chlorinated solvents associated with silk-screen photoresist;
- substituting tin for tin/lead solder on a majority of the circuit boards;
- spray-rinsing circuit boards laden with copper before bath-rinsing to differentiate rinses according to copper concentration;
- treating effluents before discharge to the sewers by:
  - adjusting pH of those free of copper, and
  - ion-exchanging and electrowinning copper-containing solutions;
- air-agitating the plating tanks to improve mixing and the rinse tanks to reduce the amount of rinse water needed;
- deionizing water to eliminate calcium and magnesium sludge formation in a variety of tanks;
- mechanically scrubbing the boards and then air-drying them after plating and stripping to avoid using solvent;
- recirculating and filtering rinse water from the scrubbing operations;
- plastic-coating racks used in the plating operations to reduce the amount of hazardous rack-stripping solution needed; and
- recycling much metallic waste, especially copper.

The scope and variety of these measures presented a challenge to the WMAC's efforts to reduce still further the emission of hazardous waste. All quantities of waste stated are to be considered in proportion to the operational level of about 1000 printed circuit boards/wk.

Manufacturing Operations

Operating for a total of 5,148 hr/yr, this plant makes about 1000 printed circuit boards/wk, many of which are prototypes designed according to a customer's performance specifications. One of the plant's principal strengths is its capability to produce multilayered circuit boards, which lead to larger and more powerful circuits compressed into compact spacing. Figure 1 presents a schematic arrangement of the manufacturing operations.

Circuit patterns, after being transferred to each layer, are developed by etching unprotected copper from these layers. Individual layers, each with its specific circuit, are etched after oxidation to ensure good bonding among them. A heated hydraulic press supplies the compression. Electroless copper plating ensures electrical contact whenever it is designed, and electrolytic copper plating establishes circuit patterns on outer board surfaces according to a prior design and after photoresist application and development. Tin plating is applied to preserve the desired external circuit when the exposed photoresist is stripped away. Then the tin is removed before final application of a solder mask and solder, and finally the last rinsing and electrical testing are done.

Hazardous Waste Generation

The variety, interdependence, and complexity of the manufacturing operations in this printed circuit board plant lead to numerous sources of hazardous waste, which vary widely in quantity and in quality. Table 1 summarizes the principal sources, their amounts, the management method applied, and the associated costs.

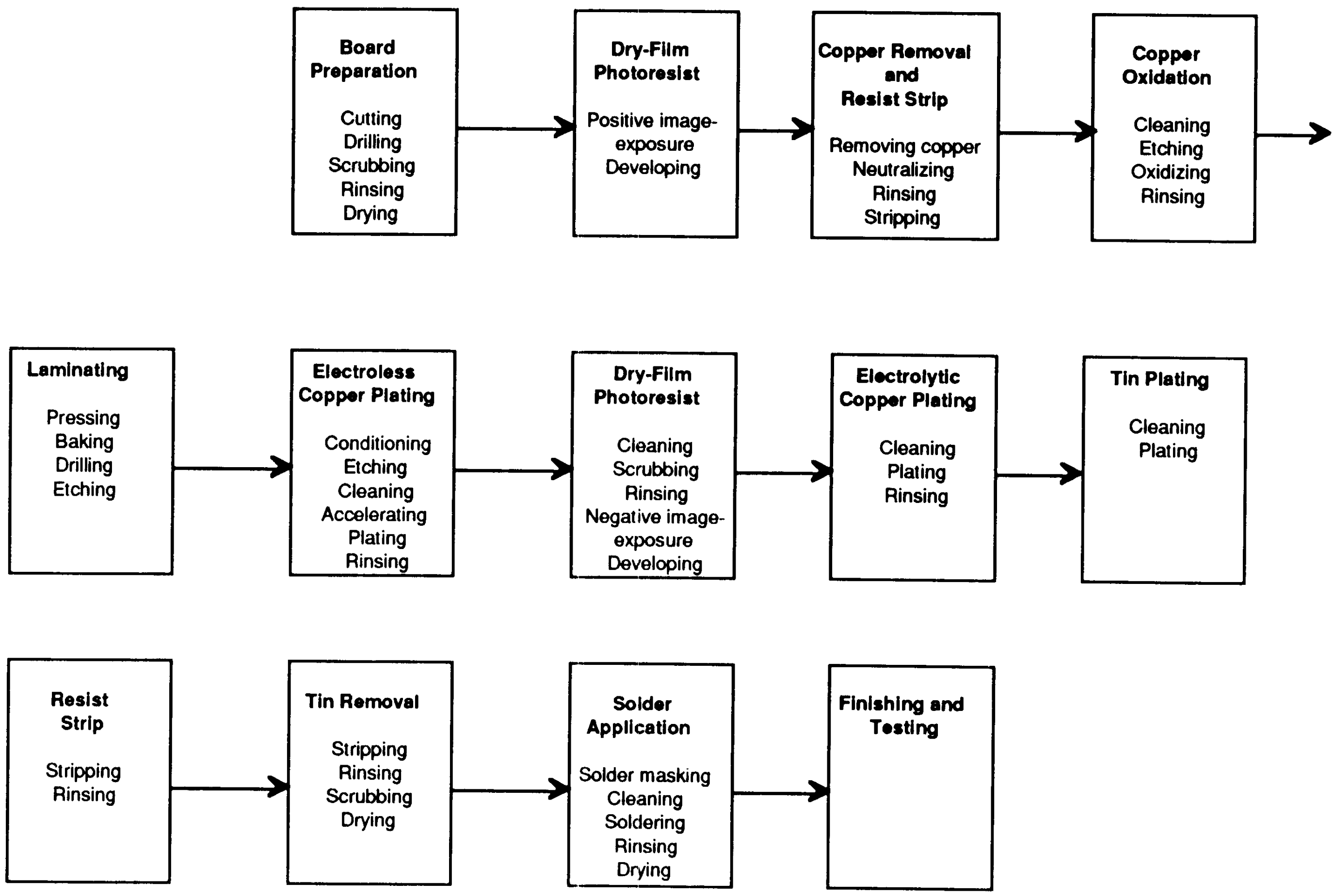

Figure 1. Sequence of Manufacturing Operations

The principal volumes of liquid hazardous waste are attributable to rinses and drag-outs. The highest cost, however, is associated with recycling 5085 gal/yr of ammoniacal copper chloride solution ($19,800/yr). Many liquid waste streams incur little or none of these costs because they involve only pH adjustment before disposal.

Summary of Recommended Waste Minimization

At this plant, total hazardous waste management costs, which had already been brought down to $46,880/yr by 10 separate measures, can be further reduced by $14,080/yr (30%) on the basis of 6 waste minimization opportunities (WMOs) identified and recommended by the WMAC team.

The greatest cost reduction would result from a proposal to segregate four liquid wastes and, by further cleaning of some, allow them to be reused and eventually sewered. Five of the WMOs recommended have simple paybacks of less than 2 yr.

Cost savings to be achieved with each of the six WMOs are summarized in Table 2, together with the waste reductions and associated costs. All savings are calculated for each WMO independently so that each can be evaluated on its own merits. Actual experience, however, will probably reveal some interdependence and lead to new cost-saving data. All data in this summary ought to be considered in relation to the operational levels stated for this plant.

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Table 1. Summary of Current Waste Generation.

Waste Stream	Hazardous Waste Generated	Annual Quantity Generated gal	Present Management Method	Annual Waste Management Costs: Treatment	Disposal	Recycling
Hazardous Liquid Waste						
A. Etch & Resist Strip:						
Copper etch	Copper ammonia chloride	5,085	Reclaimed and regenerated off-site			$19,800
Neutralizer	10% Hydrochloric acid	1,040	pH adjusted/ion exchange/disposed	$1	$0	
DI rinse	Rinse water laden with drag-out	693	pH adjusted and disposed	1	0	
Resist strip	Hydroxides, alkanolamines	2,080	Stored on-site, waiting disposal			
B. Oxide Line:						
Acid cleaner	Sulfuric acid and ethoxylated octylphenol	2,080	pH adjusted/ion exchange/disposed	2	0	
Etch	Sodium hydrogen sulfate and copper sulfate	505	Reclaimed and regenerated off-site			1,125
5% Sulfuric acid	5% Sulfuric acid	2,080	pH adjusted/ion exchange/disposed	2	0	
10% Sodium hydroxide	10% Sodium hydroxide	1,040	pH adjusted/ion exchange/disposed	1	0	
Oxide bath	Sodium hydroxide and sodium chlorite	1,043	Reclaimed once; balance waiting disposal			770
Hot deionized rinse	Rinse water with drag-out	9,733	pH adjusted and disposed	7	2	
Tap-water spray rinse	Copper-laden rinse water	186,110	pH adjusted/ion exchange/disposed	141	37	
Tap-water spray rinse	Copper-free, drag-out laden water	849,026	pH adjusted and disposed	643	170	
Tap-water bath rinses	Rinse water laden with drag-out	1,485,797	pH adjusted and disposed	1,125	297	
C. Electroless Copper Line:						
Conditioner	Ethylene glycol/sodium hydroxide	204	Stored on-site, waiting disposal			
Potassium permanganate	Potassium permanganate, sodium hydroxide and sodium hypochlorite	40	pH adjusted and disposed	0	0	
Glass etch	Dihydrazine sulfate and fluoboric acid	348	pH adjusted and disposed	0	0	
PC cleaner	10% Phosphoric acid	2,080	pH adjusted/ion exchange/disposed	2	0	
Copper etch	Sulfuric acid and copper sulfate	1,250	Reclaimed and regenerated off-site			2,588
Catalyst prep	10% Sodium bisulfate	580	Reclaimed once; balance waiting disposal			220
Catalyst	Muriatic acid, stannous and palladium chlorides, and sodium bisulfate	40	Sent to metal reclaimer for credit			8
Accelerator	10% Hydrofluoric acid	480	Stored on-site, waiting disposal			
Electroless copper plating	Sodium hydroxide, copper sulfate, and formaldehyde	80	Copper precipitated from spent soln; liquid is pH adjusted and disposed	0	0	440
D. Electrolytic Copper Line:						
5% Sulfuric acid	5% Sulfuric acid	2,080	pH adjusted/ion exchange/disposed	$2	$0	
Anti-oxidant	Propylene glycol methyl ether	480	pH adjusted/ion exchange/disposed	0	0	
Scrubber	Copper-laden deionized water	960	pH adjusted and disposed	1	0	
Acid cleaner	Sulfuric acid and ethoxylated octylphenol	2,080	pH adjusted/ion exchange/disposed	2	0	
Tap-water spray rinse	Copper-laden rinse water	186,110	pH adjusted/ion exchange/disposed	141	37	
Tap-water spray rinse	Copper-free, drag-out-laden water	849,026	pH adjusted and disposed	643	170	
Tap-water bath rinses	Rinse water with drag-out	1,273,540	pH adjusted and disposed	964	255	
Electrolytic copper plating	Copper sulfate, sulfuric acid	400	Sent once to metal reclaimer			$ 920
E. Tin Plating:						
5% Sulfuric acid	5% Sulfuric acid	1,040	pH adjusted/ion exchange/disposed	1	0	
Electrolytic tin plating	Tin sulfate, sulfuric acid, and methacrylic acid	240	pH adjusted and disposed	0	0	

Table 1. Continued

Waste Stream	Hazardous Waste Generated	Annual Quantity Generated gal	Present Management Method	Annual Waste Management Costs Treatment	Disposal	Recycling
Hazardous Liquid Waste						
F. Tin/Lead Plating:						
10% fluoboric acid	10% Fluoboric acid	480	Stored on-site, waiting disposal			
Tin/lead plating	Fluoboric acid, boric acid, tin, and lead fluoborates	188	Sent to metal reclaimer for credit			76
G. Resist Strip:						
Resist strip	Hydroxides, alkanolamines	2,080	Stored on-site, waiting disposal			
H. Tin Strip:						
Tin strip	Acid fluoride and peroxide	693	Sent to metal reclaimer for credit			280
I. Tin/Lead Solder Reflow:						
Solder brightener	Fluoboric acid and thiourea	180	Sent to metal reclaimer for credit			$ 73
Solder flux	Glycol/surfactant/organic acid	470	pH adjusted and disposed	$ 0	$ 0	
Tap-water cooling bath	Water laden with glycerin	4,695	pH adjusted and disposed	4	1	
Tap-water spray rinse	Water laden with drag-out	849,026	pH adjusted and disposed	643	170	
J. Silk Screening:						
Silk screening	Liquid epoxy resin	52	Landfill			
Developer	Sodium perborate	208	Landfill			
K. Other Processes:						
Photo developer	Potassium carbonate-laden deionized water	31,300	pH adjusted and disposed	24	6	
Pumice scrub	Metallic copper in oxalic acid	3,130	pH adjusted/ion exchange/disposed	2	1	
Pumice deionized rinse	Pumice/oxalic acid-laden deionized water	650	pH adjusted/ion exchange/disposed	0	0	
Final deionized spray	Particulate-laden deionized water	849,026	pH adjusted and disposed	643	170	
TOTAL		6,609,548		$4,995	$1,316	$26,300

Waste Stream	Hazardous Waste Generated	Annual Quantity Generated lb	Present Management Method	Annual Waste Management Costs Treatment	Disposal	Recycling
Hazardous Solid Waste						
A. Shearing:	Copper/epoxy laminate dropoffs	2,400	Landfill		0	
B. Drilling and Routing:	Copper, aluminum, and gold dust	675	Landfill		0	
C. Filters:						
Scrubber	Copper-laden filter	144	Landfill		0	
Electrolytic copper	Copper-laden filter	312	Landfill		0	
Electrolytic tin	Tin-laden filter	104	Landfill		0	
Tin/lead plating	Tin/lead-laden filter	52	Landfill		0	
TOTAL		3,687			0	

Table 2. Summary of Recommended Waste Minimization Opportunities

Present Practice	Proposed Action	Waste Reduction and Associated Savings
Several effluents and process bath rinses are treated and discharged to sewers.	Segregate liquid wastes into four streams: (1) those containing large amounts of copper, (2) those currently adjusted in pH and sewered, (3) those containing small amounts of copper and organics, and (4) spent process solutions stored for recycle and reclaim. These steps are mostly modifications of present practices, not totally new operations. Further treat (1) and treat (3) by carbon adsorption and ion exchange. Reuse much of the waste in process rinses and baths. Savings will result from lower water and sewer costs but, at present, their combined cost is only $3.13/1000 gal.	Waste reduction = 2,615,300 gal/yr Cost reduction = $7,230/yr Implementation cost = $13,000 Simple payback = 1.1 yr
Some current water flow rates for rinsing appear to be excessive, according to observations of the WMAC team.	Install flow reducers on process rinses and determine optimum flow rates on: • three oxide line rinses • three electrolytic copper rinses • solder reflow rinse	Waste reduction = 851,900 gal/yr Cost reduction = $2,360/yr Implementation cost = $250 Simple payback = 2 mo
Spent copper solutions are returned to a reclaimer.	Reduce the volume by evaporation, since the reclaimer has said the more concentrated solution is acceptable.	Waste reduction = 878 gal/yr Cost reduction = $1,790/yr Implementation cost = $4,500 Simple payback = 2.5 yr
Cutting, drilling, and routing the thin sheets of resin, fiber glass, and copper produce "drop-offs" containing copper, aluminum, and gold. Conventional disposal is in a landfill.	Collect and recycle the waste.	Waste reduction = 3,075 lb/yr Cost reduction = $1,050/yr Implementation cost = $0 Simple payback = immediate
Waste from the final spray rinse (deionized) is sewered, even though it contains small quantities of suspended hazardous waste (copper, tin, lead, and epoxy resin).	Install a filter system (0.1-micron) for the final spray rinse. Recycle the water, collect the solids, and dispose of the particulates as hazardous waste.	Waste reduction = 846,600 gal/yr Cost reduction = $1,280/yr Implementation cost = $650 Simple payback = 6 mo
Operators hold circuit boards over the electroless copper tanks to reduce drag-out to the rinse baths.	Put drip bars over the electroless copper tanks and use timers to lessen drag-out and standardize drain times.	Waste reduction = 30 gal/yr Cost reduction = $370/yr Implementation cost = $480 Simple payback = 1.4 yr

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