Aqueous and Semi-Aqueous Alternatives for CFC-113 and Methyl Chloroform Cleaning of Printed Circuit Board Assemblies

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AQUEOUS AND SEMI-AQUEOUS ALTERNATIVES FOR CFC-113 AND METHYL CHLOROFORM CLEANING OF PRINTED CIRCUIT BOARD ASSEMBLIES

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FOREWORD

This manual has been developed jointly by the International Cooperative for Ozone Layer Protection (ICOLP) and the U.S. Environmental Protection Agency (EPA) to aid the phaseout of ozone-depleting substances (ODSs) in printed circuit board (PCB) cleaning applications. It will prove useful to manufacturers world-wide because the procedures used to clean PCB assemblies apply to all manufacturers, regardless of location or size. The manual has been prepared by the U.S. EPA and an international committee of experts from the solvent cleaning industry. Committee members represent both developed and developing countries.

The manual describes a step-by-step approach for characterizing the use of ozone-depleting solvents and identifying and evaluating alternatives. It is a "how-to" document which describes all of the steps necessary to successfully phase out the use of CFC-113 and methyl chloroform (MCF) in PCB cleaning applications. Many of the alternatives described are currently in use at major companies around the world. The manual addresses primary cleaning applications and gives brief descriptions of the commercially available aqueous and semi-aqueous alternatives to CFC-113 and MCF. The manual provides sufficient technical information on the solvent alternatives to enable users to gather more detailed information on their alternatives of choice. A list of equipment and materials vendors is provided to facilitate such further research.

The Montreal Protocol

The 1987 Montreal Protocol on Substances that Deplete the Ozone Layer and subsequent 1990 and 1992 amendments and adjustments control the production and consumption of ODSs internationally. As a result of the most recent meetings in Copenhagen in November 1992, two chemicals commonly used as solvents are scheduled to be phased out. The chlorofluorocarbon 1,1,2-trichloro-1,2,2-trifluoroethane (commonly referred to as CFC-113) and 1,1,1-trichloroethane (commonly referred to as methyl chloroform or MCF), will be completely phased out in developed countries by 1996, and in developing countries between 2006 and 2015 depending on decisions taken by the Parties to the Protocol in 1995. In addition, the 1992 amendments include a developed country production freeze and reduction schedule for hydrochlorofluorocarbons (HCFCs), with a phaseout in developed countries by the year 2030.

Exhibit 1 lists the countries that are Parties to the Montreal Protocol as of February 1994. In addition, many companies world-wide have corporate policies to expedite the phaseout of ozone-depleting chemicals. Exhibit 2 lists corporations around the world that have successfully phased out their use of ODSs.

In addition to providing regulatory schedules for the phaseout of ODSs, the Montreal Protocol established a fund that will finance the agreed incremental costs of phasing out ODSs by eligible developing countries that are Party to the Protocol. Eligible countries are defined as those developing countries having a total annual consumption of CFCs of less than 0.3 kg per person, and of MCF and carbon tetrachloride of 0.2 kg per person.

International Phaseout Schedules

Several countries have passed legislation to phase out CFC-113 and MCF earlier than target dates set by the Montreal Protocol in an effort to slow ongoing depletion of the stratospheric ozone layer. Their policies are summarized below.

Canada

Environment Canada, the federal agency responsible for environmental protection in Canada, enacted a CFC phaseout program more stringent than the Montreal Protocol. Environment Canada has also announced a series of target dates for the phaseout of CFCs in specific end uses. For solvent cleaning applications such as metal and precision cleaning, it mandates a phaseout of CFC-113 by the end of 1994. Production, imports, and exports of CFCs are to be eliminated by January 1, 1996, with a 75 percent reduction by January 1, 1994. For carbon tetrachloride, the phaseout date is January 1, 1995 -- one year earlier than that mandated by the Montreal Protocol. Halons were eliminated by January 1, 1994. Production, imports, and exports of MCF will be halted by January 1,

1996, with interim reductions of 50 percent by January 1, 1994, and 85 percent by January 1, 1995.

European Community

Under the Single European Act of 1987, the twelve members of the European Community (EC) are subject to environmental directives issued by the EC Governing Council. Members of the EC are Belgium, Denmark, Germany, France, Greece, Great Britain, Ireland, Italy, Luxembourg, the

Exhibit 1

PARTIES TO THE MONTREAL PROTOCOL

Algeria	Ecuador	Luxembourg	Seychelles
Antigua and Barbuda	Egypt	Malawi	Singapore
Argentina	El Salvador	Malaysia	Slovakia
Australia	EEC	Maldives	Slovenia
Austria	Fiji	Malta	Solomon Islands
Bahamas	Finland	Marshall Islands	South Africa
Bahrain	France	Mauritius	Spain
Bangladesh	Gambia	Mexico	Sri Lanka
Barbados	Germany	Monaco	Sudan
Belarus	Ghana	Morocco	Swaziland
Belgium	Greece	Myanmar	Sweden
Benin	Grenada	Namibia	Switzerland
Bosnia/Herzegovina	Guatemala	Netherlands	Syrian Arab Republic
Botswana	Guinea	New Zealand	Tanzania
Brazil	Guyana	Nicaragua	Thailand
Brunei Darussalam	Honduras	Niger	Togo
Bulgaria	Hungary	Nigeria	Trinidad & Tobago
Burkina Faso	Iceland	Norway	Tunisia
Cameroon	India	Pakistan	Turkey
Canada	Indonesia	Panama	Turkmenistan
Central African Republic	Iran	Papua New Guinea	Tuvalu
	Ireland	Paraguay	Uganda
Chile	Israel	Peru	Ukraine
China	Italy	Philippines	United Arab Emirates
Colombia	Jamaica	Poland	
Congo	Japan	Portugal	United Kingdom
Costa Rica	Jordan	Romania	United States
Cote d'Ivoire	Kenya	Republic of Korea	Uruguay
Croatia	Kiribati	Russian Federation	Uzbekistan
Cuba	Kuwait	St. Kitts and Nevis	Venezuela
Cyprus	Lebanon	St. Lucia	Viet Nam
Czech Republic	Libyan Arab Jamahiriya	Samoa	Yugoslavia
Denmark		Saudi Arabia	Zambia
Dominica	Liechtenstein	Senegal	Zimbabwe

Date: February 1994

Exhibit 2

SUCCESSFUL CORPORATE OZONE-DEPLETING SOLVENT PHASEOUTS

A-dec
ADC Telecommunications
Advanced Micro Devices
Alcatel Network Systems
Apple Computer
Applied Magnetics
Aishin Seiki
Alps Electric
AT&T
Cadillac Gage
Calsonic
Canon
Corbin Russwin Hardware
Casio Computer
Chip Supply
Citizen Watch
Clarion
Compaq Computers
Conner Peripherals
Commins Engine
Diatek
Fuji Photo Film
Fujitsu
Funac
Harris Semiconductors
Hewlett Packard
Hitachi
Hitachi Metals
IBM
Iki Electric
Isuzu Motors
ITT Cannon
Japan Aviation Electronics
Kilovac
Kohyo Seiko
Kyocera
Mabuchi Motor
Matsushita
MDM
Minebea
Minolta Camera
Mitsubishi Electric
Mitsubishi Heavy Industry
Mitsubishi Motors
Mitsui High-tech
Motorola
Murata Erie N.A.
Murata Manufacturing
National Semiconductor
NEC
NHK Spring
Nihon Dempa Kogyo
Nissan
Nissan Diesel Motor
Northern Telecom
NRC
NSK
Olympus Optical
Omron
OTC/SPX
Pacific Scientific EKD
Ricoh
Rohm
Sanyo MEG
Sanyo Energy
Seagate Technology
Seiko Epson
Seiko-sha
Sharp
Shin-etsu Polymer
SMC
Sony
Stanley Electric
Sumitomo Electric
Sumitomo Special Metals
Sun Microsystems
Suzuki Motor
Symmons Industries
Taiyo Yuden
Talley Defense Systems
Thomson Consumer Electronics
3M
Toshiba
Toshiba Display Devices
Toyota Motor
Unisia JECCS
Victor Japan
Yamaha
Yokogawa Electric
Zexel

Netherlands, Portugal, and Spain. Council Regulation number 594/91 of March 4, 1991 includes regulatory provisions for the production of substances that deplete the ozone layer. The EC phaseout schedule for CFC-113 production is more exacting than the Montreal Protocol. It called for an 85 percent reduction of CFC-113 production by January 1, 1994 and a complete phaseout by January 1, 1995. For MCF, the schedule called for a 50 percent cut in production by January 1, 1994 and a complete phaseout by January 1, 1996. While all members must abide by these directives, Council Regulation number 3322/88 of October 31, 1988 states that EC members may take even more extensive unilateral measures to protect the ozone layer.

European Free Trade Agreement Countries

The European Free Trade Agreement (EFTA) countries of Austria, Finland, Iceland, Norway, Sweden, and Switzerland, have each adopted measures to completely phase out fully-halogenated ODSs. Austria, Finland, Norway, and Sweden will completely phase out their use of CFC-113 in all applications by January 1, 1995. Sweden plans to phase out MCF by this date as well. In addition, some EFTA countries have set sector-specific interim phaseout dates for certain solvent uses. Austria phased out CFC-113 in a number of solvent cleaning applications by January 1, 1994. Norway and Sweden eliminated their use of CFC-113 on July 1, 1991 and January 1, 1991, respectively for all applications except textile dry cleaning.

Japan

On May 13, 1992, the Ministry of International Trade and Industry (MITI) requested its 72 Industrial Associations to phase out CFC and MCF usage by the end of 1995.

United States

The U.S. Clean Air Act (CAA), as amended in 1990, contains several provisions pertaining to stratospheric ozone protection. ODSs are categorized by the CAA as either Class I or Class II substances. Class I substances include MCF, three types of halons, carbon tetrachloride, and all fully-halogenated CFCs, including CFC-113. Class II substances include 33 types of hydrochlorofluorocarbons (HCFCs). The sections of the CAA important to users of this manual are discussed below.

- ***Section 112: National Emission Standards for Hazardous Air Pollutants***

  This section of the CAA requires the EPA to develop emissions standards for 189 chemical compounds listed as hazardous air pollutants (HAPs). The list of HAPs includes the chlorinated solvents as well as many organic solvents likely to be used in cleaning metal parts.

- ***Section 604 and Section 605: Phaseout of Production and Consumption of Class I and Class II Substances.***

  These sections detail the phaseout schedule for both Class I and Class II substances. EPA accelerated the schedule in response to both former President George Bush's call for a more rapid phaseout and the recent amendments made to the Protocol in Copenhagen.

- ***Section 610: Nonessential Products Containing Chlorofluorocarbons***

  This provision directs EPA to promulgate regulations that prohibit the sale or distribution of certain "nonessential" products that release Class I and Class II substances during their manufacture, use, storage, or disposal.

- ***Section 611: Labeling***

  This section directed EPA to issue regulations requiring the labeling of products that contain or were manufactured with Class I and Class II substances. Containers in which Class I and Class II substances are stored must also be labeled. The label will read "Warning: Contains or manufactured with [*insert name of substance*], a substance which harms public health and environment by destroying ozone in the upper atmosphere". The label must clearly identify the ODS by chemical name for easy recognition by average consumers, and must be placed so that it is clearly legible and conspicuous.

  Labeling regulations affecting Class I substances took effect on May 15, 1993. Products containing or manufactured with a Class II substance must be labeled no later than January 1, 2015.

- ***Section 612: Safe Alternatives Policy***

  Section 612 establishes a framework for evaluating

the overall environmental and human health impact of current and future alternatives to ozone-depleting solvents. Such regulation ensures that ODSs will be replaced by substitutes that reduce overall risks to human health and the environment. As a result of provisions set in Section 612, the Environmental Protection Agency:

- Issued rules in November 1992 that make it unlawful to replace any Class I and Class II substance with a substitute that may present adverse effects to human health and the environment when the EPA has identified an available or potentially available alternative that can reduce the overall risk to human health and the environment.

- Has published a list of prohibited substitutes, organized by use sector, and a list of the corresponding alternatives;

- Will accept petitions to add or delete a substance previously listed as a prohibited substitute or an acceptable alternative;

- Requires any company that produces a chemical substitute for a Class I substance to notify EPA 90 days before the new or existing chemical is introduced into commerce as a significant new use of that chemical. In addition, EPA must be provided with the unpublished health and safety studies/data on the substitute.

To implement Section 612 EPA has (1) conducted environmental risk characterizations for substitutes in each end use and (2) established the Significant New Alternatives Program (SNAP) to evaluate the substitutes for Class I substances. EPA also initiated discussions with NIOSH, OSHA, and other governmental and nongovernmental associations to develop a consensus process for establishing occupational exposure limits for the most significant substitute chemicals.

The environmental risk characterizations for the substitutes involve a comprehensive analysis based on the following criteria: ozone-depleting potential, flammability, toxicity, exposure effects, energy efficiency, degradation impacts, air, water, and solid waste/hazardous waste pollution effects, and global warming potential. Economic factors are also considered. EPA has organized these assessments by use sector (i.e. solvents, refrigeration, etc). The risk characterizations result in risk-management strategies for each sector and substitute. EPA has also categorized each substance as unacceptable, acceptable with limitations on use or quantity, acceptable without comment, or delayed pending further study. Petitions are allowed to change a substance's status with the burden of proof on the petitioner.

In early 1994, the EPA issued a list of alternatives it found to be acceptable and unacceptable according to this framework in its Significant New Alternatives Policy (SNAP) Program ruling. The list will be updated regularly as new alternatives become available.

Excise Tax

As an incentive to reduce the production and consumption of ODSs in the U.S., Congress placed an excise tax on ODSs manufactured or imported for use in the U.S. Taxes do not apply to recycled chemicals. This tax provides a further incentive to use alternatives and substitutes to CFC-113 and MCF and to recycle used chemicals. The tax amounts are based on each chemical's ozone-depleting potential. These taxes have recently been increased as a part of the U.S. Congress' comprehensive energy bill of 1992.

Calendar Year	Tax Amount Per Pound	
	CFC-113	MCF
1991	$1.096	$0.137
1992	$1.336	$0.167
1993	$2.68	$0.211
1994	$3.48	$0.435
1995	$4.28	$0.535

Cooperative Efforts

Japan

The Japanese Ozone Layer Protection Act gives its Ministry of International Trade and Industry (MITI) the authorization to issue restrictions on ODSs. MITI and the Environmental Agency have established the "Guidelines for Discharge Reduction and Use Rationalization." Based upon these guidelines, various government agencies have provided administrative guidance and advice to the industries under their respective jurisdictions. Specifically, MITI worked with the Japan Industrial Conference for Ozone Layer Protection (JICOP) to prepare two manuals that provide technical information on alternatives to CFC-113 and MCF. The manuals are titled:

- Manual for Phasing-Out 1,1,1-Trichloroethane; and
- Manual for Reduction in the Use of Ozone-Depleting Substances.

MITI also encourages industry to reduce consumption of ODSs through economic measures such as tax incentives to promote the use of equipment to recover and reuse solvents.

Sweden

The Government/Industry/Research Institution sectors are conducting two major cooperative efforts targeting the phaseout of ODSs and chlorinated solvents:

- The TRE-project (Technology for Clean Electronics); and
- The AMY-project (Cleaning of Metallic surfaces).

In addition, direct support is being provided to industry for industrial scale introduction of new technologies. These are, to name a few, closed loop systems, microbiological cleaning systems, ion exchange technologies, electrochemical cleaning systems, vacuum evaporation systems, reverse osmosis, and alternative solvent-based systems.

United States

EPA has been working with industry to disseminate information on technically-feasible, cost-effective, and environmentally-sound alternatives to ODSs. As part of this effort, the Agency, along with ICOLP, prepared a series of manuals that provide technical information on alternatives to CFC-113 and MCF. Additional information about ICOLP can be found in Appendix A. The manuals are based on actual industrial experiences and serve as a guide to users of CFC-113 and MCF worldwide. These manuals will be updated periodically as technical developments occur.

The complete set of manuals produced includes:

- Alternatives for CFC-113 and Methyl Chloroform in Metal Cleaning.
- Aqueous and Semi-Aqueous Alternatives to CFC-113 and Methyl Chloroform Cleaning of Printed Circuit Board Assemblies.
- Conservation and Recycling Practices for CFC-113 and Methyl Chloroform.
- Eliminating CFC-113 and Methyl Chloroform in Aircraft Maintenance Procedures.
- Eliminating CFC-113 and Methyl Chloroform in Precision Cleaning Operations.
- No-Clean Soldering to Eliminate CFC-113 and Methyl Chloroform Cleaning of Printed Circuit Board Assemblies.

This particular manual provides those in an organization currently cleaning with ODSs with a simply-structured program to help eliminate their use of CFC-113 and/or MCF. Moreover, it presents aqueous and semi-aqueous processes that can be used in cleaning PCB assemblies. Many of these processes are currently in use around the world. The goal of the manual is to:

- Warn users of CFC-113 and MCF of the impending halt in production and the consequences to their operations;
- Identify the currently available and emerging alternatives for CFC-113 and MCF;
- Provide an overview of the tasks that are required to successfully implement an alternative process or chemical;
- Provide an overview of the environmental, health,

safety, and other factors associated with alternatives and the benefits achievable from the phaseout of CFC-113 and MCF;

- Present detailed case studies on the actual industrial applications of these technologies to:

  -- Identify unresolved problems in eliminating CFC-113 and MCF; and

  -- Describe the equipment configuration of a typical facility after it has eliminated its use of CFC-113 and MCF.

This manual will benefit all users of CFC-113 and MCF in the PCB manufacturing industry. Ultimately, however, the success of a CFC-113 and MCF elimination strategy will depend upon how effectively reduction and elimination programs are organized. Experience has also shown that a strong education and training program for workers using new processes results in greater efficiency and a smooth transition away from CFC-113 and MCF. The development and implementation of alternatives to CFC-113 and MCF for PCB cleaning present a challenge for most organizations. The rewards for success are the contribution to global environmental protection and an increase in industrial efficiency.

STRUCTURE OF THE MANUAL

This manual is divided into the following sections:

- **METHODOLOGY FOR SELECTING A CLEANING PROCESS**

  This section discusses technical and economic issues that should be considered when selecting a cleaning process.

- **SUMMARY CHARTS**

  This section presents two summary charts that match cleaning processes with the evaluation criteria presented in the methodology section. The first chart explains that all process selection begins by matching assembly technology to a fluxing system and to potential cleaning methods. The second chart presents an overview of process advantages and constraints.

- **CHARACTERISTICS OF THE CLEANING PROCESS**

  This section presents three cleaning choices: water, water with the addition of a saponifier, and hydrocarbon/surfactants.

- **PROCESS AND EQUIPMENT CHARACTERISTICS**

  This section describes the mechanical systems that are typically associated with aqueous and semi-aqueous cleaning.

- **WATER AND WASTEWATER HANDLING**

  This section presents information on pre- and post-treatment of water.

- **CASE STUDIES OF INDUSTRIAL PRACTICES**

  This section provides specific examples of actual industrial applications of aqueous and semi-aqueous cleaning processes.

METHODOLOGY FOR SELECTING A CLEANING PROCESS

The methodology used to select a cleaning process for printed circuit boards (PCBs) must take into account a host of important considerations. These can be grouped into two categories: technical and economic.

Technical

The factors that determine the technical feasibility include:

- Compliance with specifications
- Defect rate
- Customer return issues
- Industry direction
- Cosmetics of the PCBs cleaned
- Process flexibility
- Ability to clean surface mount assemblies
- Fallback position
- Process control
- Process throughput
- Time scale
- Health, safety, and environmental concerns
- Future costs

- Availability of the process
- Process installation
- Process compatibility
- Floor space requirements
- Operating and maintenance requirements
- Other selection criteria related to the specific application

- ***Compliance to Specifications.*** Military or civilian contracts or specifications may strictly define process parameters and performance. For example, military specifications very frequently require conformal coatings. Poor cleaning causes a special category of surface defect, vesication. A military contractor would have to ensure that the chosen cleaning process/system will decrease or eliminate this type of defect, whereas this would not be a concern for manufacturers of non-military products. Before you select a new process you should consider existing and possible future contracts/provisions.

- ***Defect Rate.*** This is defined as the rate that parts fail to meet inspection standards. If the soldering process is totally unchanged and only the cleaning portion is affected, defect rates will likely not increase. Do not be short-sighted. Question the impact of a different cleaning process on downstream processes such as test and post-wave assembly. Consider the possibility that a change in the cleaning process may affect the cost of components that are compatible with the new process.

- ***Customer Return Issues.*** The choice of cleaning process can influence how easily a returned unit can be repaired or how well repairs and modifications can be done in the field.

- ***Industry Direction.*** Investing in a process that is counter to existing industry direction may be necessary, but using standard equipment sold to many customers costs less. Parts and service become costly; resources to answer waste stream issues or reliability issues are limited; and risks tend to be higher for custom equipment.

- ***Cosmetics of the PCBs Cleaned.*** Although visual appearance is becoming less important, some customers may still impose standards on visual appearance of electronic components.

- ***Process Flexibility.*** The number of different types of technology that can be cleaned efficiently with the new process is a consideration for some parties. One must consider the compatibility of the process with typical materials. What are the viable options if the process fails? Production can recover if the process is sufficiently flexible.

- ***Ability to Clean Surface Mount Technology (SMT).*** The ability to penetrate close tolerance spaces typical to SMT applications is a major advantage. SMT applications are rapidly expanding.

- ***Process Control.*** This issue refers to the degree of difficulty of operating the entire process. Simple processes are better from a process control standpoint. A process that can be easily monitored and controlled is desirable.

- ***Process Throughput.*** Throughput is extremely important to the economic feasibility of a system. The level of emissions from solvent systems is directly related to throughput. As workloads are processed faster than intended in the original design of the equipment, solvent emissions increase. This consideration is important when selecting an alternative system.

- ***Time Scale***. Converting an existing process to CFC-free alternatives cannot be expected to be completed overnight. Physically removing old equipment, installing new equipment, connecting the services, performing acceptation trials, establishing manufacturing protocols and integrating the new process into production all take time. Production projections during the conversion should be estimated realistically: zero production should be expected initially; low- to mid-levels of production should be expected during the adjustment period; and full production after all parties are fully educated. This schedule also should take into account possible fallback positions.

- ***Health, Safety, and Environmental Concerns.*** While methyl chloroform and CFC-113 are being phased out due to the concern over stratospheric ozone depletion, these chemicals were initially chosen over many other candidates because of their low flammability properties and relatively benign toxicological profiles. In order to move forward, alternatives should offer similar or better performance, safety, health, and environmental aspects. The U.S. EPA has conducted an overall risk characterization for many substitutes under Section 612: Safe Alternatives Policy of the Clean Air Act of 1990. This assessment has involved a comprehensive analysis based on ozone-depletion potential, flammability, toxicity, exposure effects, energy efficiency, degradation impacts, air, water, solid waste/hazardous waste pollution effects, environmental releases, and global warming potential.

- ***Future Costs.*** Factors such as escalating solvent costs or anticipated major expenditures associated with pending control legislation should be considered.

- ***Availability of Process.*** "Availability" is not the same as "industry direction." "Availability" concerns the ease with which vendors can supply the process. For example, some alternatives might be available only from a few vendors.

- ***Process Installation.*** This is the work that will be required to put the system into production and includes physical installation of the process, material handling considerations, and employee training.

- ***Process Compatibility.*** The fewer the number of changes required by the proposed process, the more likely that the changeover will be successful. Form, fit, and function of the product should not change. Upstream and downstream process adjustments required for a changeover should be considered. For example, the reliability of the pin test is an important concern.

- ***Floor Space Requirements.*** The total amount of space available and its value have a significant impact on process selection. Compact units are often preferred. Allow extra space for related items such as

water heaters, storage tanks, treatment facilities, and added process control tools. In some instances permits may be required before installing a new process.

- ***Operating and Maintenance Requirements.*** Each new process will require establishing unique operating and maintenance procedures. In some instances a new process could be significantly different in operation and would require special operator training.

  Depending on the process chosen, maintaining process equipment on a regular basis may be critical to preventing product defects. For example, it is necessary to clean spray nozzles to remove contamination that would make spraying less effective. Pumps and leaky valves should also be checked regularly.

Economics

Process economics is a key factor in the selection of alternative processes. Analysis of initial costs associated with the alternative process should include capital costs of equipment, capital costs associated with installation and waste treatment/handling equipment, and costs associated with obtaining local permits. In addition, ongoing operating costs should be projected and include materials, labor, maintenance, and utilities, such as energy and water. The cost estimates for the alternative process can be developed during preliminary process design.

One simple approach to compare processes is to calculate net present value (NPV) based on the discount rate and period of investment your company uses. The NPV is calculated as follows, where (n) is the number of years, (i) is the discount rate, and $cost_n$ represents the investment that occurs each year over the life of the new process.

$$NPV = Cost_{ø} + Cost_1/(1+i) + Cost_2/(1+i)^2 + \ldots + Cost_n/(1+i)^n$$

While traditional economic considerations such as rate of return and payback period are important, environmental protection and solvent supply reliability can justify the CFC-113 and MCF usage reduction program. An important component of the analysis should be a recognition that the price of CFC-113 and MCF will increase rapidly as supplies are reduced and taxes are increased. Economic analysis should also include the cost savings resulting from savings in solvent consumption; for example, some new alternative processes have much lower operating costs than the current CFC-113 and MCF processes.

SUMMARY CHARTS

The charts on the following page highlight aspects of the most promising new technologies for specific applications and present an overview of the options presented in this manual. The remainder of the manual provides additional detail.

Cleaning Options

The cleaning options chart, Exhibit 3, presents the fluxing and cleaning combinations that have been demonstrated to be successful with different types of product. Assessing these combinations is a first step in process selection.

When rosin fluxes are used, cleaning with hydrocarbon/surfactants or with saponifiers is an effective choice. With water soluble flux/paste, plain water cleaning is preferred although aqueous saponified or semi-aqueous cleaning also are applicable.

Summary Matrix

The second chart, Exhibit 4, provides brief, relevant comments on the costs, applicability, strengths, and weaknesses associated with eight machine and solvent combinations discussed in this manual.

A brief explanation of some of the criteria displayed in Exhibit 4 follows:

Possible Military Specifications Approval. While every process listed in this text has exhibited a good level of performance and control, some may not yet have been approved by the military. Military specifications should be considered when evaluating alternative cleaning technologies.

Component Issues. Concerns include corrosion, failure of seals, effects on plastics, effects on functional performance, removal of markings, and the potential to trap flux or detergent residues. Underbrush cleaning with no topside exposure has a "low" concern rating. Plain water systems have a "high" concern rating if organic fluxes that are very active are used. Entrapment of flux residue in components is a high risk for long-term reliability unless resolved by proper component design/ selection. Second, immersion/spray cleaning systems, typically using elevated temperatures, can stress poorly sealed or designed components and lead to failure.

Defect Rate. This concern refers to the soldering defect rate associated with a flux selection. Plain water cleaners typically used with the stronger organic fluxes probably would have better solder yields. It is conceivable that the other systems do not change the solder process, hence, the defect rate would be unchanged.

Waste Stream Issues. Process control, volume, local water quality, local regulations, and management decisions influence this locality-specific issue. Every process in this text has an identified, effective control mechanism applicable to the effluent. Waste stream considerations must be an important part of process implementation.

Health and Safety Issues. These issues include toxicity, flammability, odor, VOC concerns, and occupational long-term exposure of semi-aqueous and aqueous cleaners.

Idle Time Cost. The cost to sustain heated baths, ventilation, and operating pumps during idle time is important for applications with part-time usage. In most instances terpene units are effective without added heat, but some large facilities include chiller or cold water packages to reduce flammability. In-line water units must be ready during the entire shift while batch units can be shut down. Idle time can represent costs particularly to low volume operations that might choose to use in-line machines.

exhibit 3

exhibit 4

Processing Cost. This manual does not cover the associated cost of cleaning per square foot of product produced because this is determined by a number of variables at the local level. The manual does present an approximation of what the processing cost might be compared to CFC-113 systems.

CHARACTERISTICS OF THE CLEANING PROCESS

The effectiveness of a cleaning system depends on the cleaning chemistry and the cleaning mechanics. The selection of cleaner depends on the contaminants being removed, the material being cleaned, the level of cleanliness required, and the method used to apply the cleaners. Cleaners may be formulated and used for one application or for several. This diversity accounts for the many cleaner formulations that are commonly available for use in the electronics industry.

In this text, the discussion of cleaning begins with aqueous cleaning including sections on cleaning with plain water and cleaning with alkaline saponified water. It next considers the hydrocarbon/surfactants followed by water rinse, commonly referred to as semi-aqueous cleaning.

Aqueous Cleaning

Water is an excellent solvent for removing ionic contaminants and water-soluble flux. In combination with a saponifier, water can remove non-polar substances such as oil and rosin flux. Aqueous cleaning systems generally consist of washing, rinsing, and drying stages. Although waste disposal is clearly an issue, local conditions determine its impact.

Water-Based Cleaning

By itself, tap water would seem to be the perfect solvent. This notion, however, is false for two basic reasons:

- Untreated water carries a variety of trace elements and particles. The use of untreated water to clean electronic assemblies can result in inadequate cleaning.
- Most water-soluble fluxes are corrosive and incomplete removal can lead to problems. Many saponifiers applied to treat this problem also cause concerns if they are not adequately removed. Complete rinsing is more difficult with surface mount technology.

In reviewing plain water cleaning, consider the following points:

- The method is not effective for water immersible product designs.
- Reverse osmosis is a pre-treatment step commonly-used to prepare the water used in the washing and the rinsing stages.
- Plain water (tap and soft) does not effectively remove fingerprint residues.
- Plain deionized water has a high surface tension. A surfactant (wetting agent) may need to be added to improve close tolerance cleaning. Some water soluble flux residues contain surfactants that may aid water penetration under components and reduce the need for additional surfactants.
- Deionized water must be used, especially for final rinse.
- Drying using air knives or heated air is often necessary to speed drying times.
- Most applications require waste stream treatment, reducing the cost-effectiveness of the project.
- In specific installations, plain water cleaning may be compatible with closed loop water recycling packages discussed later in this document.

Alkaline Saponified Water Cleaning

This method can be used in applications with almost any flux, including water-soluble formulations. The removal of rosin flux by aqueous cleaners always requires using a strongly alkaline saponifying detergent. The saponification process uses the alkaline chemical to convert rosin into a water-soluble soap that rinses freely with water. Alkaline cleaners formulated for use in the electronics industry generally consist of alkanolamines such as monoethanolamine. The amines saponify the rosin acids.

Quality cleaners provide the following process advantages:

- Low surface and interfacial tension to aid detergent action;
- Alkalinity to neutralize acidic soils (or flux);
- Dispersion properties to assist in solid soil removal and to prevent redeposition;
- Emulsification properties to prevent redeposition of oils;
- Inhibitors to minimize attack on metals or other surfaces while cleaning;
- Post-cleaning minimization of corrosion.

Electronic cleaners tend to be formulated with an alkanolamine, combined with a builder such as ethyl butyl glycol ether, and some amount of a nonionic surfactant. Sodium hydroxide or potassium hydroxide may be included to add alkalinity. These ingredients perform the following functions:

- Monoethanolamine minimizes the possibility of creating electrolytes that can cause conductivity problems on circuit boards. Monoethanolamine generally comprises 30 to 90 percent of the cleaner concentrate.
- Builders improve the overall cleaning performance.
- Surfactants improve the cleaning solution's ability to penetrate close tolerance spaces, and they prevent the released contaminants from recontaminating the cleaned surface.
- Nonionic surfactants are used widely because they are a widely-compatible, non-electrolyte-forming chemical with a large variety of molecular structures.

Pitfalls to avoid when considering a saponified water-based system include:

- Inadequate control of detergent concentration and operating temperatures can lead to uncontrolled foaming which hinders cleaning.
- Improper selection of detergent can result in poor cleaning, unnecessary costs, or poor product quality.
- Detergents can have a high pH, as well as a high biological oxygen demand; therefore wash water with concentrated detergent solution should be checked for compliance with sewer discharge requirements. Discharging into a sanitary drain without warning can have a major impact on the microbacterial population used in treatment facilities. The biodegradability of surfactants should also be evaluated.
- Some detergent formulations include builders that are complexing agents for heavy metals. The complexing property tends to make metal separation difficult.
- If closed loop water supply packages are considered, it should be noted that detergents significantly reduce the efficiency of the carbon adsorption bed media and ion exchange columns.

Semi-Aqueous Cleaning

A semi-aqueous process uses a hydrocarbon solvent to clean the product by dissolving the contaminants, followed by a water rinse to remove the hydrocarbon solvent residue. In addition, a surfactant component is generally added to the hydrocarbon solvent to provide wetting, emulsification, and rinsing properties.

The advantages of hydrocarbon/surfactant cleaners include:

- Excellent cleaning of surface mount technology;
- Low viscosity, low foaming properties;
- Some have low vapor pressure (thus, evaporative loss is minimized);
- Polar and nonpolar contaminant removal capabilities;
- Excellent surface insulation resistance (SIR), solvent extract conductivity, and cosmetic results, including a low tendency to form white residue (see Exhibit 5);
- Specific cleaning characteristics can be enhanced with blending;
- Effective at room temperature;
- Effectively rinsed with room temperature water;
- Solvent extract conductivity measurements, using the standard DI/alcohol mixture at room temperature (MIL-P-28809), indicate ionic levels typically below 1.53 micro gram NaCl equivalent per square centimeter. That level is also typical whenever a water rinsing operation is used (see Exhibit 6);
- Excellent rosin-loading capacity;
- Typically no corrosion in copper mirror tests.

In considering the use of hydrocarbon/surfactants for cleaning, note the following points:

- While rinsing may cause corrosion of the assemblies, not rinsing can lower SIR by two orders of magnitude;
- Material compatibility with plastics and rubbers used in equipment should guide equipment selection;
- Use of spraying that results in the formation of mist or finely atomized droplets can increase hazard of flammability or loss of the hydrocarbon to the exhaust. This can result in a major source of loss of the hydrocarbon. This selective loss of hydrocarbon can increase the concentration of surfactant in the wash tank;
- Limonene-based terpenes have a strong citrus odor that may be objectionable;
- Concentrated rinse water should not be discharged without prior treatment;
- When mixed with water at concentrations of approximately 75 to 97 percent, some limonene-based terpene cleaners form a gel that is incompatible with most cleaning processes;
- Some hydrocarbons could be classified as volatile organic compounds which contribute to the formation of smog -- an air quality concern in some areas;
- Current formulas that decant very easily from water have significantly reduced earlier concerns regarding water pollution and system control.

exhibit 5

exhibit 6

PROCESS AND EQUIPMENT CHARACTERISTICS

This section presents some key process and equipment issues that should be considered before selecting an aqueous or semi-aqueous cleaning process.

The technologies are presented in the following order:

- Underbrush Cleaning (Aqueous and Semi-Aqueous);
- Hydrocarbon/Surfactant Spray Cleaning;
- Batch Hydrocarbon/Surfactant Cleaning;
- In-Line Aqueous Cleaning; and
- Batch Aqueous Cleaning.

Provision of this material in no way constitutes EPA or ICOLP recommendation or approval of any company or specific offering. These technologies require case-by-case evaluation. A list of vendors and references that can be used as additional sources of information is provided in the back of this manual.

Underbrush Cleaning

Underbrush cleaning scrubs only one side of the printed circuit board assembly, typically the fluxed solder side (see Exhibit 7). Because any fluxing and soldering technique will result in the presence of top-side flux, this cleaning process has been used only in conjunction with very mild fluxes leaving residues that need not be completely removed. This cleaning process is not designed or suited for either SMT or total cleaning of the printed circuit assembly. Reflowed surface mount residues have not been effectively removed by either detergent or hydrocarbon/surfactant underbrush equipment.

Key features of underbrush cleaning are:

- Equipment costs range from $40,000 to $70,000;
- In-line or batch processes can be used;
- Not recommended for SMT;
- Solvent, detergent, and hydrocarbon/ surfactant can all use the same equipment.

A typical underbrush cleaner has a conveyor carrying product across the two separate stainless steel tanks (see Exhibits 8 and 9). The washing section ranges in length from 3 to 6 feet. Seals and gaskets use Teflon® and Viton®. Most plastics and silicone rubbers are avoided.

A pair of rotating brushes in the first tank pick up the wash solution from the sump, and mechanically scrub the flux-covered bottom of the printed circuit board. The concentration of the wash solution can range from 2 to 8 percent detergent in the aqueous process and 35 to 50 percent hydrocarbon in the semi-aqueous process. The cleaning section of the tank can be heated to enhance the cleaning action. For example, the aqueous wash solution can be heated to between approximately 140° and 160°F and the semi-aqueous solution can be heated to approximately 105°F. The solution is added automatically to maintain operating levels of the cleaning tank.

A second tank with rotating brushes rinses the bottom of the boards. The temperature of the rinse water may be anywhere from 75° to 160°F. Fresh tap or deionized water is added constantly while the used rinse is discharged.

The following are some important characteristics of underbrush cleaning:

- Wave-soldered assemblies can be processed at four to eight feet per minute.
- Terpene emulsions can last two months before showing signs of deterioration when running 400 sq. ft. of product per shift.
- Monthly replacement of the aqueous solution in the wash tank avoids saturation of the cleaning solution with rosin and subsequent decrease in cleaning efficiency.
- This process usually applies only to noncorrosive rosin fluxes.
- The amount of terpene consumed is generally about 50 percent of the quantity of solvent used in underbrush processing.
- Monoethanolamine is a typical detergent used in underbrushing. The detergent consumption rate is approximately two drums a week when producing about 1,000 sq. ft. of product per day.
- The conveyor system must be designed to suit the product.
- Hydrocarbon/surfactant emulsion rinses well at a variety of temperatures, but warm water enhances the drying of the printed circuit board. This drying is an advantage to downstream assembly and test functions. Water quality will affect SIR results.
- The rinsing section uses a continuous supply of 0.5 to 1.0 gallons of water per minute. The flow cascades forward in the cleaning machine and excess rinse overflows through a particle filter. Local regulations should be consulted prior to discharge to the drain. The choice of deionized

exhibit 7

exhibit 8

exhibit 9

water or tap water depends on the quality of the local plant water supply.

Operation and Maintenance

In a manufacturing environment, the ability to continue operations often depends on backup strategies and options.

- In general, the basic design and control of underbrush systems is simple, clear-cut, and easily-managed. The use of a noncorrosive flux simplifies process control.

- Fire and odor are usually the main concerns when a hydrocarbon cleaner is suggested. A 50-50 hydrocarbon-water emulsion used in the wash stage, however, reduces any fire hazards. Applying standard operational methods for ventilation control reduces odor problems.

- Important process factors to control are the selection of brushes and the water supply.

- Brush material, brush size, and level of cleanliness required determine how aggressive the cleaning should be.

Hydrocarbon/Surfactant Spray Cleaning

This type of cleaning process is analogous to grease-removing hand cleaners commonly used in the home. The cleaner dissolves the soil, even in difficult to clean areas, but it is not volatile enough to evaporate. The solvent contains a surfactant that allows the solvent/soil mixture to be rinsed away with water.

Typically, these cleaning systems have the following sections:

- Wash section with hydrocarbon/ surfactant spray;
- Water rinse section;
- Drying section.

Concentrated hydrocarbon/surfactants have been shown to be more effective cleaners than either CFC-113 or aqueous cleaners for cleaning printed circuit board assemblies, especially those with SMT (see Exhibit 10).

The key points to note are:

- Equipment costs range from $90,000 to $225,000;
- Applicable for in-line systems;
- Excellent for SMT cleaning;
- More than adequate for through-hole cleaning;
- Retrofit of aqueous systems to terpene systems may be unsafe because of flammable mist formation;
- 9 fpm run rate potential;
- Flammability and waste stream issues are manageable.

These units look much like any in-line, conveyorized aqueous or solvent cleaner. The cabinets are made out of stainless steel and are usually at least 15 feet long. The first half of the system is the hydrocarbon/surfactant solvent wash module, and the second half is the rinse and dry section. The equipment can be configured as one long cabinet or as two in-line modules. Services must include fire control, ventilation, power, drain, and water. The rinse module may utilize an additional cabinet to recycle the water. If the cleaning facility uses a water-immiscible hydrocarbon/surfactant solvent, a separation chamber is added to allow the solvent to decant from the water (see Exhibit 11). All hydrocarbon/surfactant spray washing systems use a hydrocarbon solvent at full strength.

Virtually all hydrocarbon/surfactant spray cleaning machine manufacturers adequately manage the important concerns listed below:

- Flammability can be controlled in the cabinet by:

  -- Avoiding heat input to the system from both the solder process and from the spray pumps;

  -- Avoiding formation of hydrocarbon aerosol caused by a spray stream impinging on a surface.

  -- Using under-surface spraying. This technique avoids mist formation by spraying the circuit while it is immersed in the liquid. In some cases, it can be used without inert gas fire protection.

- Because some of the hydrocarbons are considered VOCs, adequate containment is necessary. In the case of terpenes, odor also can be objectionable and may need to be controlled.

exhibit 10

exhibit 11

- Segregation of hydrocarbon/surfactant concentrate from water makes handling waste solvent and wastewater more manageable.

- Machines must be constructed with compatible materials.

Hydrocarbon/Surfactant Wash Section

Because spray-under-immersion reduces emissions and fire hazards, new in-line semi-aqueous facilities are moving away from direct spray cleaning. The wash module sprays concentrated hydrocarbon from a room temperature recirculating sump. To avoid forming a terpene gel, this section must be separated from the water rinse module. This segregation is accomplished by using separate conveyor sections for each module. Dragout of nearly 9 grams of solvent per square foot of board area has been reported. An air knife is one method used to remove excess surface liquid from the wash module. It should be noted that an air knife can produce a mist of the hydrocarbon. The use of an air knife is not recommended in spray machines as it can make it difficult to design a nitrogen inerting system. In a nitrogen-type system, the goal is to prevent air from getting into the spray zone so that the oxygen stays at a safe level, usually 6-8 percent compared to air which is 20 percent oxygen. An air knife will inject air into the system and the oxygen concentration will rise to unsafe levels.

The wash area, not the rinse section, will present the fire hazard. An incoming burning printed circuit board could be an ignition source. The atomized spray and the impact of the solvent against the printed circuit boards create flammable atmospheres even though the temperature of the solvent is below its flash point. These hydrocarbon materials are conductive enough that a static electric charge is not a problem in properly bonded and grounded systems.

Water Rinse Section

As in most water wash systems, the cleanest water enters the system closest to the exit and cascades forward in the machine. The first rinse is always done with the worst quality water that often overflows from that point to a drain. Air knives in the rinse module remove the bulk of the rinsing water on the surface.

The rinse module often sprays deionized water from a recirculating sump. The use of deionized water is an internal decision, affected by local water quality and product cleanliness requirements. Before exiting the rinse module, assemblies are sprayed with a final rinse of fresh deionized water at a flow rate of approximately 0.75 gpm. A flammable atmosphere is unlikely in the rinse module.

The rinse step is a critical parameter in cleaning because an improper rinse can result in SIR dropping by two orders of magnitude when hydrocarbon/ surfactant residues are left on the board.

Drying Section

Although the use of infrared heaters aid in drying the printed circuit boards, the drying process in these systems usually emphasizes blowing off residual water rather than drying entrapped water and residue.

Operation and Maintenance

In cleaning SMT products, the wash sump should be drained once or twice a year, and the spent hydrocarbon/surfactant should be barrelled and disposed of as fuel. The larger machines have a wash sump capacity of 110 gallons; the hydrocarbon/surfactant cost is about $40/gal, and the disposal cost will be nearly $75/drum. The frequency of change will increase if more than average amounts of soil must be removed.

The vent system and air knives used in the wash section affect the amount of solvent consumed per board. Unless exhaust ventilation is excessive, hydrocarbon/surfactant loss is almost entirely a result of solvent dragout either by entrapment around board-mounted devices or by surface film residue. Evaporation usually accounts for only a small portion of hydrocarbon/surfactant losses. Typical dragout should be between 9 and 13 grams per square foot of product.

Typical servicing procedures for cleaning equipment include lubrication of drives and bearings, belt and tensioner adjustment, tightening or replacement of seals and gaskets, and replacement of filters.

These units should be no more difficult to operate than any other in-line system. An enforced preventive maintenance program and a spare parts program are desirable.

Using an existing water cleaner for the rinsing and drying portion of the operation would significantly reduce the capital outlay.

WARNING: THIS MANUAL DOES NOT RECOMMEND THE USE OF ANY FLAMMABLE SOLVENT IN EQUIPMENT THAT IS NOT PROPERLY PROTECTED AGAINST FIRE. Using a hydrocarbon/surfactant solvent in equipment not designed for its use (e.g., putting the solvent in unmodified aqueous cleaning equipment that generates mists in air from the sprays) would represent an extreme fire hazard and cause potential for personal injury. Equipment such as an unmodified aqueous sprayer is commonly found in printed circuit board assembly shops, and there is a natural desire to utilize existing equipment before deciding to purchase new equipment.

Batch Hydrocarbon/ Surfactant Cleaning

The first cycle in a hydrocarbon/surfactant batch cleaning machine is the wash step and the second cycle is a water wash and rinse step. The units tend to be very simple and durable. The capital cost is low but the operating costs are relatively high. This combination makes the units best suited for low volume cleaning.

The performance of these batch cleaners is similar to the hydrocarbon/surfactant in-line machine, except for throughput capacity.

The following points should be noted:

- Average equipment costs range from $10,000 to $70,000;
- Batch cleaning is applicable for SMT and through-hole technology;
- In most instances drying with air knives or heated air is necessary. This requirement increases the cycle time of the cleaning process.
- Overloading reduces the cleaning or rinsing effectiveness of these units;
- Capacity will vary by board size and racking configuration. Maximum panel size is about 18" x 20";
- Unlike the in-line units, these small packages can be quickly and conveniently brought on-line as required;
- Some units utilize nitrogen blankets over the solvent as a fire control feature;
- Transfer between machines can be manual or automated;
- Typical water usage is about 1-5 GPM at a temperature between 90° and 140°F.

In-Line Aqueous Cleaning

Aqueous cleaning of printed circuit boards relies on the spray cleaning process. Cleaning per-formance depends on the quality of process water. Plain water is effective for ionic cleaning and water-soluble fluxes. With the addition of saponi-fiers, water can remove nonpolar substances such as oil and rosin flux as well. Although difficult, cleaning of surface mount assemblies is possible with this method.

Virtually every available in-line system has the same configuration (see Exhibit 12), and most systems are designed to be used with saponifiers. Most of these machines can be used as the rinse module for a hydrocarbon/surfactant system. This flexibility reduces the capital outlay for a process change to hydrocarbon/surfactant systems. However, full conversion of in-line aqueous machines would require new wash sections.

Factors to consider in evaluating in-line aqueous cleaning systems are listed below:

- Expect average in-line aqueous system capital costs ranging from $40,000 to $150,000;
- Be aware of applicability for SMT processing with limitations;
- Because water treatment is expensive, first try cleaning with tap water and then shift to purified water if the boards are not sufficiently clean;
- Prewash sections can remove 70 to 80 percent of the soils on a recently soldered printed circuit board, thereby extending the life of the wash tank solution. However, the water stream from the wash section must be filtered to remove heavy metals that might result from overextending the wash tank bath life;
- Anticipate process water temperatures up to 160°F;
- Match flux to saponifier using a chemical analysis. Experiment only when adequate support is provided;
- Blowing off excess solution from the board is effective as a first stage in the drying process, especially when saponifier is used;
- Construction materials can be either stainless steel or plastic (usually polypropylene). Each has advantages and disadvantages. When making a selection, consider durability, resistance to heat, fire resistance, heat retention, chemical resistance, aging, and repair;
- Build in access to frequently-maintained components, such as sumps, filters, drains, and float switches. Consider the quality of hardware and seals;
- Anticipate using mechanical and chemical descalers. Use sheet tube heaters and easily replaced spray assemblies;
- Install a pressure piston head on the water supply to reduce hammering in the line caused by fast actuating water supply solenoids;
- As a first choice, use stainless steel vents, and verify that condensate leaks will not be a problem;
- Include filters on all water lines, especially the drain line, and change the filters as recommended. Protect all solenoids with filters;
- Secure necessary permits before purchasing systems. Maintain waste stream monitoring logs after installation. Keep abreast of relevant regulations;
- Recirculate water to insulated tanks with low gradient immersion heaters where possible, or use closed loop water recycling;
- Product sensing systems are recommended to reduce operating costs by shutting down the pump when no product is being cleaned;
- Consider modular units that allow reconfiguration as needs change;

exhibit 12

- Separate baths with splash curtains, notched conveyor rails, drain areas, and air knives to maintain machine efficiency.

Aqueous cleaners rely on spray nozzles to clean printed circuit board assemblies. Innovative nozzle schemes are emerging to provide better cleaning performance. For example, one available nozzle design uses high velocity, high volume water curtain systems to direct water at a 90° angle to the conveyor. In this system, water does not bounce back or splash after impinging the conveyor. Instead, the water is directed radially outward, thus enabling flow directly under conventional PCB and SMT devices.

Batch Aqueous Cleaning

"Dishwasher"-type batch spray machines are similar in appearance to household dishwashers. These machines have several cleaning stages. Electronic assemblies are loaded into the machine in racks, and the machine fills with water to a designated level. The water then heats up and sprays onto the electronics assemblies. These machines are fairly effective but they tend to operate on long cycles. A typical dishwasher batch machine has a throughput of 10 square meters of boards per eight hour shift. This throughput rate can be a disadvantage because most soldering machines have at least twice this throughput.

High throughput batch machines are two to three times more expensive than conventional batch machines and require more floor space. However, they also have the following benefits compared to a dishwasher batch machine:

- A higher throughput and three to eight times more thorough cleaning;
- 75 percent less water consumption;
- 20 percent lower electricity usage because the wash water remains in the tank and is not drained each cycle, thus saving in heating costs; and
- The full output of most wave soldering and reflow machines can be managed.

During the two to three minute wash cycle, 120°F water is pumped to high pressure jet sprays that wash the printed circuit board assemblies. The machine stops for a 15 to 30-second period to drain the water and then fan sprays rinse the boards with water for 20 to 40 seconds.

Batch machines are not equipped with a drying unit. A dryer is generally installed in addition to the batch machine to avoid having to dry the walls of the batch machine itself, to allow better heat accumulation (saving energy), and because the physical movement of the electronic assemblies from the batch machine to the dryer shakes off considerable quantities of water. Drying machines generally consist of upper and lower rotary air knives fed from a large centrifugal blower. When the cycle is started, these air knives blow off 90-98 percent of the residual water. Next, hot air blows across the parts to remove the excess water by evaporation. After cooling, the printed circuit boards are generally dry and can be tested immediately.

The effectiveness of batch cleaning machines depends a great deal on the operator. To improve process control and reduce the chance of operator error, batch machines are equipped with automated controls for temperature, cleaning solution dispensation, wash and rinse cycle times, and rinse water cleanliness. Proper dispensation and temperature control of saponifiers is especially important because this type of cleaner can leave flux residue or attack the electronic assembly if used incorrectly. Automated machinery also is available to load and unload batch machines.

WATER AND WASTE STREAM HANDLING

Pre-Treatment of Water

The quality of the water used in aqueous and semi-aqueous processes is important to achieve high cleanliness. Therefore, the requirements for water supply and water quality must be understood. In some areas, water is in short supply and in others areas, the quality of water is not suitable for cleaning printed circuit boards.

Factors to consider for water supply, quality, and pre-treatment are:

- Water supply requirements vary between machines and with various recycling schemes;
- Water supply requirements range from 0.5 gpm to 10 gpm with 3 to 5 gpm being most common. Systems that recycle water require water only to make up for evaporation and dragout;
- Pre-treatment of water may be required to reduce hardness and suspended particulates, or to reduce machine maintenance. Water softening can be done with off-the-shelf water softening packages;
- Water with hardness greater than four should not be used with saponifiers;
- Tap water costs less and wets better than purified deionized water, but can introduce contaminants or interfere with the cleaning chemistry;
- Highly deionized water can cause problems.

Typically, aqueous and semi-aqueous cleaning will use tap water and/or deionized water. If the tap or deionized water is inadequate for the specific application, water treatment may be required. The cleanliness of assemblies rinsed with water is largely determined by the quality of the rinse water.

The following treatments can adjust water quality.

- Mechanical filtration to remove suspended particles;
- Sedimentation (to allow suspended particles to settle);
- Coagulation (to remove fine particles in colloidal suspension);
- Carbon filtration (to adsorb gases, vapors, organic substances, and colloidal solids);
- Bacteria filtration (to remove bacteria and other microorganisms);
- Irradiation with ultraviolet light (to destroy bacteria and other microorganisms);
- Water softening (to exchange calcium and magnesium). Softened water must never be used for final rinse, as the sodium ions are hygroscopic and thus incompatible with electronic assemblies;
- Reverse osmosis (to remove dissolved solids and colloids).
- Ion exchange (to remove ions of all types except hydrogen and hydroxy ions). This type of water treatment can be either mixed-bed or separate-bed, and have on-site or off-site regeneration. Ion exchange is ideal for polishing reverse osmosis water, or for providing rinse water for small- to medium-size installations.

Depending on the water quality, different combinations of the above units are used to achieve the desired water quality.

Post-Treatment of Wastewater

Wastewater generated from aqueous and semi-aqueous cleaning processes may require treatment before being discharged to local sanitary drains or publicly owned treatment works (POTWs).

Wastewater can contain: (1) organic matter such as flux residue and chemicals used in cleaner formulations (monoethanolamines, terpenes, and other hydrocarbon/surfactants); and (2) metals present either as dissolved metals or as suspended metal (dissolved metals will be present in saponified aqueous cleaning processes due to the alkalinity of the solution). The wastewater generated from a saponified aqueous cleaning process also can have a high pH.

Note the items below in determining the disposition of wastewater:

- Local, state, and federal regulations on wastewater may require treatment prior to discharge into sewer or septic systems.
- Wastewater discharge standards are expected to become more stringent. Systems should be designed to minimize or eliminate water discharge.
- Most saponified aqueous wastewater contains alkanolamines, raising the pH of the wash tank to between 10.5 and 11.8.
- Rinse water from saponified aqueous cleaners and hydrocarbon/surfactant cleaners will have a high biological oxygen demand, unless cleaner dragout from the wash section is minimized.
- Process water temperatures range from 120° to 165°F.
- Wastewater can be removed from the site by a contract waste hauler.
- Closed loop water packages are available for many, but not all, applications.

Metal Contamination Control

Dissolved metals, primarily copper, tin, and lead, are toxic to both people and to the microorganisms that are part of wastewater treatment facilities. Metals appear in wastewater as a result of dissolution of the metal oxides on parts being soldered, the flux activators, and etching by the alkaline cleaner. More metals will be dissolved when metal particulates, or metal fines, are allowed to soak in the cleaning solution. Solder balls, solder splash, and component parts are common types of metal particulate found in wash tank sumps.

Metal contamination can be controlled by the methods listed below:

- Ion exchange beds are the most commonly used technology to reduce concentration of dissolved metals in wastewater. This technology is well developed and established. Resins are available for removing a wide range of cation and anion types. Regeneration of the bed results in the production of a salt solution which must be disposed of properly. Eventually, resin beds lose their efficiency and must be replaced, thereby producing additional waste to be managed properly. Relative energy costs for this system are low, but the ion exchange process is fairly capital intensive. However, it can handle a high volume stream and has a long useful life.
- Filters are an inexpensive and effective way to remove metal fines. When filtration efficiency drops off, it is necessary to backwash the filter bed to remove accumulated solids. These solids must be disposed of as a sludge or mud, and may present a disposal problem. Relative energy costs and other requirements are low.
- Lime and caustic soda can precipitate metals out of

solution.

The following suggestions also will help control metal contamination:

- Monitor the alkalinity of the saponified aqueous solution to avoid increases in dragout of heavy metal contaminants.
- Limit the amount of saponifier in the wash system to the minimum required for the process.
- Minimize the period of time a product is in the wash system.
- Include particle filters on the wash tank.
- Change the filters as required.

Organics

Organic materials found in process wastewater are generated from hydrocarbon chemicals and from surfactants found in the chemical cleaners and fluxes used in soldering.

Carbon adsorption is commonly used to remove organics. It is important to note the items listed below when considering carbon adsorption:

- Carbon adsorption is one of the most efficient organic removal processes available;
- Carbon adsorption is reversible and the carbon beds can be regenerated;
- Control of the effluent stream entering the carbon bed is critical to both the cost of operation and the resultant quality of treated water. A mixed, low concentration waste stream is very difficult and expensive to treat;
- Some organics such as rosin can quickly exhaust the carbon, thus reducing the effective life of the bed;
- If the dragout of organics from the cleaning process is minimized, carbon adsorption may not be required.

Ultrafiltration is another membrane filtration process that is used to separate high molecular weight solutes or colloids from a solution or suspension. Pressure is applied to force the solvent through the membrane after which the solute is collected upstream, and the solvent (containing very small molecular weight solutes) is collected on the downstream side of the membrane. The process concentrate and filter media may require treatment prior to disposal. Relative energy costs tend to fall in the medium range, whereas relative capital costs would be on the high side due to the custom-designing of the filter media to a specific range of solutes to be controlled.

Reverse osmosis is used to remove dissolved materials from water by filtration through a thin membrane. Pressure is applied to force pure water molecules through the membrane, leaving the larger contaminant molecules behind. Reverse osmosis has been used to purify brackish/sea water for drinking water purposes. It has also been used to separate and concentrate heavy metals, cyanide, ammonia, nitrates, and a variety of organic materials such as glycols, organic acids, higher molecular weight alcohols and carbohydrates. A concentrated liquid waste containing the removed contaminant must be disposed of properly. Careful pilot testing is often required to tailor the porosity of the membrane for each specific application. Many solvents and oxidizing agents may damage or destroy particular kinds of membranes. Compatibility of the membranes and the proposed solvents should be tested prior to implementing the alternative technology. Relative energy costs are in the medium range. Capital and operating costs vary depending on the pre-treatment required, stream volume and level and type of contaminant(s) to be removed. In general, the relative costs are expected to be high. This process requires sophisticated pre-treatment and operating equipment as well as sophisticated control devices.

pH

Saponified aqueous wastewater is alkaline, having pH levels between 7 and 12, depending on the cleaning process. The type and strength of the chemical cleaner used also has a direct bearing on the alkalinity of the wastewater. Since the effluent is alkaline, corrective treatments include the addition of sulfuric or hydrochloric acid. The neutralizing process can be carried out continuously or in batches and is economical. The primary expense is the cost of the mixing tank. The operating cost is essentially the cost of the acid.

Recycling Equipment

Recycling equipment can be used to purify and

recirculate the rinse water used in rosin flux cleaning operations, to purify all the wash and rinse water used in a water-soluble flux cleaning operation, and to purify the rinse water generated from semi-aqueous cleaning processes. Recycling reduces energy use and avoids disposal treatment costs. Exhibit 13 shows the concept of a recycling treatment scheme.

A recycling system consists of filtration media that remove particles and suspended matter (such as solder balls), an ion exchange bed that removes dissolved metals, and carbon adsorption that removes organic matter. The water regenerated from the recycling system is used as process water. Recycling equipment can be retrofitted to existing cleaning machines. Different recycling equipment and chemistry are required for rosin and water-soluble fluxes because ion exchange beds are rapidly exhausted by saponifier residue.

Recycling systems for semi-aqueous cleaning processes can be used with hydrocarbon/surfactant solvents that easily phase separate from water (Exhibit 14). The advantage of the hydrocarbon/surfactant system over an aqueous cleaning process is that the contaminants (soils) removed from the printed circuit board are present in the solvent phase that can be separated from the water phase. This separation reduces the soil content in the recycled water. The hydrocarbon/surfactant phase is separated from the water phase using a unit such as a decanter. The water phase is then recycled in a unit such as the one described in Exhibit 14.

Contract Hauling

In certain cases, especially for small users of aqueous and hydrocarbon/surfactant cleaning processes, it might be more economical and efficient to enlist contractors to haul the waste instead of recycling or reusing the wash water. In recent cleaning system designs, the volume of wastewater discharged is relatively small compared to continuous, once-through systems (no recycling). This is particularly true of the hydrocarbon/ surfactant processes, especially if the system uses a concentrated solution in the wash cycle. Waste from the hydrocarbon/surfactant wash stage is a fuel source for incinerators or kilns.

exhibit 13

exhibit 14

RECAP ON MANUAL

This manual has identified a structured program that provides basic information and identifies key items that must be considered when selecting an aqueous or semi-aqueous cleaning process. The manual has provided:

- Key technical and economic issues that must be considered while selecting an alternative cleaning process;
- Major characteristics of three types of cleaning processes: water, water with the addition of a saponifier, and hydrocarbon/surfactants;
- Detailed description of machines used with these types of cleaning processes; and
- Information on pre- and post-cleaning treatment of water.

The next section builds on this basic understanding of aqueous and semi-aqueous cleaning processes and presents detailed case studies of these cleaning applications being implemented in industry.

CASE STUDIES OF INDUSTRIAL PRACTICES

The following section presents actual industrial experiences with some of the alternative technologies discussed earlier in this manual.

Mention of any company or product in this document is for informational purposes only and does not constitute a recommendation of any such company or product, either express or implied by EPA, ICOLP, ICOLP committee members, and the companies that employ the ICOLP committee members.

- ***Case Study #1:*** Terpene Cleaning of Surface Mount Assemblies;
- ***Case Study #2:*** Terpene Cleaning of Printed Circuit Board Assemblies;
- ***Case Study #3:*** Micro-Droplet Aqueous Cleaning of Surface Mount Technology;
- ***Case Study #4:*** Organic Acid Flux Qualification for Aqueous Cleaning;
- ***Case Study #5:*** Heavy Metals Removal System
- ***Case Study #6:*** Conversion from CFC-113/Methanol Cleaning to Aqueous Cleaning for Medium-Sized Surface Mount Device Assembler

CASE STUDY #1: TERPENE CLEANING OF SURFACE MOUNT ASSEMBLIES

Case study #1 describes AT&T's terpene process for total immersion cleaning of surface mount assemblies. Traditionally AT&T and most of the industry has relied on CFC-113 solvents for removing residues from surface mount components. For both performance and environmental reasons, however, AT&T selected an in-line terpene spray cleaner.

The formulation of the d-Limonene/surfactant material known as Bioact® EC-7 and the associated development of a cleaning process to effectively utilize this new semi-aqueous material constitute a cleaning technology that provides the benefits of both solvent and aqueous cleaning. The process for using EC-7 in cleaning printed circuit board assemblies involves spraying the assembly with EC-7 concentrate. The EC-7 spray removes the bulk of the flux residue by emulsifying or dissolving the constituents of the flux residue. The remaining EC-7/flux residue is rinsed from the assembly with water.

The unique properties of EC-7 determine its mode of use and the design of the facility. The material has a strong citrus odor, a boiling temperature of about 350°F, a vapor pressure of 1.6 mm Hg and a closed cup flash point of 117°F. Since EC-7 has a deteriorating effect on some elastomers and plastics, construction materials and component qualifications demand considerable attention. These factors resulted in the need for a machine different from any system used before at AT&T.

AT&T determined that commercially-available systems were not adequate for cleaning surface mount components with EC-7 based on results obtained from material characterization process studies. Therefore, equipment vendors were approached regarding their willingness to undertake a customized project. Based on discussions with the individual manufacturers on the project and the quotes received on the proposed equipment, it was decided that Detrex Corporation would build, per AT&T specifications, the first production EC-7 spray cleaning machine.

Cleaning equipment must meet the following requirements:

- All construction materials including seals and gaskets must be compatible with EC-7 (such as stainless steel, Viton®, and Teflon®);
- Mechanisms to control dragout and contain the spray aerosol are required to minimize material loss and odor;
- High pressure spray is needed to facilitate cleaning under low stand-off components;
- System throughput, in continuous operation, should be suited to the soldering operation used;
- Product must be washed and rinsed with maximum isolation between wash and rinse sections;
- Fire safety measures are required to maintain EC-7 below its flash point. These measures include an inerting system to prevent ignition and an automatic system to shut down the facility in case of a problem.

The spray machine was designed to function adequately in a production environment, yet be flexible enough to determine optimal cleaning parameters. The machine incorporated a programmable logic controller, separate controls for each individual component in the system, and both high and low pressure spray sections. Two conveyorized spray modules are arranged end-to-end in the pass-through system. Schematics of the modules are shown in Exhibit 15 and Exhibit 16. Each module has a 60 gpm low pressure (approximately 30 psi) and a 40 gpm high pressure (approximately 90 psi) spray section followed by an air knife to remove excess surface liquid. The low

exhibit 15

exhibit 16

pressure spray zone is approximately three feet long and has 27 individually adjustable nozzles in six spray headers. The wash module sprays concentrated (100 percent) EC-7 from a 110-gallon recirculating sump maintained below 77°F. The rinse module sprays deionized (DI) water from a 110-gallon recirculating sump. The rinse module differs from the wash module in that the rinse module sump overflows to a sanitary drain. Before exiting the rinse module, assemblies are sprayed with a final rinse of fresh DI water at a flow rate of approximately 0.75 gpm. The final rinse water cascades forward into the rinse sump. The rinse module is also equipped with air knives to remove the bulk of the surface rinsing water. The dryer is made up of an air knife section, a recirculated hot air section, a series of infrared dryers with high air flow convection, and a series of infrared dryers with low air flow convection.

Other features incorporated into the design focus on issues involving EC-7 material compatibility. Although EC-7 tends to swell certain plastics and elastomers. Teflon and Viton have been found to be acceptable materials.

Due to the relatively large size (approximately 32 ft. x 6 ft.) and number of features included in the new machine's design, extensive preparation was needed to install the machine in the factory.

The following services were required for this customized machine:

- Nitrogen Supply: The design specification required a nitrogen supply of approximately 2,000 cfh. At present, consumption of nitrogen is about 1,200 cfh and it is anticipated that the consumption can be reduced further.
- Chilled Water: Chilled water (approximately 50°F) is supplied to the machine at 5 gpm to maintain the 110-gallon sump of EC-7 below 70°F and the recirculating air knife below 95°F.
- Rinse Water: Deionized rinse water is supplied at 0.75 gpm at 125°F from a deionized water heater.
- Electricity: This facility requires a 200 amp, 480 volt, 3-phase electrical service.
- Exhaust: The exhaust was specified to be 2,800 cfm maximum so that all recirculating air flow could be 100 percent exhausted if required.
- Drain: Disposal of the rinse water is to a sanitary drain. The effluent flow is approximately 0.75 gpm. Test ports are provided to sample water quality.
- Eye Wash Station: Because chemicals are being used, an eye wash station in the area is necessary.

When assessing the key items to implement a cleaning technology, it is important to consider cleaning effectiveness, qualification issues, material usage, wastewater and disposal requirements and process economics. These factors are discussed below.

Cleaning Effectiveness

The spray facility has been successfully used to clean SMT printed circuit boards with up to 5,000 surface mount reflowed interconnections. Omega-Meter® 600-SMD testing of one production code with 1,350 interconnections indicated an average decrease in ionic residue from 6.1 micrograms NaCl equivalent per square inch of surface area before cleaning to 1.8 after cleaning. This printed circuit board code contained a mix of 68 to 84 pin plastic leaded chip carriers, 8 to 28 pin small outline integrated circuits, and 1205 to 1210 size ceramic chip capacitors. Measurements show that not only are terpenes effective cleaners but they also provide improved ionic cleaning results when compared with CFC solvent cleaning.

Qualification Issues

During the trial of the EC-7 spray machine, interdigitated, metallic-conductor comb-patterned test coupons were processed through the cleaning system using various rinse water temperatures. It should be noted that only the rinse water temperature was varied since the EC-7 spray is maintained below 77°F. After processing, these boards were maintained at 95°F, 90 percent relative humidity and 50 volt DC bias for 24 days. Once each day, the bias was removed and an opposite polarity of 100 volt DC potential was applied and the SIR measured.

The average log SIR for these FR4 test boards are shown in Exhibit 17. The rinsing temperature was varied from 77°F to 105°F to 150°F. No degradation of SIR was observed over this range of temperature. SIR values for boards underbrushed with a 35 percent emulsion of EC-7 maintained at approximately 110°F are plotted as dashed lines in Exhibit 17. These boards were underbrushed with 35 percent concentration EC-7 at 135° F and underbrush rinsed with either 65°F or 150°F water. Neither the EC-7 emulsion, brushing action, nor the rinsing temperature degraded the SIR.

Exhibit 17 also plots the SIR for boards sprayed with concentrated EC-7 and not rinsed. These EC-7 sprayed boards were processed through the infrared drying section of the rinsing module. Exhibit 17 shows a decrease in log SIR to about 8 for these boards. This drop is most likely due to polymerized EC-7 and surfactant remaining on the surface. Although the SIR is "low" in value, the trajectory is positive, indicating that there is no metal migration or corrosion taking place. This test does indicate that the effective rinsing of EC-7 residues is necessary to maintain process control.

In order to test the effect EC-7 has on solder mask material, boards fabricated with stripes of the various solder masks, oriented perpendicular to the interdigitated metallic conductors, were processed. The average log SIR for the boards processed through the EC-7 spray machine at the normal conveyor speed of 9 feet per minute are shown in Exhibit 18. The log SIR for "bare" FR4 boards is typically in the range of 11 to 12. Whenever SIR measurements are used to show the effect of a process or material, control boards must be processed. The log SIR shown in Exhibit 18 indicates that although using solder mask lowers the SIR from the base value of the FR4 boards, the value does not fall below the lower value of 9.5. The log SIR values for the solder mask striped boards exposed to EC-7 are the same or better than the value for their respective controls.
Rather than processing boards at various conveyor speeds to investigate longer exposures to EC-7, it was decided to soak boards in EC-7 for an extended period (24 hours) and measure the change in SIR over maximum EC-7 exposure and minimum rinsing. If boards were processed in the EC-7 spray machine using various conveyor speeds, the rinse duration as well as the EC-7 spray duration would be varied. Because of unforeseen experimental interruptions and scheduling, the test boards soaked in EC-7 for 7 days. After this extremely long soak, the boards were processed through the EC-7 spray machine. The average log SIR for the boards is presented in Exhibit 19. The SIR of the solder mask striped boards was not degraded. The average values for the log SIR were 10 to 11.5. The SIR for the bare FR4 boards decreased approximately two orders of magnitude. This decrease may be due to the absorption of EC-7 into the surface during the extremely long soak. Although the SIR decreased, the trajectory is positive. It should be noted that the 7-day soak in concentrated EC-7 followed by spraying with 90 psi EC-7 and rinsing water did not remove the striped solder mask material from the compounds as judged by visual observations at 20X magnification.

Material Usage

The consumption of EC-7 depends on the amount of EC-7 dragout from the wash module to the rinse module coupled with evaporative losses. Although EC-7 is biodegradable, it has a high biochemical oxygen demand value and could overload a waste treatment system if disposed of in large quantities.
Initial evaluations during acceptance testing indicated that the air knives, if positioned immediately above and below the board surface, could reduce the EC-7 dragout to about 4 grams of EC-7 per square foot of projected board area. Without an air knife, the maximum dragout of EC-7 was measured to be about 29 grams per square foot. With various height components, the air

exhibit 17

exhibit 18

exhibit 19

knives have been adjusted to accommodate the current product code mix. This configuration results in a dragout of approximately 9 to 12 grams per square foot of board area.

Wastewater and Disposal Issues

Because EC-7 residue is noncorrosive, rinsing of EC-7 from assemblies is not as important as the removal of water soluble flux or detergents. Consequently, not only is the rinsing temperature in EC-7 cleaning machines reduced, but the flow rate of rinsing water can also be reduced. Final rinse flow rates of 0.5 to 1.0 gpm are typical in EC-7 cleaning facilities. With these rinsing rates, the concentration of EC-7 in the rinsing sump is in the order of hundreds of ppm. Concentrations of these proportions have presented no biological treatability problems.

The concentration of lead and copper in the rinse water that has been filtered with in-line filters (e.g., 100 micron paper filters) has been measured to be less than 20 ppb and tin has been measured at less than 100 ppb. The metals concentration in EC-7 rinse water continues to be monitored to ensure that high concentrations of EC-7 are not inadvertently delivered to a sanitary drain.

Although the number of reflowed interconnections on boards can number in the thousands, the actual amount of solder paste flux residue needed to be removed is small. The typical volume of solder paste per interconnection is less than one-thousandth of a cubic inch and the paste is only 11 percent flux by weight. Considering the "small" amount of flux and the "large" rosin loading capability of EC-7, it is anticipated that the initial 110-gallon sump charge of EC-7 will not become saturated with flux until after an entire year of production operation. The concentrated EC-7 disposal cost is approximately $50 per 55-gallon drum, and the effluent is recycled by a fuel blender to fire a cement kiln.

Process Economics

The final and one of the most important considerations is the cost of the cleaning technology. Exhibit 20 illustrates the cost of various cleaning technologies based on square foot of board processed. Although we have focused on the elimination of CFC cleaning, we have included costs for aqueous processes to allow the relative baseline costs for cleaning to be determined.

Exhibit 20

SUMMARY OF SPRAY CLEANING COST PER SQUARE FOOT OF BOARD CLEANED FOR VARIOUS PROCESSES

	Water	Terpene	Alkaline Saponified Water	CFC-113	
Chemical	$0.000	$0.121	$0.041	$0.178	
Water	$0.017	$0.002	$0.018	$0.000	
Disposal	$0.003	$0.001	$0.067	$0.000	
Energy	$0.049	$0.026	$0.045	$0.042	
Maintenance	$0.008	$0.008	$0.008	$0.008	
Nitrogen	$0.000	$0.007	$0.000	$0.000	
TOTAL	$0.077	$0.165	$0.179	$0.228	

Source: AT&T.

CASE STUDY #2: TERPENE CLEANING OF PRINTED CIRCUIT BOARD ASSEMBLIES

In mid-1989, one of Motorola plants began an active program to reduce its use of CFC-113 to zero by August 1990. As of July 20, 1990, this plant had accomplished this goal. In 1988, there were 29 active CFC-113 systems in operation using 250,000 pounds of CFC-113 annually (valued at $700,000 at 1990 prices). This Motorola plant accomplished this reduction by taking the following four major steps.

The first step was to repair/retrofit existing stills to prevent excessive solvent loss. In conjunction with this process, a number of CFC-113 stills were also removed from production based on re-evaluation of production needs. New machines and new CFC material technologies were implemented where possible. A 50 percent reduction in the use of CFC-113 was accomplished.

The second step was the implementation of a wave-solder "no clean" system. This action was taken early in 1990, and much work was completed to make the system run cleanly. (The boards soldered are densely populated, leaded top side and surface mount bottom side boards.)

The third step was to implement production of a "no clean" surface mount technology screen paste system. This measure was also completed early in 1990.

The fourth and final step needed to bring this location to the facility-wide CFC-113 elimination goal was the implementation of an in-line terpene cleaner. It was found that some applications could not be replaced with a "no-clean" technology. Certain products demanded a high levels of cleanliness (e.g., products with elastomeric connections, resin flux performance issues, or that needed encapsulation).

- The terpene cleaning option allowed Motorola to clean all the remaining board types, solder stencils, misprinted PCBs, etc.
- The products cleaned in this system are cleaner than their CFC-113 counterparts.
- Motorola has experienced an 80 percent cost savings by cleaning with the terpene system.

Terpene Cleaning System

The plant selected a Vitronics S-2150 semi-aqueous cleaning system. This system consists of one terpene cleaner wash section, followed by one water rinse system. A transfer conveyor couples the two sections. The system dimensions are 23 feet long by 3 feet wide by 4 feet high. The system can handle up to 18-inch wide products, with cleaning speeds exceeding 5 feet per minute. However, drying products with connectors and shields requires the system to run at a slower speed of 1.5 feet per minute.

System Requirements

Motorola's terpene cleaning system requires the following:

- A ventilation system capable of 1,500 cubic feet per minute (cfm) at a pressure of 4 inches of water equivalent.
- Electrical service of 208V at 80 amperes (240V, 380V, and 480V models are also available).
- Chilled water flow of 4 gallons per minute at 65°F or less (for cooling the terpene wash stage). This is necessary to remove heat generated by the terpene pump. Hot boards are not allowed to enter the terpene section since this will trip the unit for terpene overheat.
- Compressed air at 100 psi (20 cfm may be required, according to your drying configuration and need).
- Heated deionized water at 120° and 3 gallons per minute. This site uses water heated by a 54 KV

commercial-grade 120-gallon water heater and purified by the reverse osmosis method. The purity of water required for specific applications varies widely, from city water (this may be a high risk if circuits are high impedance) to greater than 1 mega ohm heated deionized water.

- Terpene-compatible materials in construction. Because terpene can dissolve PVCs, CPVCs, and natural rubbers, only stainless steel, Viton, Teflon, and polypropylene plastics come in contact with the terpene. Motorola uses a polypropylene sump system with a backup pump and sensors. The sump system is an in-house design using a Teel 3/4 H.P. stainless steel pump and a second backup pump as well. A polypropylene water level sensor with alarm and backup switching to the second pump is also used in case of failure. The water container is made of polypropylene plastic.

Operational Issues

Some operational issues that Motorola has experienced are:

- The new system's hourly cost has typically been $7.50 per running hour as compared to $38.50 per hour for CFC-113. This cost is based on a recyclable terpene cleaner (EC-7R).
- Production downtime is near zero.
- The parts are cleaner than their CFC-113 counterparts.
- Flammability is a minor issue, and there are redundant on-board fire detection and suppres-sion systems on the Vitronics equipment.

Future Plans

This site of Motorola plans to install and run a complete stand alone terpene/water recycling system. This requires installing a water scrubber/separator system to capture and recondition the wastewater effluent for reuse. These engineers have chosen a water/terpene separator made by Separation Technologists. This system is designed to separate the terpene from water, clean and filter the heated water to deionized purity, and recycle it for reuse in the water rinse section.

The advantages of such a recycling system are:

- Very low lead or any heavy metal discharge;
- Very low discharge of organic matter (terpene);
- Savings in water and energy costs to heat the water.

In addition, preliminary results have shown that cleaning solder screens and misprinted PCBs in the in-line terpene system unnecessarily and prematurely load the terpene solvent with contaminants and severely shorten the bath life. Therefore, this Motorola plant has decided to use batch cleaning capability to clean both screens and misprinted PCBs. An Electronic Control Design batch terpene system has been chosen at this location.

CASE STUDY #3: MICRO-DROPLET AQUEOUS CLEANING OF SURFACE MOUNT TECHNOLOGY

Since 1974 Digital Equipment Corporation has pioneered aqueous-based cleaning processes for through-hole component modules. However, as surface mount techniques for components emerged, results from traditional aqueous cleaning chemistries and equipment fell short of the expected cleanliness criteria generally accepted in the electronics industry. The failure mechanisms were attributed to more densely packed components and the general topography of surface mounted solder joints as opposed to through-hole solder joints.

Many vendors and users of surface mount processes have been trying to devise methodologies to overcome problems associated with surface mounted components and to extend aqueous cleaning techniques into the surface mount space. Marginal successes have been limited to surface mount architectures with coarser pitches.

Digital perfected and patented a new cleaning process that controls water droplet size and angle of impingement for effectively cleaning rigid leaded surface mount components. The process referred to as "Micro-Droplet" aqueous cleaning will be made available to users of CFCs worldwide, without any charge as part of Digital's corporate commitment to protect the ozone layer.

Micro-Droplet Process Overview

Digital embarked on a program aimed at identify-ing the critical process parameters that assure success for aqueous cleaning of fine pitch surface mount modules. They began with a rigorous engineering evaluation, based on the latest design of experiments and technology, and a strong understanding of the parameters of the printed wiring circuit modules manufacturing process.

The process development program allowed the engineers to identify (previously uninvestigated) key process parameters that would allow fine pitch surface mount modules to be cleaned efficiently without using CFC solvents. While others in the industry had concentrated on their complex chemistries and water pressure variables, Digital engineers defined the angle of impingement of the water and the water droplet size as being the key parameters driving the effectiveness of the aqueous cleaning process, specifically for finer pitch, rigid leaded surface mount components.

Working under a well-defined intellectual property protection agreement, Digital engineers and engineers from Bete Fog Nozzle Company, Inc. of Greenfield, MA (a nozzle design and manufactur-ing firm) collaborated on a combination nozzle design and water delivery system that successfully met or exceeded the cleanliness criteria set for fine pitch surface mount modules cleaned with CFC solvents.

The highlights of this system are:

- The delivery system is designed to create specific micro-sized water drop-lets and provide a continuously vary-ing angle of attack for the water spray.
- The process has been characterized for all rigid leaded surface mount modules currently manufactured for Digital products.
- Hardware to support this technology is available as a "retrofit kit."
- The retrofit kit is field installable on an off-the-shelf aqueous cleaning system.
- Other manufacturers of aqueous cleaning systems may accommodate the retrofit kit at some time in the future, but no effort has been exerted to assure this at this time.

Having successfully met extensive manufacturing qualification procedures and documentation activities, the process has been implemented in Digital's Modules Manufacturing Line. More information on this patented public domain technology can be obtained from the International Cooperative for Ozone Layer Protection (ICOLP). ICOLP's address is provided at the end of this manual in Appendix A.

Process Development

The micro-droplet aqueous cleaning process consists of a rotating arm (as shown in Exhibit 21) that allows the spray to impinge equally on all four sides of the component. This coverage is accomplished using only two nozzles compared to the many nozzles that would be required in a fixed manifold system. This design reduces the total flow rate, thereby minimizing the size of the pump (power outage) required. The need for a high flow rate combined with the high pressure needed in this system would have otherwise required a very large electric motor to power the pump.

The rotation of the arm causes the saponified solution to be delivered intermittently to a particular section on the surface of the circuit board. This intermittence caused by the rotating arm allows the solution that has been sprayed on the particular section of the board to drain from the board surface. Thus, when the spray pattern returns, it will be in direct contact with the surface of the board, not the barrier layer of water that has flooded the surface of the board as in more conventional cleaning operations.

The system uses a helically vaned spiral hollow cone nozzle with a spray pattern angle of 50 degrees. This angle along with the droplet size and flow characteristics causes the water to strike the surface of the circuit board and be redirected under the SMT components without giving up its velocity upon impact, thereby improving the cleaning performance.

The combination of high pressure and low flow rate yields a small droplet size that is needed to penetrate the tight spaces that are a by-product of utilizing surface mount technology. Digital has qualified the process on component packages down to 25 mil lead spacing.

Process Parameters

Digital is now operating the process at the parameters listed below. These parameters were arrived at using experimental design techniques for parametric optimization during nearly two and one-half years of process development work.

Process parameters include:

- Saponifier concentration: 7 percent (in both pre-wash and wash sections).
- Water temperature: 150°F.
- Conveyor belt speed: 3 feet per minute.
- Micro-droplet spray pressure: 400 psi. (All other spray pressures were per equipment vendor's recommendation.)

The new cleaning process uses a Stoelting cleaning machine (model CBW 224) modified with a retrofit kit supplied by Bete Fog Nozzle.

Process Qualification

Based on the optimum process parameters, Digital conducted a number of tests to qualify the process. The tests focused on three areas: cleanliness, joint integrity, and component and module functional testing.

For the cleanliness portion of the qualification the boards were tested for ionic contamination. The results were favorable and the conclusion was that the micro-droplet system removed more potassium while leaving sodium levels only slightly higher. It was clear that the micro-droplet system was removing more contamination than the conventional aqueous cleaner.

The joint integrity testing was conducted by performing pull and peel tests of the leads on 25 mil parts and comparing this data to the empirical data from earlier testing on solvent cleaned

exhibit 21

assemblies. There was no discernable difference in the test data.

Several tests were performed to determine component integrity. Results of the High Acceleration Stress Testing, which is a functional test of the component after accelerated thermal cycling, showed that there were no failures on several different component types.

To check for delamination, an x-ray of the die attach was performed. To further verify that no delamination had occurred, C-Scan was also performed. All test results were negative.

A gross leakage test for violation to hermetic seals was conducted by placing the components in a fluoro-inert solution at 125°C and observing the bubbles that would indicate outgassing in the component. No bubbles were observed during this testing.

Module functional testing at ambient temperature was conducted for over 1 million component hours and nearly 200,000 module hours with no failures.

Process Economics

Process economics includes the capital costs of acquiring the process, the operating cost, and the cost of the treatment of the waste stream that is a by-product of the process. Costs of operating this system will vary widely.

Capital Costs

Capital costs are as little as $30,000 to retrofit an in-line aqueous cleaner and $150,000 to purchase a new cleaner with this modification installed.

Operating Costs

Operating costs are based on a 16 hr/day production of 500 to 700 square feet (which is well below maximum production capacity). Operating costs for this system are broken out in the following categories:

- Cost of saponifier: $125 per day per machine.
- Cost to supply softened water: $3 per day (based on four aqueous cleaning machines).

Waste Treatment Costs

The treatment costs for a system that accommodates four aqueous cleaners are broken out in the following categories:

- Cost to neutralize wastewater: $18 per day.
- Cost of wastewater discharge: $35 per day.

It is important to understand that there is a wide diversity in the costs of dealing with a waste stream and the amount and type of treatment that must be performed to be in compliance with local ordinances. Before selecting a non-CFC alternative, check with local and municipal authorities on requirements.

CASE STUDY #4: ORGANIC ACID FLUX QUALIFICATION FOR AQUEOUS CLEANING

Overview

Case study #4 describes how Company A conducted a program to develop process methods for organic acid (OA) flux usage and to select OA flux candidates for qualification testing. This case study shows how Company A took steps to change from using a rosin flux and solvent cleaning of printed wiring boards to the proposed water soluble OA flux and water cleaning process. Part of this test also required the successful application of a polyurethane conformal coating.

Current processes in Company A utilize a rosin flux (RA or RMA) at the machine soldering area, followed by cleaning with methyl chloroform. A final process requires coating the printed wiring assemblies with a polyurethane. The study was limited to glass/epoxy PWAs with and without permanent solder mask.

Five OA fluxes were tested and two of these were selected for further qualification testing. OA fluxed assemblies were be cleaned to the current cleanliness levels of the rosin based fluxes used in the factory. Solderability defects of OA fluxed assemblies were significantly reduced.

Scope

This case study describes the test program conducted to evaluate OA fluxes for wave soldering. The test program consisted of two subsets. The first flux evaluated was Superior 30 by using a process similar to the existing manufacturing method. The second test procedure evaluated the characteristics of four other OA fluxes and a rosin flux in regard to cleanability and solderability. This program examined flux compatibility with current assembly processes and equipment. Long-term corrosion reliability tests will be performed by Company A during additional flux qualification testing.

Test Plan

The fluxes selected for testing were cleaned with a saponifier and deionized water.

A mil-spec rosin flux was selected as the control to be cleaned with methyl chloroform.

A data package will be developed in the qualification phase of this test program to support specification changes for the use of OA fluxes.

The criteria included:

- Cleanability of post-solder residues

  Visual inspection
  Ionic contamination testing
  Humidity/moisture resistance testing

- Solder yield performance

  Quality Assurance visual inspection per MIL-P-28809A

- Material hazards and safety
- Shelf life
- Equipment requirements
- Compatibility to SMD adhesives, part marking, and tapes

The following machine settings were the same for all fluxes:

- Conveyor speed of 3 fpm;
- Solder pot temperature of 500° F;
- Topside board temperature of 190-200° F;
- Wave solder air knife.

Aqueous cleaning was performed on an in-line machine, at 2 fpm, using the following process conditions:

- Saponifier concentration (Wash 1 stage): 0.4 - 0.6 percent by volume
- Conveyor speed: 2 fpm
- Wash 1 solution temperature: 150 ± 10°F
- Wash 2 solution temperature: 170 ± 10°F
- Final rinse water temperature: 160 ± 10°F
- The recirculating tanks were drained, cleaned, and refilled after the wash solution had been in use 20 hours.

Solvent cleaning was performed using a methyl chloroform in-line solvent machine with a conveyor speed of 2 to 4 fpm and with the following temperature requirements and recommended pressure settings:

- Boil sump temperature: 167 ± 10°F
- Distillate sump temperature: 155 ± 10°F
- High pressure sump temperature: 165 ± 10°F
- Spray-over-immersion sump temperature: 164 ± 10°F
- Pre-clean upper spray pressure: 20 psi
- Pre-clean lower spray pressure: 15 psi
- High-pressure upper spray pressure: 30 psi
- High-pressure lower spray pressure: 25 psi
- Immersion spray pressure: 25 psi
- Distillate upper spray pressure: 20 psi
- Distillate lower spray pressure: 15 psi

With the exception of fluxing, which was hand dipped, was applied to all samples, in a controlled manner, by foaming, Superior 30.

All samples were 0.062 inch thick epoxy glass material. All test samples underwent a solder pre-bake cycle of 200°F for 16 hours. Each flux group consisted of eight boards. Six of the boards were PTH, populated with DIPs and axial parts, and having half of the board covered by a permanent solder mask. Two boards were cleanliness tested for ionic contamination, and four were humidity/moisture resistance tested, with one of these boards having three components removed to check for cleanliness under parts. The remaining two boards were SMT configurations populated with LCCs, SOICs, and chip components. One of these boards was tested for ionic contamination and one for humidity/moisture.

Test Procedure

The following steps constitute the test procedure:

- Label PWAs.
- Apply part marking/overcoating materials on DIPs and cure in accordance with the appropriate specifications. Label the parts accordingly. Apply adhesive dots to boards. This test will be performed to check material compatibility with OA flux. Test boards used for this testing will be separated from the ones outlined above.
- Apply solder paste to PWB and place SMDs.
- Vapor phase solder and clean PWAs.
- Apply OA flux to SMD PWAs and process through wave solder and clean.
- Insert DIPs and axial on PTH PWB
- Flux and wave solder PWA.
- Clean PWAs per aqueous process.

- Quality assurance inspection of PWAs per MIL-P-28809A (must wear gloves).
- Omega meter test two PTH PWAs and one SMD PWA per flux.
- Remove three components from one PTH PWA (schedule for humidity testing) per flux type and check for contaminants underneath parts.
- Conformally coat assemblies with polyurethane.
- Submit all coated samples to quality assurance for visual inspection. Inspection performed at 10X. Record and photograph any anomaly.
- Submit samples to 10-cycle Moisture Resistance testing in accordance with MIL-STD-202, method 106. Measure insulation resistance before and after the first, fourth, seventh, tenth, and post-conditioning cycles of testing.
- Submit all samples for visual inspection after completion of testing. Document and photograph coating anomalies, if necessary.
- Analyze test results.

Test Results and Discussion

Solder Joint Visual Inspection

Using MIL-P-20809A, the ranking of candidates, beginning with the best, was as follows: Kester 2331-ZX, LONCO 3355 NB, ROSIN, Gardiner 5735, Alpha Metal 857, and Superior 30.

Kester 2331-ZX fluxed boards had the lowest solder defect rate and showed a 60 percent improvement over the rosin flux system used in the factory. All OA fluxes were able to solder marginally solderable parts -- parts which are defined as axial parts in storage over 3 years without pre-tinning. Different fluxes exhibited different types of problems, and those noted included solder balls on permanent mask areas, voids, and insufficient fill.

Ionic Contamination

Using the Omegameter 600, all samples passed with readings well below the allowable limit.

Conformal Coat/Moisture Resistance

Polyurethane conformal coating was applied by spray and by dipping. Spray did not provide consistent results.

Tests applied were MIL-I-46058C, MIL-STD-202F, and visual inspection.

While many of the initial readings were lower than expected, these values recovered, and except for 4 specifically identified faults, the post conditioning results were above the minimum requirement of 5.0XE9 ohms.

The visual inspection results revealed that the best OA candidate had slight mealing on one sample, with the rest being acceptable. Coating adhesion was acceptable. On the rosin flux control, one sample had a high degree of mealing and minor delamination on another coating adhesion was acceptable.

DIP Removal/Flux Residue Inspection

There was no evidence of flux residue remaining underneath DIPs after cleaning for all tested fluxes.

Materials Evaluation

Materials used to test OA flux compatibility to completed board assemblies were polyurethane adhesive, epoxy adhesive, marking ink, overcoat materials, and solder stop. No deleterious effects resulting from OA flux interaction with process materials were observed.

Material Hazards/Safety

The prime ingredient in the evaluated fluxes was isopropyl alcohol. Various activators included mild organic acids, hydrohalides, and amines.

Controls similar to those in effect presently would be suitable for safe use of the OA products.

Some fluxes emitted strong odors when soldered. Other samples did not.

Facility Requirements

The flux application equipment should be made of epoxy, polyethylene, polypropylene, or Teflon.

Preliminary investigations indicated that the effluent from cleaning OA fluxes was acceptable for discharge per environmental control. Further analysis of effluent disposal, tied to production levels, will be investigated.

Conclusions and Recommendations

OA flux can be a viable alternative to the currently used rosin-based fluxes for soldering high reliability, mixed technology printed wiring boards.

Screening flux candidates is required to confirm that the most appropriate product is selected, thereby increasing the likelihood of successful process change.

A primary flux candidate and an alternate were presented from this study. Further qualification, such as corrosion testing, and the result of higher volumes of effluent on the waste handling facility should be conducted.

All process materials used in assembling PWAs and all conformal coating products should be evaluated for use with OA fluxes.

Industrial Engineering should conduct a method and cost study for the implementation of OA fluxes to the factory.

CASE STUDY #5: HEAVY METALS REMOVAL SYSTEM

In using the heavy metals removal system, Digital Equipment Corporation's objectives were twofold: (1) to reduce the level of heavy metals in wastewater from several of its aqueous manufacturing processes and (2) to reduce the costs of waste disposal. In addition to meeting these objectives, Digital was required to comply with all applicable federal, state and local regulations. This required, for example, preventing the introduction of pollutants into Publicly Owned Treatment Works (POTWs), establishing point source controls within the manufacturing processes, and designing systems for controlling and monitoring pollutant discharges.

This process should not be confused with a closed loop water supply package for aqueous or semi-aqueous cleaners. No organic matter removal takes place in this process and the wastewater exiting after metal removal and pH balancing is discharged to a local municipal waste treatment facility. The ion beds used in this facility were designed to hold the strong positive metal ions of copper, tin, and lead. These beds do not get saturated with the saponifier. The heavy metal removal package described here is not intended to be used as a closed loop water supply system.

Overview of Removal Process

The three key components of the process are: neutralization, filtration and ion exchange (see Exhibit 22).

Neutralization

The waste effluent first discharges into a pH-waste holding tank for neutralization. The tank control system monitors and controls all process waste effluent within the holding tank. Parameters that are controlled include pH, liquid level, equipment power, and drainage. After neutralization, the discharge effluent enters a second stage heavy metal filtration system.

Filtration System

The filtration system is designed to remove soluble and insoluble metals from the wastewater. It consists of a series of filters of selected type and particle size retention.

Ion Exchange Resin

The ion exchange resin system consists of two down flow cartridges containing 2-4 cubic feet of a specially treated ion exchange resin operating at a flow rate of 4 gallons per minute per cubic feet of resin. The resin is especially designed to remove heavy metals while resisting the adverse effects of organics in the wastewater. The system has demonstrated effective lead removal while processing in excess of 200,000 gallons of aqueous waste effluent from wave solder/surface mount processes.

Maintenance

The primary/final filters have a useful service life of about two to three months. Changing filters takes approximately 30 minutes. Analysis of depleted filters indicate that they are hazardous waste. The service life of ion exchange resin is estimated to be three to five years.

Economics

The annual cost of disposal before installation of the heavy metal treatment system was approxi-mately $36,500. This figure includes disposal costs for 75 drums of hazardous waste. This figure should be compared to the post-installation annual cost of approximately $2,750, a sizeable annual savings of approximately $33,750. Exhibit 23 presents additional information on process economics.

exhibit 22

exhibit 23

CASE STUDY #6: CONVERSION FROM CFC-113/METHANOL CLEANING TO AQUEOUS CLEANING FOR MEDIUM-SIZED SURFACE MOUNT DEVICE ASSEMBLER

Company L in Geneva, Switzerland, is a manufacturer of miniature industrial controls. The reliability of the finished articles is an important feature, bearing in mind that they may be used anywhere in the world and under any conditions. The majority of the products are manufactured on panels about 190 x 160 mm and then cut out. Nearly all of them are surface mount assemblies, using various passive components and SOT-23 and SOIC outlines. Although these components are not the most difficult type to clean under, they are sometimes placed very close together (spacings occasionally less than 0.5 mm). A small number of power circuits are also hand-soldered, using through-hole components.

The SMD circuits are manufactured using screened solder-paste, automatic placement on one side and infra-red reflow. Until recently, the process used an RMA solder paste and a two tank vapor degreaser with a stabilized CFC-113/MeOH azeotrope cleaned the circuits. The hand-soldered circuits were cleaned in the same manner after assembly using an RA flux-cored solder wire. Cleanliness levels obtained were sometimes considered as marginal for the application. After cleaning out the machine and refilling it with fresh solvent, Contaminometer levels obtained on the SM circuits were typically about 0.3-0.4 ug/cm^2 eq. NaCl as general surface contamination and twice this figure for under-component levels. This measurement was related to the surface of the whole panel, including supporting margins. The real circuit surface area was less than half this total. After a few hours of solvent use, the residual contamination levels started to rise rapidly, forcing frequent changes. The throughput did not justify in-house off-line redistillation of the solvent. This was a costly process.

In 1988, Company L decided to examine other possibilities to reduce the cost of the highly competitive articles while equally bearing in mind environmental factors. Initial studies encompassed three potential techniques: no-clean soldering, alcohol cleaning and water-cleaning.

No-Clean Soldering

No-Clean Soldering was examined carefully, but none of the rosin based solder pastes were considered to be satisfactory for SMT because the residues were found to cause malfunctioning under hot, humid conditions. The paste types examined were RMA and DIN 8511 F-SW32 (carboxylic acid activated), mainly with ponderal metal contents in the range of 85-90 percent.

On the other hand, the through-hole hand-soldered circuits were considered reliable when soldered with carefully selected RMA fluxes. Special low-residue flux wires were rejected as being too difficult to use.

Alcohol Cleaning

This process was only briefly examined because of the flammability and toxicity problems associated with using isopropanol. Experimental hand cleaning did seem to produce good results. This study also tested hydrocarbon/surfactant solvents as they became available, but no serious work has been done on them. They were retained as a possibility for future study if all else failed.

Water Cleaning

This part of the study was divided into two sections: (1) using water soluble fluxes and plain water cleaning and (2) using rosin fluxes and saponifier cleaning. The latter process was examined first as experience had already been gained with rosin flux pastes and this option offered the possibility of maintaining status quo on this difficult variable. Concern was expressed that the saponifiers would present difficulties with waste water treatment and with operator safety, due to their high pH odor was also considered a difficulty.

Initial trials with water-soluble solder pastes were far from convincing with respect to three criteria: tack, soldering quality and cleanliness (with experimental manual cleaning). In late 1989, a new solder paste was proposed and that seemed to fulfill all the requirements. This option was retained as a strong possibility.

Practical Implementation

In Spring 1990, the Management of Company L decided to take the next step. Various machine types were examined for aqueous cleaning, keeping in mind the need for flexibility with the possibility of adding saponifier and hydrocarbon/surfactant methods if the process was not initially successful. The machine types examined included modified dishwasher, high throughput batch, and smaller conveyorized types. This last type was the most practical but least flexible and odd demonstration trials did not produce entirely convincing results, although some of the conditions of the trials were questionable. The modified dishwasher type was rejected although economically interesting, because two or three machines would be required to handle the production volume. This configuration would entail difficult manipulation of heavy loaded baskets. The most satisfactory system appeared to be the high-throughput batch system. The manufacturer installed a line on loan in late August 1990.

Numerous practical trials were done using this line, with simple mixed-bed deionization as water purification. The retained water-soluble solder paste demonstrated excellent cleanliness with a six-minute cycle (4.7 minute wash, 0.5 minute drain, 0.7 minute rinse). As the estimated total production would initially entail less than ten cycles per day, adequate spare capacity was provided for planned tripling of the production over the following two years. After the cleaning/rinsing cycle, rotary air-knife drying was done in a basket. After cooling, the dried circuits could be tested immediately. It was estimated that eight baskets each containing 33 panels 160 x 190 mm could be practically cleaned and dried per hour, allowing time for the necessary manipulation.

Contaminometer tests showed the worst achieved cleanliness levels to be about 0.2 ug/cm^2 eq. NaCl as general surface contamination and 0.3 ug/cm^2 under the components. The best figures obtained were about half these levels. This range was considered acceptable. Hand soldered circuits, using a water-soluble flux cored solder wire, demonstrated slightly higher contamination levels, typically under 0.4 ug/cm^2 both as general surface and under-component contamination. This contamination level also was considered acceptable. Other accelerated reliability tests were also positive in all cases.

The decision was made in late November 1990 to purchase this equipment on the basis of the practical trials under real, on-site conditions. As full production has not yet been implemented, it is premature to give too many figures, but estimated water and electricity consumptions are about 8 liters and 750 watt hour per basket and it is expected that overall costs of soldering/cleaning/ drying/maintenance will fall to about 60 percent of the CFC-113 reference production method.

Future plans include automating the cleaning line and probably introducing wave soldering with water-soluble flux, to replace the hand soldering.

Environmental Aspects

No wastewater treatment has been found to be necessary. The wastewater has been tested by the Geneva authorities and conforms entirely to the requirements of the severe Swiss law. The authorities have indicated they will tolerate monthly pH excursions outside the limits during maintenance cleaning of the machine with a descaling product.

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GLOSSARY

Acute toxicity -- The short-term toxicity of a product in a single dose. Can be divided into oral, cutaneous and respiratory toxicities.

Adsorption -- Not to be confused with absorption. Adsorption is a surface phenomenon which some products can exhibit, whereby they can form a physicochemical bond with many substances.

Alcohols -- A series of hydrocarbon derivatives with at least one hydrogen atom replaced by an -OH group. The simplest alcohols (methanol, ethanol, n-propanol, and isopropanol) are good solvents for some organic soils, notably rosin, but are flammable and can form explosive mixtures with air: their use requires caution and well-designed equipment.

Aqueous cleaning -- Cleaning parts with water to which may be added suitable detergents, saponifiers or other additives.

Biodegradable -- Products in wastewater are classed as biodegradable if they can be easily broken down or digested by, for example, sewage treatment.

BOD -- An abbreviation for biochemical oxygen demand.

CFC -- An abbreviation for chlorofluorocarbon.

CFC-113 -- A common designation for the most popular CFC solvent, 1,1,2-trichloro-1,2,2-trifluoroethane, with an ODP of approximately 0.8.

Chelation -- is the solubilization of a metal salt by forming a chemical complex or sequestering. One way of doing this is with ethylenediaminetetra-acetic acid (EDTA) salts which have a multi-dentate spiral ligand form that can surround metallic and other ions.

Chlorofluorocarbon -- An organic chemical composed of chlorine, fluorine and carbon atoms, usually characterized by high stability contributing to a high ODP.

Chronic toxicity -- The long-term toxicity of a product in small, repeated doses. Chronic toxicity can often take many years to determine.

COD -- An abbreviation for chemical oxygen demand.

Conformal coating -- A protective material applied in a thin, uniform layer to all surfaces of a printed wiring assembly including components.

Defluxing -- The removal of flux residues after a soldering operation. Defluxing is a part of most high-reliability electronics production.

Detergent -- A product designed to render, for example, oils and greases soluble in water, usually made from synthetic surfactants.

Fatty acids -- The principal part of many vegetable and animal oils and greases, also known as carboxylic acids which embrace a wider definition. These are common contaminants for which solvents are used in their removal. They are also used to activate fluxes.

Flux -- An essential chemical employed in the soldering process to facilitate the production of a solder joint. It is usually a liquid or solid material, frequently based on rosin (colophony).

Greenhouse effect -- A thermodynamic effect whereby energy absorbed at the earth's surface, which is normally able to radiate back out to space in the form of long-wave infrared radiation, is retained by gases in the atmosphere, causing a rise in temperature. The gases in question are partially natural, but man-made pollution is thought to increasingly contribute to the effect. The same CFCs that cause ozone depletion are known to be "greenhouse gases", with a single CFC molecule having the same estimated effect as 10,000 carbon dioxide molecules.

HCFC -- An abbreviation for hydrochlorofluorocarbon.

HFC -- An abbreviation for hydrofluorocarbon.

Hydrocarbon/surfactant blend -- A mixture of low-volatile hydrocarbon solvents with surfactants, allowing the use of a two-phase cleaning process. The first phase is solvent cleaning in the blend and the second phase is water cleaning to remove the residues of the blend and any other water-soluble soils. The surfactant ensures the water-solubility of the otherwise insoluble hydrocarbon. Terpenes and other hydrocarbons are often used in this application.

Hydrochlorofluorocarbon -- An organic chemical composed of hydrogen, chlorine, fluorine and carbon atoms. These chemicals are less stable than pure CFCs, thereby having generally lower ODPs.

Inert gas soldering -- A soldering process done in a relatively oxygen-free atmosphere. The process greatly reduces oxidation of the solder, so that less flux is required, thereby easing or eliminating the need for cleaning.

Leaded surface mount component -- A surface mount component (SMC) whose external connection consists of formed leads.

Leadless surface mount component -- A surface mount component (SMC) whose external connection consists of metallized terminations that are an integral part of the component body.

Low-solids flux -- A flux which contains little solid matter, thereby easing or eliminating the need for cleaning. See no-clean flux.

MEA -- An abbreviation for monoethanolamine.

Methyl chloroform -- See 1,1,1-trichloroethane.

Monoethanolamine -- A saponifier capable of eliminating rosin fluxes and fatty acids. Also abbreviated to MEA.

No-clean flux -- A flux whose residues do not have to be removed from an electronics assembly, therefore, no cleaning is necessary. This type of flux is usually characterized by low quantities of residues.

ODP -- An abbreviation for ozone depletion potential.

Organic acid (OA) flux -- See water-soluble flux.

Ozone -- A gas formed when oxygen is ionized by, for example, the action of ultraviolet light or a strong electric field. It has the property of blocking the passage of dangerous wavelengths of ultraviolet light.

Whereas it is a desirable gas in the stratosphere, it is toxic to living organisms at ground level (see volatile organic compound).

Ozone depletion -- Accelerated chemical destruction of the stratospheric ozone layer by the presence of substances produced, for the most part, by human activities. The most depleting species for the ozone layer are the chlorine and bromine free radicals generated from relatively stable chlorinated, fluorinated, and brominated products by ultraviolet radiation.

Ozone depletion potential -- A relative index indicating the extent to which a chemical product may cause ozone depletion. The reference level of 1 is the potential of CFC-11 and CFC-12 to cause ozone depletion. If a product has an ozone depletion potential of 0.5, a given weight of the product in the atmosphere would, in time, deplete half the ozone that the same weight of CFC-11 would deplete. The ozone depletion potentials are calculated from mathematical models which take into account factors such as the stability of the product, the rate of diffusion, the quantity of depleting atoms per molecule, and the effect of ultraviolet light and other radiation on the molecules.

Ozone layer -- A layer in the stratosphere, at an altitude of approximately 10-50 km, where a relatively strong concentration of ozone shields the earth from excessive ultraviolet radiation.

PCB -- An abbreviation for printed circuit board.

Printed circuit -- A printed circuit is an electronic component designed for interconnecting the other components. It usually consists of a metallic conductor pattern on an organic insulating substrate. After fabrication, it is known as a printed circuit board (PCB); after assembly where components are added, it is known as a printed wiring assembly (PWA).

PWA -- An abbreviation for printed wiring assembly.

Reflow soldering -- A method of electronics soldering commonly used with surface mount technology, whereby a paste formed of solder powder and flux suspended in an organic vehicle is melted by the application of external heat.

Rosin -- A solid resin obtained from pine trees which, in a pure form and usually with additives, is frequently used as a flux.

Rosin flux -- A flux whose main constituent is rosin. There are several categories of rosin flux, often designated by the codes R (pure rosin), RMA (rosin, mild activation), RA (rosin, activated usually with free chloride ions), RSA (rosin, super activated), SA (synthetic resin, activated).

Saponifier -- A chemical designed to react with organic fatty acids, such as rosin, some oils and greases etc., in order to form a water-soluble soap. This is a solvent-free method of defluxing and degreasing many parts. Saponifiers are usually alkaline and may be mineral (based on sodium hydroxide or potassium hydroxide) or organic (based on water solutions of monoethanolamine).

SMC -- An abbreviation for surface mount component.

SMD -- An abbreviation for surface mount device.

Solvent -- Although not a strictly correct definition, in this context a product (aqueous or organic) designed to clean a component or assembly by dissolving the contaminants present on its surface.

Surface mount technology (SMT) -- A technique of assembling SMDs or SMCs on the surface of PCBs and PWAs, as opposed to wiring them through holes. Surface mount technology offers a number of important advantages, but also some disadvantages, such as difficulty in defluxing under certain types of SMD.

Surface mount component (device) -- A component capable of being attached to (device) a PCB by surface mount technology. The device may be either leaded or leadless.

Surfactant -- A product designed to reduce the surface tension of water. Also referred to as tensio-active agents/tensides. Detergents are made up principally from surfactants.

Terpene -- Any of many homocyclic hydrocarbons with the empirical formula $C_{10}H_{16}$, characteristic odor. Turpentine is mainly a mixture of terpenes. See hydrocarbon/surfactant blends.

Volatile organic compound (VOC) -- These are constituents that will evaporate at their temperature of use and which, by a photochemical reaction, will cause atmospheric oxygen to be converted into potential smog-promoting tropospheric ozone under favorable climatic conditions.

Water-soluble flux -- A flux, which itself may be free from water, but whose residues after soldering may be entirely eliminated by a water wash. Such fluxes are usually very active so adequate defluxing is an essential part of their use. They are also known as Organic Acid (OA) fluxes or inorganic acid fluxes.

Wave soldering -- Also known as flow soldering, a method of mass soldering electronics assemblies by passing them, after fluxing, through a wave of molten solder.

APPENDIX A

INTERNATIONAL COOPERATIVE FOR OZONE LAYER PROTECTION

The International Cooperative for Ozone Layer Protection (ICOLP) was formed by a group of industries to protect the ozone layer. The primary role of ICOLP is to coordinate the exchange of non-proprietary information on alternative technologies, substances, and processes to eliminate ozone-depleting solvents. By working closely with solvent users, suppliers, and other interested organizations worldwide, ICOLP seeks the widest and most effective dissemination of information harnessed through its member companies and other sources.

ICOLP corporate members include:

AT&T
British Aerospace Defense
Ford Motor Company
Hitachi
Honeywell
IBM Corporation
Mitsubishi Electric Corporation
Motorola Corporation
Ontario Hydro
Northern Telecom
Texas Instruments
Toshiba Corporation

In addition, ICOLP has a number of industry association and government organization affiliates. Industry association affiliates include American Electronics Association, Association Pour la Research et Development des Methodes et Processus Industriels, CANACINTRA (Mexico), Center for Global Change, Electronic Industries Association, Halogenated Solvents Industry Alliance (U.S.), Industrial Technology Research Institute of Taiwan, Japan Electrical Manufacturers Association, Korea Anti-Pollution Movement, and Korea Specialty Chemical Industry Association. Government and NGO affiliates include the City of Irvine (CA), National Academy of Engineering, Research Triangle Institute, Russian Institute of Applied Chemistry, Russian Ministry of Environmental Protection and Natural Resources, Swedish National Environmental Protection Agency, Technology Development Foundation of Turkey, Turkish Ministry of the Environment, United Nations Environment Programme, U.S. Air Force, and U.S. Environmental Protection Agency (EPA). The American Electronics Association, Electronic Industries Association, City of Irvine, California, Japan Electrical Manufacturers Association, Swedish National Environmental Protection Agency, U.S. EPA, U.S. Air Force, and the Russian Institute of Applied Chemistry have signed formal Memorandums of Understanding with ICOLP. ICOLP will work with the U.S. EPA to disseminate information on technically feasible, cost effective, and environmentally sound alternatives for ozone depleting solvents.

ICOLP is also working with the National Academy of Engineering to hold a series of workshops to identify promising research directions and to make most efficient use of research funding.

The goals of ICOLP are to:

- Encourage the prompt adoption of safe, environmentally acceptable, nonproprietary alternative substances, processes, and technologies to replace current ozone-depleting solvents;
- Act as an international clearinghouse for information on alternatives;
- Work with existing private, national, and international trade groups, organizations, and government bodies to develop the most efficient means of creating, gathering, and distributing information on alternatives.

One example of ICOLP's activities is the development and support of an alternative technologies electronic database "OZONET." OZONET is accessible worldwide and has relevant information on the alternatives to ozone-depleting solvents. OZONET not only contains technical

publications, conference papers, and reports on the most recent developments of alternatives to the current uses of ozone-depleting solvents, but it also contains:

- Information on the health, safety and environmental effects of alternative chemicals and processes;
- Information supplied by companies developing alternative chemicals and technologies;
- Names, addresses, and telephone numbers for technical experts, government contacts, institutions and associations, and other key contributors to the selection of alternatives;
- Dates and places of forthcoming conferences, seminars, and workshops;
- Legislation that has been enacted or is in place internationally, nationally, and locally.

Information about ICOLP can be obtained from:

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APPENDIX B

LIST OF VENDORS FOR CFC-113 AND METHYL CHLOROFORM SOLVENT CLEANING SUBSTITUTES

This is not an exhaustive list of vendors. Vendors can be cited in any subsequent editions of this document by sending information to ICOLP. ICOLP's address is provided in Appendix A. Listing is for information purposes only, and does not constitute any vendor endorsement by EPA, ICOLP, or the committee members, either express or implied, of any product or service offered by such entity.