Alternatives for Cleaning Printed Circuit Boards

In the past, chlorofluorocarbons (CFCs) and chlorinated hydrocarbons (CHCs) were widely used to clean printed circuit board assemblies. However, these compounds are being phased out because they deplete the stratospheric ozone layer. Therefore, other cleaning options must be implemented.

Several printed circuit board assembly cleaning alternatives have been evaluated by Sandia National Laboratories (Albuquerque, New Mexico). The results of the evaluation are summarized in “Non-CFC Cleaning of Printed Wiring Boards,” by P. J. Nigrey et al. The paper is available from NTIS, 5285 Port Royal Road, Springfield, Virginia 22161, (703) 487-4650, Order No. DE91-009252, for $15.00.

CFC Alternatives

A number of alternatives for cleaning printed circuit boards are available, including:

- Chlorinated solvents,
- CFC and CHC self-contained cleaning systems,
- Hydrogenated chlorofluorocarbons (HCFCs),
- Aqueous-based cleaning processes, and
- Hydrocarbon-based solvents.

Chlorinated Solvents

Chlorinated solvents, such as perchloroethylene, trichloroethylene (TCE), trichloroethane (TCA), and dichloromethane are excellent cleaning compounds and exhibit low flammability. However, most of these solvents can pose serious health risks to workers unless they are used in self-contained cleaning systems. Unfortunately, such systems are not practical for high-volume printed circuit board operations. In addition, TCA (also known as methyl chloroform) is also being phased out by EPA because it has been found to cause ozone layer depletion.

CFC and CHC Self-Contained Cleaning Systems

Some CFC and CHC manufacturers claim that these solvents can still be used in self-contained cleaning systems without adversely affecting the ozone layer. However, this option is not cost-effective in the long-term because the cost of CFCs and CHCs will continue to increase until they are phased out.

Switching to HCFCs

In response to the CFC and CHC phase-out, many CFC manufacturers have been searching for substitute solvents with low ozone depletion potentials (ODPs), such as HCFCs. HCFCs have lower ODPs because of their reduced chemical stability in the upper atmosphere. As a result, these compounds are more easily degraded and consequently are less likely to reach the stratospheric ozone layer. Although HCFCs may seem to be an ideal substitute, they do not represent a long-term solution because EPA plans to phase them out as well.

Aqueous-Based Cleaning Processes

Aqueous-based cleaning methods, which were used long before CFC and CHC cleaning techniques became available, are becoming popular again because they typically do not use toxic or environmentally damaging chemicals. In these processes, aqueous-based cleaning agents (e.g., detergents, alkaline cleaners) are sprayed onto the printed circuit boards to dissolve resins and other contaminants or remove them as small particles. However, detergent or alkaline cleaning may not be adequate for hard-to-remove deposits. To circumvent this problem, a two-step process can be used in which a solvent cleaning step is followed by a detergent cleaning step.

Hydrocarbon-Based Solvents

Several types of hydrocarbon-based solvents (e.g., alcohols, alkyl esters, mineral spirits, and terpenes) can also be used to clean printed circuit boards. The advantage of these solvents is that most of them are environmentally safe and relatively non-toxic. However, they do represent fire hazards due to their flammability. As a result, they are inappropriate for vapor degreasing. Instead, they are typically used in immersion or spray-cleaning applications.

Four Cleaning Agents Evaluated

In order to identify an effective CFC alternative for cleaning nuclear weapons electronic components, Sandia National Laboratories evaluated four non-halogenated, environmentally safe solvents:

- Terpene-based BIOACT EC-7,
- N,N-dimethylacetamide-based ACT-100,
- Decyl acetate-based EXXATE 1000, and
- Isopropyl alcohol.

During the first part of the evaluation, the cleaning efficiency of these solvents for removing oils (WD-40), greases (Apiezol L grease), and mold release compound (RMA 225 mold release) from copper printed circuit board coupons was studied. Then, the ability of the solvents to remove three products representative of body oils (water-soluble hand creams SANI-TUFF and SANI-FRESH, and lanolin) was determined. TCE was also used in the body oil study to establish baseline cleaning data.

In both portions of the evaluation, the performance of each solvent was studied using two cleaning processes:

- Cleaning process #1—Ultrasonic cleaning of the soiled coupons with the appropriate solvent for one minute at ambient temperature, followed by a water rinse and/or an isopropanol rinse.
- Cleaning process #2—Immersion of the soiled coupons in the respective solvents heated to 120ºF for one minute, followed by a water rinse and/or an isopropanol rinse.

Cleaning effectiveness was determined from weight loss data and MESERAN (Measurement and Evaluation of Surfaces by Evaporative Rate Analysis) values. The MESERAN method turned out to be a much more accurate measurement of surface cleanliness than weight loss data. In the MESERAN technique, a volatile radioactive compound (labeled-tetrabromoethane dissolved in a cyclohexane) is placed on the surface to be analyzed. The rate of evaporation of a volatile material (such as the
**FIGURE 1**
EFFECTIVENESS OF CLEANING AGENTS FOR REMOVING OILS, GREASES, AND MOLD RELEASE COMPOUNDS

**FIGURE 2**
EFFECTIVENESS OF CLEANING AGENTS FOR REMOVING BODY OILS
radioactively labeled compound) from a surface is inversely proportional to the quantity of preexisting contamination. Therefore, the "dirtier" the surface, the lower the rate of evaporation, and the higher the level of radioactivity on the surface. In other words, high MESERAN values will be observed for contaminated surfaces, while low MESERAN values will be observed for clean surfaces.

**EXXATE 1000 and BIOACT EC-7 Out Perform Other Solvents**

The results of the solvents’ ability to remove oils, greases, and mold release compounds are shown in Figure 1. This data indicates that both BIOACT EC-7 and EXXATE 1000 were effective in removing these contaminants. ACT-100 and isopropanol were not capable of removing Apiezon L grease; additionally, isopropanol could not be used in Process #2 due to safety concerns associated with the elevated temperatures.

Results of the body oil study (shown in Figure 2) indicate that only EXXATE 1000 was able to remove all of the contaminants effectively. The other solvents worked well for some compounds, but not as well for others.

**Conclusions**

The study showed that EXXATE 1000 and BIOACT EC-7 were more effective for cleaning oils, greases, and mold release compounds from copper printed circuit board coupons. However, EXXATE 1000 was more effective for removing body oils. Nevertheless, since cleaning equipment is commercially available for use with BIOACT EC-7 and not for EXXATE 1000, Sandia National Laboratories selected BIOACT EC-7 for use at its facility.

**DOW Chemical Shares Waste Reduction Ideas**

In these times of high waste disposal costs, stringent regulations, and increased public awareness, companies are realizing that waste reduction is the smartest solution to many disposal problems. However, nonsense advice on how to minimize waste generation is often hard to come by.

Numerous practical suggestions for reducing waste generation are offered by Kenneth E. Nelson of Dow Chemical U.S.A.’s Louisiana Division (Plaquemine, Louisiana) in a paper entitled, “Process Modifications that Reduce Wastes.” The paper was presented at the 1991 AIChE Summer National Meeting in Pittsburgh, Pennsylvania (August 21, 1991). Based on experience gained in Dow Chemical plants, Nelson has compiled a list of waste reduction alternatives concerning 1) raw materials, 2) reactors, 3) heat exchangers, 4) pumps, 5) furnaces, 6) distillation columns, 7) piping, 8) process control, and 9) miscellaneous processes. According to Mr. Nelson, most of the improvements had a return on investment greater than 30 percent and some paid for themselves in less than a year.

**Raw Materials**

Typically, impurities or unnecessary constituents in raw materials end up as wastes. In order to reduce waste generation, each raw material should be evaluated to determine how it affects the amount of waste produced by a plant. Several other steps may also be taken:

- Reduce the level of impurities present in raw materials by consulting with the suppliers or installing new purification equipment.
- Use off-specification material that would otherwise be a waste instead of raw materials whenever possible.
- Improve the quality of your products because impurities in them may be creating waste in your customers' plants.
- Use inhibitors to prevent unwanted side reactions or polymer formation.
- Make sure that incoming raw materials and outgoing products are shipped in reusable containers or bulk shipments.
- Evaluate each process to determine if it can be modified to reduce or eliminate the need for certain raw materials that ultimately end up as waste. For example, the need for algae inhibitors in a cross-flow cooling tower can be reduced by shielding the water distribution decks from sunlight.

**Reactors**

Reactors can be major sources of waste products if process conditions (mixing, temperature, etc.) are not optimal. Waste generation in reactors can usually be minimized if the plant takes steps to:

- Improve mixing by adding or improving baffles, installing a higher-rpm motor on the agitator(s), using a different mixer blade design (or multiple impellers), or adding/increasing pumped recirculation.
- Improve feed distribution. As shown in Figure 1a, reactants entering a fixed catalyst bed may be poorly distributed. Part of the feed short-circuits down through the center of the reactor and does not have enough time to completely convert to the desired products. The remainder of the feed stays closer to the walls and remains in the reactor too long, causing the formation of unnecessary by-products. In order to improve feed distribution, a distributor can be added to force the feed to move uniformly through the reactor (Figure 1b). A special collector at the bottom of the reactor may also be required to prevent the flow from necking down to the outlet.

**FIGURE 1**

**REACTOR FEED DISTRIBUTION**

Source: K.E. Nelson.
• Constantly search for better catalysts. Changes in the chemical composition of a catalyst, the method by which it is prepared, or its physical characteristics (size, shape, porosity, etc.) can lead to substantial improvements in catalyst life and effectiveness.

• Improve reactant mixing so that ideal reactant concentrations are reached before the feed enters the reactor. Individual reactants should not be added directly to the reactor, as shown in Figure 2a, because inadequate mixing causes secondary reactions to occur and consequently causes unwanted by-products to form. In particular, a consumable catalyst should be diluted in one of the feed streams (one that does not react in the presence of the catalyst) before it is introduced into the reactor. In this situation, the process can be improved by using three in-line static mixers (Figure 2b) to thoroughly mix the reactants before they enter the reactor.

• Evaluate the method used to heat or cool the reactor to ensure that hot-spots or overheated feed streams are avoided. These situations usually cause the formation of unwanted by-products.

• Provide a separate reactor for handling recycled by-products and waste streams because ideal reactor conditions for converting recycle streams back to usable products are significantly different from conditions in the primary reactor. Use of a separate reactor, as shown in Figure 3, allows temperatures, pressures, and concentrations in both reactors to be optimized.

• Consider changing the reactor design if a stirred backmix reactor is currently in use. A plug flow reactor may be a better choice because it can be staged and each stage can be run under different conditions (e.g., temperatures). In this manner, the reaction can be closely controlled for optimum product mix and minimum waste generation.

• Improve the control system so that optimum operating conditions can be ensured with minimal fluctuation, thereby reducing the production of unwanted by-products.
Heat Exchangers

The formation of waste products in heat exchangers can be reduced by several methods:

- Desuperheat high-pressure plant steam, which may contain several hundred degrees of superheat, when it enters a process or just upstream of a heat exchanger. This will reduce tube wall temperatures and increase the effective surface area of the exchanger because the heat transfer coefficient of condensing steam is ten times greater than that of superheated steam.

- Use lower pressure steam to reduce tube wall temperatures and thereby minimize formation of waste products.

- Install a thermocompressor to reduce tube wall temperature (Figure 4). A thermocompressor, which operates on an ejector principle, combines high- and low-pressure steam to produce an intermediate-pressure steam. Variable throat models are available that operate like control valves, automatically mixing the appropriate amounts of high- and low-pressure steam.

- Utilize on-line cleaning devices (e.g., recirculated sponge balls, reversing brushes) to reduce exchanger maintenance and keep tube surfaces clean so that a lower temperature heat source can be used.

- Install scraped-wall heat exchangers, which consist of a set of rotating blades inside a vertical, cylindrical jacketed column. They can be used to recover saleable products (e.g., monomer) from viscous streams (e.g., polymer tars).

- Use staged heating to reduce degradation when heating heat-sensitive fluids. In this process, several heat exchangers are installed in series and incrementally hotter sources of heat/steam (waste heat, low pressure steam, and then high pressure steam) are introduced in each exchanger (Figure 5).

- Continuously monitor the exchanger fouling factor to pinpoint the cause of fouling, which may be due to a change in conditions or upset somewhere else in the process.

- Install noncorroding tubes to reduce fouling.

Furnaces

Mr. Nelson recommends contacting furnace manufacturers for information on new techniques for optimizing furnace operation and reducing tar formation. Several options that may be chosen include:

- Install a furnace coil that has improved design features (e.g., tubes with low residence times or split-flow design) to optimize furnace operation and reduce tar formation.

- Eliminate direct heating in the furnace, which exposes the heated fluid to high tube wall temperatures, by using an intermediate heat transfer medium, such as

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Pumps

In order to reduce pump leaks, plants can:

- Recycle pump seal flush and purge streams back to the process.

- Use can-type sealless pumps or magnetically driven sealless pumps to eliminate leaking pump seal wastes.

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Dowtherm™ (Figure 6). In fact, the furnace may be eliminated completely if sufficient superheat is available in the plant steam.

Distillation Columns

Distillation columns can be a source of wastes when 1) impurities are allowed to remain in the product; 2) wastes form within the column, usually because high reboiler temperatures cause polymerization; and 3) condensing is inadequate, resulting in vented or flared product. Suggestions for reducing waste generation from distillation columns include:

- Increase the reflux ratio to improve separation and consequently remove impurities from the product.
- Add a new section to the column to increase capacity and improve separation if the column is operating close to flood. The new section does not have to use the same type of packing/trays that exist in the original part of the column.
- Retray or repack part or all of the column using high efficiency packing, which can reduce column pressure drop and, hence, reboiler temperature.
- Insulate the column to prevent heat loss, thus allowing lower reboiler temperatures, and preventing column conditions from fluctuating radically with weather changes.
- Improve feed distribution (especially in packed columns) to ensure that distribution anomalies are not lowering overall column efficiency.
- Preheat the feed to improve column efficiency.
- Increase the size of the vapor line in low-pressure or vacuum columns to reduce pressure drop and decrease reboiler temperature.
- Modify reboiler design by installing a falling film reboiler, a pumped recirculation reboiler, or high-flux tubes to minimize product degradation.
- Reduce reboiler temperature by desuperheating plant steam, using lower pressure steam, installing a thermocompressor, and/or using an intermediate heat transfer fluid.
- Lower column pressure to decrease the reboiler temperature. (However, the overheads temperature will also be reduced and may create a potential condensing problem.)
- Retube/replace the condenser or add a supplementary vent condenser to reduce overheads loss caused by an undersized condenser. The vent may be rerouted back to the process if the process pressure is stable. However, the tubes must be maintained above 32°F if a refrigerated condenser is used and there is moisture in the stream.
- Improve process controls.
- If the overheads stream is sent to another column for further separation, use a partial condenser and introduce a vapor stream to the downstream column.
- Recycle/reuse individual waste streams before they are mixed with other waste streams en route to the wastewater treatment facility.
- Avoid overheating or freezing lines that contain temperature-sensitive materials.
- Cool hot materials before they are transferred to storage.
- Eliminate leaks. Leaks of products that cannot be seen or smelled can be documented by measuring the quantity of raw materials that must be bought to replace "lost" streams.
- Use more inert types of metal for vessels and/or piping if the existing material is acting as a catalyst for the formation of unwanted by-products or is causing a color problem. Alternatively, lined pipes or vessels can be utilized.
- Paint all pipes and vessels before they are insulated and maintain all external painted surfaces to avoid external pipe/vessel corrosion.

Process Control

Waste generation can be reduced by placing tighter control on process conditions. Specific ideas for improving process controls are listed below:

Piping

Waste generation from pipes and vessels can be minimized by implementing the following suggestions:
High-Temperature Recovery of Nickel and Cadmium from Spent Batteries

INMETCO (Ellwood City, Pennsylvania) uses a pyrometallurgical process to recycle metals from spent nickel- and cadmium-containing batteries. When INMETCO began operation in 1978, the high-temperature metal recovery process was originally designed to reclaim flue dust, mill scale, and swarf from stainless steel manufacturing plants. Since then, the process has been expanded to recycle spent batteries, pickling cakes and solutions, plating sludges, nickel- and chrome-containing solutions, and spent catalysts. In 1990, the plant processed about 55,000 tons of waste, including 130 tons of nickel-iron and nickel-cadmium batteries. More than 22,000 tons of metal were recycled for reuse.

The INMETCO process has been described by M.E. Schweers et al. in "A Pyrometallurgical Process for Recycling Cadmium-Containing Batteries." The paper appears in the proceedings of HMC-North-east '91 held July 10-12, 1991 in Boston, Massachusetts. The proceedings are available from HMCRI, 7237 Hanover Parkway, Greenbelt, Maryland 20770-3602, (301) 982-9500, $59.00.

The Pyrometallurgical Process

A schematic diagram of the metal recovery process is illustrated in Figure 1 (page 1.28). Prior to treatment, solid wastes (e.g., mill scale, swarf, and flue dust) are subjected to size reduction and mixed with coke or coal in a screw conveyor. Then they enter a disc pelletizer where liquid wastes (e.g., waste chromic acid, spent nickel stripper solutions) are added. In the pelletizer, pellets about 0.5 inch in diameter are formed.

Meanwhile, spent nickel-cadmium and nickel-iron batteries are drained and shredded into strips (3 inches by 2 inches). Potassium hydroxide electrolyte from the drained batteries is stored for reuse as a neutralizing agent in the facility's wastewater pretreatment plant. The shredded battery pieces are mixed with the pellets formed in the disc pelletizer and the mixture proceeds to a rotary hearth furnace.

In the rotary hearth furnace, which is operated at 2,300°F (1,260°C), metal oxides are partially reduced to their metallic state when some of the coke or coal present in the pellets reacts with oxygen. Reduced zinc, lead, and cadmium present in the flue dust are subsequently collected in a high energy, wet venturi scrubber. The scrubber water is treated in the facility's wastewater treatment plant. The resulting metal-containing sludge is dewatered and the filter cake, which contains zinc, lead, and cadmium, is shipped offsite to a secondary zinc producing plant for cadmium recovery. (This process is described below.) About 1,980 metric tons of filter cake are generated each year at the INMETCO facility.

In the meantime, hot, metallic, sintered pellets from the rotary hearth furnace are transferred to an electric arc smelting furnace where nickel is recovered. (Typically, 98% recovery of nickel from spent batteries is achieved.) At temperatures of 2,552°F to 2,912°F (1,400°C to 1,600°C), the pellets melt to form a nickel/chrome/lead molten metal bath and liquid slag. The metals, which are tapped periodically from the furnace, are cast into pigs and sold to stainless steel mills. The pigs typically consist of 8% nickel, 13.5% chromiu, and the balance is mostly iron. The slag, which consists of lime, silica, alumina, and magnesia, is also removed periodically. It is poured into thin shee, cooled, crushed, screened, and sold as fill and construction aggregate. Zinc, lead, and cadmium are removed from the furnace in the flue dust and are collected in a baghouse.

Offsite Cadmium Recovery

Up to this point in the process, zinc, lead, and cadmium have been concentrated in 1) scrubber water filter cake generated from treatment of offgases from the rotary hearth furnace, and 2) electric arc smelting furnace baghouse dust. The composition of these two materials is summarized in Table 1, page 1.29. INMETCO sends both offsite to a secondary zinc plant for cadmium recovery.

In the first step of the cadmium recovery process, the scrubber filter cake and baghouse dust are heated along with coal, limestone, and silica flux in a Waelz kiln at 2,372°F (1,300°C). This reduces and volatilizes virtually all of the zinc, lead, and cadmium in the presence of excess carbon from the coal. The volatilized metals are recx-
FIGURE 1
SCHEMATIC DIAGRAM OF INMETCO'S PYROMETALLURGICAL PROCESS FOR RECYCLING NICKEL AND CADMIUM FROM SPENT BATTERIES

Source: M.E. Schweers.
TABLE 1
COMPOSITION OF MATERIALS
SENT OFFSITE FOR CADMIUM RECOVERY

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Rotary hearth furnace scrubber filter cake (% dry weight)</th>
<th>Electric arc furnace baghouse dust (% dry weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2 and Al2O3</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>CaO and MgO</td>
<td>13</td>
<td>5</td>
</tr>
<tr>
<td>F</td>
<td>3</td>
<td>1</td>
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<td>Zn</td>
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<td>Fe</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>Cr</td>
<td>3</td>
<td>0.6</td>
</tr>
<tr>
<td>Cd</td>
<td>0.6</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Source: M.E. Schweers et al.

3. Zinc dust is added to precipitate copper [CuSO4 + Zn° dust = Cu° (precipitate) + ZnSO4].

4. In order to separate cadmium from zinc, zinc dust is added again in a second step to precipitate cadmium from solution [CdSO4 + Zn° dust = Cd° (precipitate) + ZnSO4].

The cadmium precipitate that results from the hydrometallurgical process is readily treated to recover refined cadmium metal.

EPA'S REASSESSMENT OF DIOXIN

In April 1991, EPA Administrator William Reilly announced that EPA would conduct a scientific reassessment of the risks from exposure to 2,3,7,8-TCDD (tetrachlorodibenzo-p-dioxin) and similar chemical compounds, known collectively as dioxin. The agency's reassessment is in response to increased scientific knowledge on the biochemical mechanisms involved in the toxicity of dioxin and new information on the human health and environmental effects of the chemical.

In a background document released in conjunction with a public meeting, EPA summarizes the elements comprising its scientific reassessment of dioxin. The paper, titled “EPA's Scientific Reassessment of Dioxin” (October 1, 1991), is available from Environmental Management Support, Inc., 010 Wayne Avenue, Suite 200, Silver Spring, MD 20910, Attention: Dioxin Reassessment.

Background

On the basis of animal studies, dioxin is considered to be one of the most potent carcinogens known to man. However, the degree to which these studies can be extrapolated to human health has long been the source of much controversy. EPA has previously completed two scientific assessments of the human health and environmental effects of exposure to dioxin. A 1985 assessment found sufficient evidence of carcinogenicity in animals to classify dioxin as a "B2" carcinogen, the classification used by EPA for probable human carcinogens.

A 1988 draft assessment suggested that the cancer potency estimate should be revised and the risk-specific dose should be decreased by a factor of 16, on the basis of new scientific evidence. However, although EPA’s Science Advisory Board agreed that the standard approach had inadequacies, not enough evidence existed to justify lowering the risk-specific dose. This panel did recommend developing a receptor-based dose-response model to generate a new carcinogenic potency estimate.

Reassessment

Two events prompted EPA to undertake this scientific reassessment of dioxin. First, in January 1991, the National Institute of Occupational Safety and Health (NIOSH) published the results of an epidemiological study of cancer mortality rates in American chemical workers in the New England Journal of Medicine. Results of the study, which...