SOURCE REDUCTION AND RECYCLING OF HALOGENATED SOLVENTS IN THE ELECTRONICS INDUSTRY

TECHNICAL SUPPORT DOCUMENT

A REPORT ON RESEARCH PERFORMED BY
THE SOURCE REDUCTION RESEARCH PARTNERSHIP
FOR THE METROPOLITAN WATER DISTRICT AND
THE ENVIRONMENTAL DEFENSE FUND

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Description of Project

This document is part of a 12-volume report on research performed by the Source Reduction Research Partnership (SRRP) over the past five years. The report as a whole, entitled *Potential for Source Reduction and Recycling of Halogenated Solvents*, covers a wide range of industries.

The Summary Report of this project, which is available separately, gives an overview and the results of the research as a whole. This is one of ten Technical Support Documents covering each of ten solvent-using industries and operations (listed below). The full report also includes a separate Lifecycle Inventory and Tradeoff Analysis, covering issues that arise in the comparison of existing halogenated solvent uses with potential alternatives. The ten categories of solvent-using industries and operations are:

- Adhesives
- Aerosols
- Chemical Intermediates
- Dry Cleaning
- Electronics
- Flexible Foam
- Paint Stripping
- Parts Cleaning
- Pharmaceuticals
- Textiles

The Source Reduction Research Partnership was formed and jointly managed by the Metropolitan Water District of Southern California (Metropolitan) and the Environmental Defense Fund (EDF). Metropolitan is a public agency, obtaining and supplying water for some 15 million consumers in Southern California. EDF is a national, not-for-profit, public interest organization with more than 200,000 members nationwide.

The research leading to this 12-volume report took place in two phases. The first phase consisted of multi-year field research, primarily in the Southern California area, involving on-site visits, site-specific data gathering, and research into individual processes for all of the affected industries, using a full-time staff employed directly by SRRP. Dr. Kathleen Wolf served as Project Manager during this phase, and staff included Richard Holland, Azita Yazdani, Pamela Yates, and Fidelia Fulmore.

The second phase involved development of a methodology to quantify potential reductions, additional research and data assessment, analysis of lifecycle and tradeoff issues, derivation of results, and preparation of all report documents. Jacobs Engineering Croup performed the work of this phase as consultants under contract. Michael Callahan served as Principal Investigator and Hector Ortiz served as Project Manager for Jacobs during this phase, assisted by Carl Fromm, Dr. Rajeev Sane, Harry Van Den Berg, David Shoemaker, Ross Teneyck, and Dr. Arthur Purcell.

Dr. Timothy Quinn of Metropolitan and David Roe of EDF served as co-administrators of the project throughout. A formal advisory committee, including over 40 representatives of solvent-using industries, industry associations, government agencies, and environmental groups, oversaw the design and development of the project.

Acknowledgments

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Additional funding to help set up the unusual partnership that made this project possible, and to help design the research format, came from the Michael J. Connell Foundation, the Andrew Norman Foundation, and Southern California Edison Company.

Metropolitan and EDF warmly thank all the sponsors of the Source Reduction Research Partnership for their support, patience, and faith in this unconventional and unprecedented research effort.

Even as originally conceived, this project's goals were ambitious; and while it was underway, unanticipated difficulties in meeting those goals regularly emerged. The results would not have been possible without the extraordinary effort of everyone involved in both phases of the project. Metropolitan and EDF gratefully acknowledge their special debt to the project's dedicated participants including staff, consultants, advisers, and supporters.

Disclaimer

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Readers Note

Note on Terminology: The definition of key terms in this field, including the term “source reduction” itself, has been subject to rapid evolution and nearly continuous debate during the period in which this study was carried out.

In 1986, when SRRP was first taking shape, the sponsors chose to focus the SRRP study on “source reduction” defined to include recycling and recovery of solvents, as well as substitution of alternative materials, equipment and process modifications, housekeeping measures, and the like. In 1990, midway through the study, Congress passed the Pollution Prevention Act which defined “source reduction” to exclude recycling.

Although this report tries to use the terminology of the 1990 Act, the fact that the scope of this study is larger than the 1990 definition of “source reduction” might be confusing to the casual reader. Definitional issues and the reasons for choosing the scope of this study are discussed at greater length in the Summary Report.

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1.0 INTRODUCTION

The focus of this Technical Support Document is on source reduction opportunities in the electronics industry. Two major electronics processes are investigated: semiconductor wafer fabrication/assembly and printed circuit board fabrication/assembly. Critical (precision) cleaning applications and in-situ generation of etchants are discussed but not investigated in detail. For information regarding source reduction options that apply to critical cleaning, the reader is referred to the companion Technical Support Document on parts cleaning.

Halogenated solvents are used in these processes for degreasing and precision cleaning of semiconductors and printed circuit boards, defluxing printed circuit boards, developing and stripping off photoresist, and in situ generation of gaseous etchants. Although all five halogenated solvents are used, three predominate: 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) l,l,l-trichloroethane (TCA), and methylene chloride (METH). SRRP staff estimate that the use of CFC-113 in 1988 was 39,900 metric tons (MT) mainly for circuit board defluxing, degreasing, and critical cleaning. The use of TCA and METH in these applications was estimated to be 16,200 MT and 16,300 MT respectively. There is minor use of trichloroethylene (TCE) and perchloroethylene (PERC).

To reduce the use of these solvents, there is a move to change military specifications which govern solvent use in the printed circuit board defluxing applications. If this change occurs, a range of alternatives will be adopted in place of CFC-113 based solvents. Alternative fluxes are being developed that will require no cleaning; also, no-flux soldering processes and water cleanable fluxes are being investigated. There is also a continuing movement toward the use of aqueous and semi-aqueous photoresist in place of solvent based formulations. Carbon dioxide “snow” and ultraviolet *(W)* photolysis/ozonation are being investigated for cleaning of semiconductor wafers. Many manufacturers are converting to aqueous cleaning for some precision cleaning applications.

By adopting these measures, overall solvent emissions are projected to be reduced by 21 to 54 percent in the short-term (0 to 5 years) and 63 to 85 percent in the long-term (10 to 20 years). Medium-term (5 to 10 year) reductions are projected to be 48 to 74 percent. In terms of tons reduced, this represents a potential reduction of 16,100 to 41,500 MT short-term, 37,200 to 57,000 MT medium-term, and 48,400 to 65,000 MT long-term. These projections are based on expectation that the main alternatives to solvents will include converting to aqueous and semi-aqueous photoresist, use of no-flux soldering and low solids flux, and adoption of good operating practices. In the 3 year period from 1988 (baseline year) to 1991, the electronics industry has reduced its use of virgin METH by 70 percent and TCA by 44 percent (CMR 1989 and 1992).

Given the phase-out of CFC-113 by 1997, users are now faced with the mandate of switching to entirely different chemistry or methodology. However, conversion to these new processes will require time. In the interim, the question arises as to whether or not economic incentives exist to improve the existing process to reduce CFC emissions. In order to obtain an economic perspective on some short-term solvent use reduction approaches, detailed economic analysis was performed for two cases. The first case involved installing a carbon bed system to control emissions from a CFC defluxer cleaning 10,000 PC boards per day for a military product. The second case involved replacing the existing defluxer with a new lower emissions model.

The cost effectiveness of these two options ranged from $1,660 per ton of CFC-113 reduced for the new fluxer to $1,990 per ton for the carbon bed system. The carbon bed system could save the facility $47,500 per year provided that the recovered solvent can be reused elsewhere on-site. Both analyses were based on a capital recovery time frame of 5 years due to the impending phase-out of CFC and a projected solvent price of $32 per gallon. At best, adding additional controls to reduce CFC losses is an interim strategy that does not replace the need to switch to non-CFC based processes after the phase-out. It is more likely that most facilities will invest in the development of the new technology rather than invest capital into the retrofit of the existing process, even though the economics may be favorable.

Section 2 provides a general discussion of the electronics market, descriptions of the electronics and printed circuit board fabrication and assembly process, and other relevant information. Section 3 describes the source reduction options that could be considered and implemented for the reduction of solvent use. Two hypothetical case studies are presented in Section 4 followed by the estimation of potential solvent use reduction in Section 5.

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2.0 BACKGROUND

In line with the significant growth in the electronics industry over the last few decades, usage of halogenated solvents has increased accordingly. This section presents an estimate of the use of halogenated solvents in various sectors of the electronics industry and a description of the processes where the solvents are used. Subsequently, the characteristics of the industry are presented and trends that may alter the future pattern of solvent use are discussed.

2.1 MARKET SEGMENTS

The electronics industry manufactures a wide range of discrete components, integrated circuits, and electronic devices. The demand for electronic systems and equipment in non-Communist countries was more than $356 billion in 1986. U.S. consumption of electronic equipment amounted to $210 billion in 1986; by 1991 it was expected to reach $370 billion (Davis et al., 1987). The end use sectors for PC boards and their share of the market are shown in Table 2.1. The values illustrate that the largest market for PC boards is computers followed by communications and government/military.

2.2 SOLVENT USE

Halogenated solvents are used in four major applications in the electronics industry. These include semiconductor wafer fabrication and assembly, printed circuit board fabrication and assembly, critical cleaning applications, and in-situ generation of etchants. Table 2.2 presents estimates of 1988 solvent use of CFC-113, TCA, METH, TCE, and PERC by application. The total amount of halogenated solvent used was 76,700 MT.

According to D'Ruiz (1991), the total production of CFC-113 in the United States in 1988 was estimated to be 79,200 MT, with electronics use consuming 50 percent and metal parts cleaning consuming another 37 percent. Broken down by operation, 65 percent was used for PC board defluxing, 12 percent was used for critical cleaning, 11 percent was used for the fabrication and assembly of semiconductors, 10 percent was used for degreasing of PC boards during fabrication, and 2 percent was used for drying the boards. These percent estimates, along with SRRP staff consultations with industry sources, were used to derive the breakdown of CFC-113 use shown in Table 2.2 Given the critical nature of these operations, it is assumed that the use of recycled solvent is relatively minor and can be neglected.

Table 2.1

Printed Circuit Board Market

Market	Percent of Market
Computer	43.2
Communications	18.9
Government/Military	12.2
Consumer	11.5
Instruments	7.0
Industrial	5.1
Business	2.1
Total	100.0

Source: Davis et al. (1987). Data is for the year 1985 but should still be representative of market profile.

The usage of TCA in 1988 by the electronics industry was estimated to range from 4 percent of total production or 12,700 MT (CMR, 1988) up to 6 percent of production or 19,700 MT (D'Ruiz, 1991). These same sources placed the use of METH at 7 percent of production or approximately 16,300 MT. The major use of TCA is in PC board fabrication for developing solvent-based photoresist while the major use of METH is for stripping off resist. Estimates of TCE and PERC use (3,000 MT and 1,300 MT) were derived by SRRP staff consultation with industry sources.

As shown in Table 2.2, it is estimated that 76,700 MT of halogenated solvent was used in the electronics industry in 1988. This amount represents the amount of virgin solvent consumed; the actual amount used when including the effects of on-site recycling and the use of recycled solvent would be larger. However, given the strict quality requirements for solvent use in electronics, it is unlikely that the use of recycled solvent is high. The use of recycled solvent was, therefore, assumed to be negligible.

2.3 NUMBER OF FACILITIES IN OPERATION

Semiconductor manufacturers can be small research and development firms that test and develop prototype products or they can be very large manufacturers that make semiconductors for their own internal products or direct sales. The American firms that are among the top ten commercial manufacturers of integrated circuits include Motorola, Texas

Table 2.2

Halogenated Solvent Use in the Electronics Industry (1988)

	Solvent (thousand MT)				
	TCE	PERC	METH	TCA	CFC-113
Semiconductor Production					
Wafer Fabrication	2.2	0.5	1.3	0.3	2.7
Wafer Assembly	0.3	0.3	0.5	1.1	1.7
PC Board Fabrication					
Developing Photoresist	--	--	--	8.0	--
Striping Photoresist	--	--	13.8	--	--
Degreasing Boards	--	-	--	--	4.0
Drying Boards	-_	--	--	---	0.8
PC Board Assembly Primarily Defluxing	0.5	0.5	0.7	6.6	25.7
Critical Cleaning of Mechanical Assemblies					4.8
In Situ Generation of Etchants					0.2
TOTAL	3.0	1.3	16.3	16.2	39.9

Source: CMR (1989); D'Ruiz (1991); SRRP staff; and Industry Sources.

Instruments, and Intel. Other firms such a AT&T and IBM are also very large producers, but their production is used captively only in their own products. The production of semiconductors falls under SIC code 3674, "Semiconductors and Related Devices". In 1986, there were 804 establishments that were classified in this SIC code (USDC, 1986a). In that same year in California, there were 281 such establishments (USDC, 1986b).

The printed circuit board industry is composed of large facilities that produce only boards, both large and small captive facilities, small job shops which do contract work, and specialty shops which do low-volume and high-volume precision work. Printed circuit board producers fall into SIC Code 3679, "Electronic Components, not elsewhere classified." This SIC code is not limited to the PC board industry because that particular SIC code aggregates a number of electronics industries. In 1986, there were 3,483 establishments nationwide in this SIC code (USDC, 1986a). In California, there were 997 establishments (USDC, 1986b). In terms of PC board producers, one source reports that there are only about 900 total producers nationwide; more than 750 of these firms are small shops with less than $5 million in annual sales (Davis et al., 1987).

2.4 PRODUCTION PROCESSES AND SOURCES OF RELEASE

Halogenated solvents are used in the electronics industry in four primary operations: semiconductor and integrated circuit (or wafer) manufacture; printed circuit/wiring board manufacture and assembly; critical component cleaning; and in-situ generation of etchants. Each of these processes and their solvent use characteristics are discussed below.

Semiconductor Manufacture

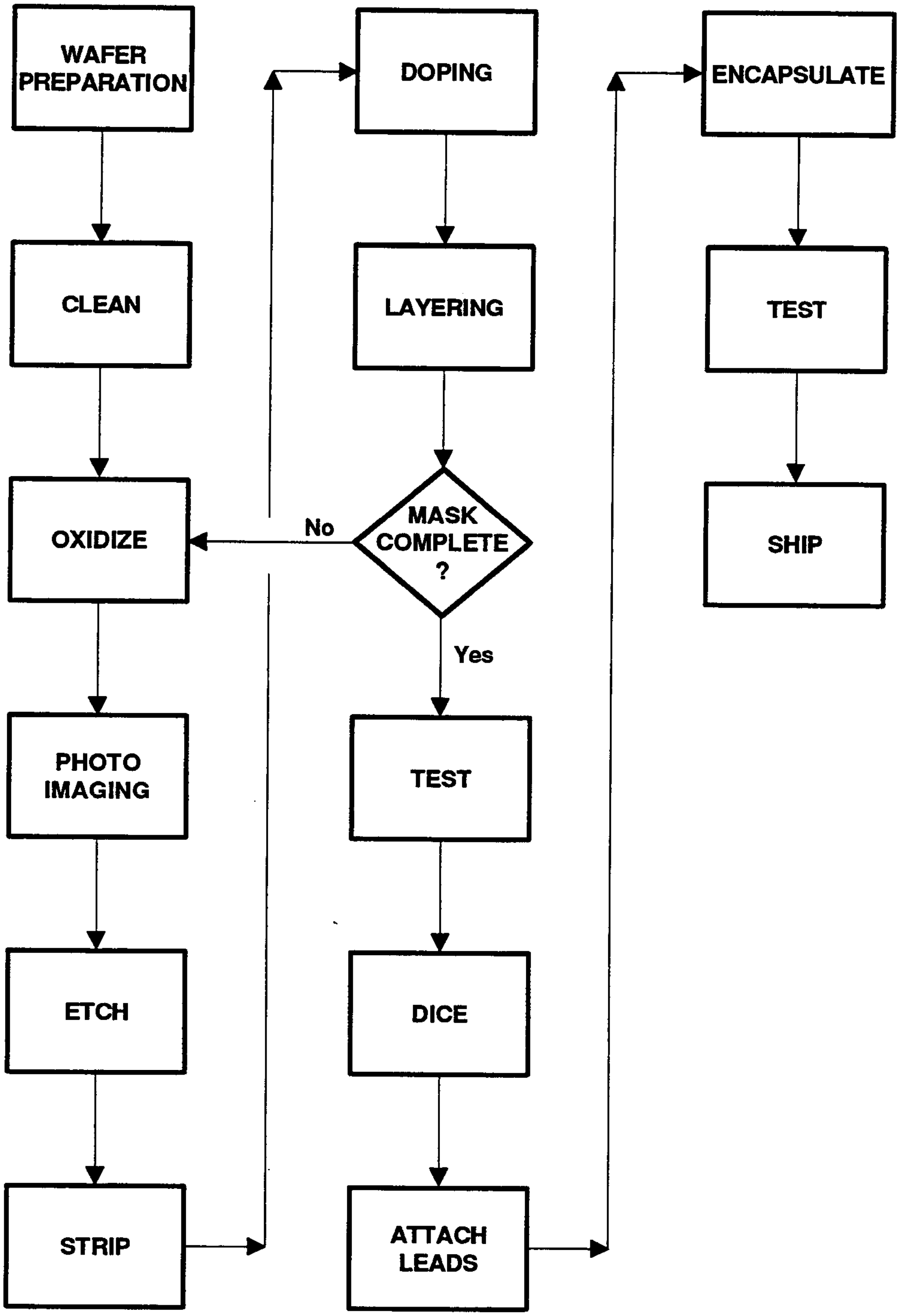
Integrated circuits (ICs) are the major product of the semiconductor industry. Unlike discrete devices such as resistors, capacitors, or transistors, ICs are combinations of such devices contained in a single package. IC production processes may employ more than 200 different materials and 100 proprietary methods (Foecke, 1988). Figure 2.1 illustrates the semiconductor production process. Note that the oxidation, photolithography, etching, stripping, doping, and layering steps are repeated until the desired number of circuit layers is achieved. Then the circuits go on to wafer assembly.

The first step in the fabrication process is to grow a single crystal or ingot from a seed crystal. Materials that are used for this purpose include silicon, germanium, gallium arsenide, gallium phosphide, or gallium arsenic phosphide. The vast majority of the crystalline material used today, 80 to 90 percent, is silicon (Foecke, 1988). Once the ingot is grown, it is sliced into wafers, smoothed and polished (the so-called lapping process), and cleaned.

In the next stage which involves six fundamental steps, the semiconductor devices are built onto the wafers. The wafers are first cleaned with an acid plus an oxidant (the most common method), with deionized water, with alkaline cleaners, or with solvent. After cleaning, the silicon wafers are oxidized. Oxidation produces a silicon dioxide layer which provides a base for the photolithography process and prevents the diffusion of dopants to the silicon wafer during doping. Oxidation is achieved by exposing the wafers to oxygen in a high temperature

Figure 2.1

Semiconductor Production Process



Source: Van Zant (1986) and Foecke (1988).

furnace. After oxidation, wafers are cleaned with strong acids and bases. In some cases, TCA is injected into the furnace as a source of chlorine which cleans the wafers.

In the second step, a uniform film of photoresist is spun onto the-wafer. The photoresist used may be a negative resist polymer or, more commonly today, a positive resist consisting of resin. Next, a photomask of the desired pattern is placed over the resist coated wafer and then exposed to an energy source such as ultraviolet light, deep ultraviolet light, or x-rays. During the development step, the unwanted pattern areas are removed or stripped off. In the case of positive resist, areas exposed to the light are removed. With negative resist, unexposed areas are removed. Organic solvents are used for stripping positive photoresist while halogenated solvents are used from stripping negative photoresist (Van Zant, 1986).

The third and fourth steps involve etching and stripping. Inorganic acids are used to etch the oxide layer from the exposed pattern area. After etching, the remaining resist pattern is stripped off the wafer with liquid or dry strippers. In certain cases, the strippers used may be halogenated solvents or acids, but dry stripping using oxygen plasma is becoming the method of choice. After etching and stripping, the fifth step is to dope the lattice with impurities to change the electrical conductivity of silicon. This step is followed by layering where a thin layer of material which may be a conductor, semiconductor, or insulator is deposited over the whole surface of the wafer. The oxidation, photolithography, etching, stripping, doping, and layering steps are repeated over and over until the desired circuit is fabricated.

Following fabrication, the chips are tested for defects and the wafers cut into individual chips. Leads are soldered to the chip and the device encapsulated. Common means of encapsulation include small metal cans if lead count is low and dual in-line packages or DIPs. Following encapsulation, the devices are marked with part numbers and other proper means of identification. It is during this operation that CFC-113 combined with METH is used to test the ink nomenclature on the circuit to verify that it has properly cured. The military specification for mark permanency testing requires the use of either a 50 percent CFC-113 and 50 percent METH azeotrope or a 35 percent/65 percent mixture. An alternative marking method employs the use of a laser to etch the case. After marking, the chips are retested and then packaged for shipment.

Many different machines are used in the wafer fabrication step. These machines need to be cleaned periodically and the cleaning is mainly done with CFC-113. TCA and CFC-113 are often used for cleaning parts during assembly. When soldering, isopropyl alcohol is the most commonly used solvent for removing flux although CFC-113 and TCA may also be used. A mixture of CFC-113 and METH is used to test the ink nomenclature on the circuit.

Printed Circuit Board Manufacture

There are two main types of printed circuit (PC) boards currently in use today: rigid boards and flexible boards. Rigid boards may be made of glass epoxy, plastic, ceramic, or paper-based phenolic resin substrate. These boards, which account for roughly 90 percent of the market, can be single sided, double sided, or multilayered. Flexible boards are made of a polyester and polyimide substrate. Most boards are clad with copper, and the desired circuit pattern consists of fine traces of conductive metal. Figure 2.2 presents a block flow diagram of the PC board fabrication process. Discussion of the fabrication and assembly process are presented below.

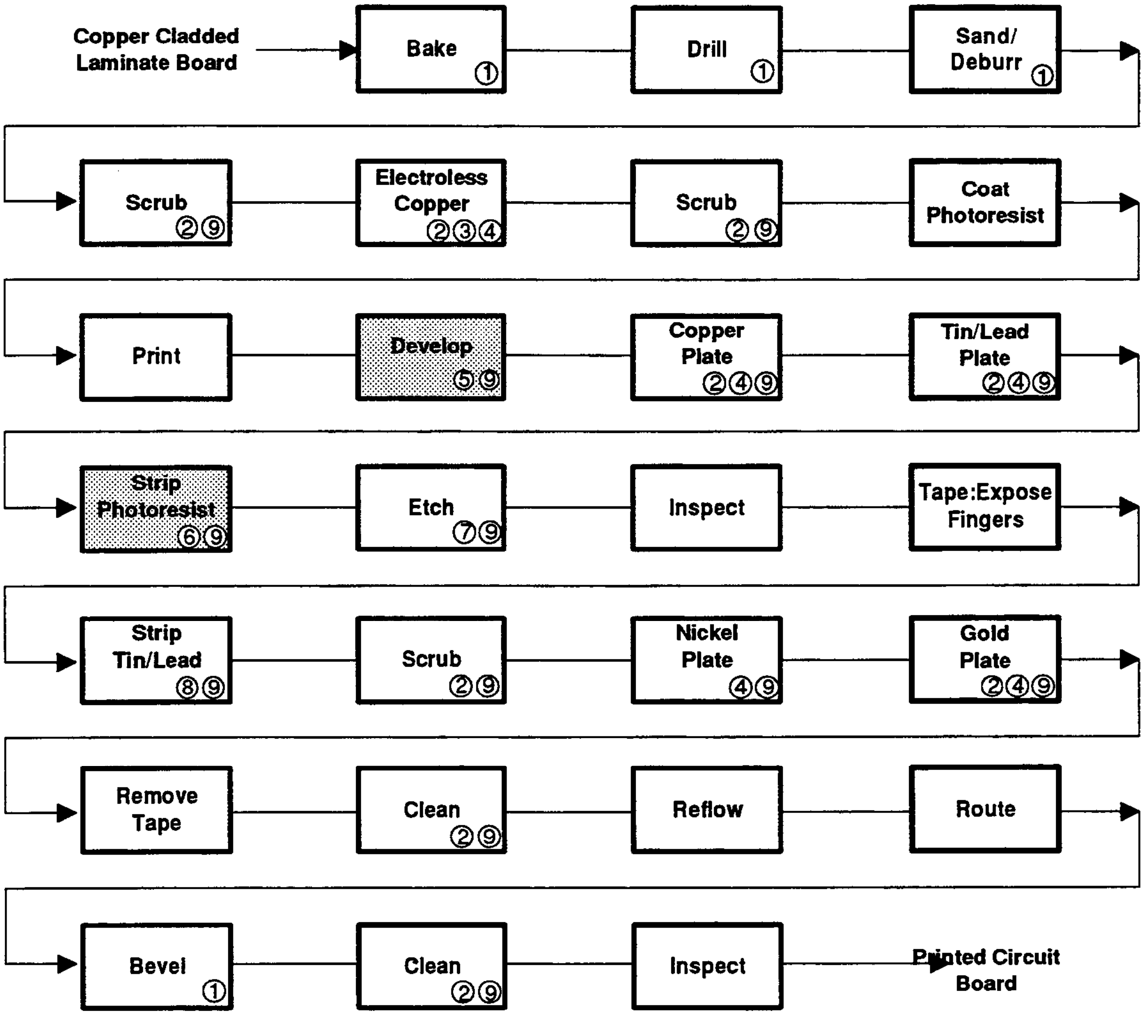
There are three methods for producing PC boards: additive, subtractive, and semi-additive. The additive method involves electroless plating the desired circuit pattern onto the bare board substrate. Only 5 to 10 percent of the boards manufactured today employ this method. The second method, the subtractive technique, accounts for nearly 80 percent of the board market. It involves etching metal from the copper clad board and leaving the desired circuit pattern. The semi-additive method is a combination technique. The bare board is metalized as in the additive method and is then etched to produce the desired pattern as in the subtractive method. The following discussion focuses on the subtractive process only.

Fabrication begins by cutting the copper clad boards from sheet material and then drilling component holes. Mechanical cleaning to remove cuttings and burrs is followed by chemical cleaning with acids and then with alkaline cleaners, electrolytic cleaners, abrasive cleaners, or halogenated solvents. Once clean, the boards are electroless plated with copper so as to obtain a continuous metallic surface from one side of the board to the other and inside the just drilled holes.

Silk screening, offset printing, or photolithography is then used to transfer the circuit pattern from a master to the board. The circuit pattern may be positive or negative depending on the type of photoresist employed. In silk screening and offset printing, the circuit image is printed directly onto the board using resist. In photolithography, the boards are first coated with photoresist, dried, and then placed beneath the photocopy master, a transparent pattern of the circuit printed on Mylar film. The board is then exposed to ultraviolet light and after

Figure 2.2

Subtractive Process for the Production of Double-sided Printed Circuit Boards



PROCESS WASTE CATEGORIES

① Airborne Particulates
② Spent Surface Cleaning Solutions
③ Spent Catalyst Solutions
④ Spent Plating Baths
⑤ Spent Developing Solutions
⑥ Spent Resist Removal Solutions
⑦ Spent Etchants
⑧ Spent Metal Stripping Solutions
⑨ Rinse Wastewater

exposure, sent to the developer. Depending on the type of resist used, the exposed areas may either remain on the circuit board or be removed by the developer. In this discussion, it is assumed that the photocopy master is a positive image and that the exposed resist remains on the board.

Since the resist pattern on the board is a negative image, the desired circuit pattern is exposed copper. The exposed areas are then built-up by copper plating followed by solder plating. The solder plating acts as a resist during subsequent etching operations. Once the board is solder plated, the old resist pattern is stripped off and the board etched. This removes the unwanted copper from the board. Additional masking, etching, and plating of the boards may be performed to produce nickel and gold plated edge connectors. As a final part of fabrication, the boards may be degreased and dried with CFC-113.

In addition to the choice between positive and negative photoresists, a fabricator must also choose among solvent, aqueous, and semi-aqueous photoresist formulations. TCA is used to develop solvent-based resist while aqueous resist is developed with carbonate-based solution (DuPont, 1988) and semi-aqueous resist is developed with glycol ethers and alcohols (SRI, 1985). Removal or stripping off of solvent-based resist is accomplished with METH or aqueous formulations. Aqueous resists can be stripped off with sodium or potassium hydroxide solutions (DuPont, 1988). Alkylamides, glycol ethers, and other water soluble components are used to strip semi-aqueous resists-

In the assembly process, the circuit boards are populated with the desired components and then soldered either by hand or by passing through a wave, dip, or drag soldering machine. Flux is used to remove oxides from the metal surface and to reduce the surface tension of the solder so that it flows evenly and provides a good electrical bond. Three major types of flux are employed. Rosin flux accounts for about 55 percent of the flux used. It can be removed with saponifier and water, CFC-113, or TCA Organic acid flux, representing 40 percent of the market, is removed with aqueous cleaners. The remaining 5 percent of the flux market is synthetically activated flux which must be removed with halogenated solvents. A listing of fluxes available for use and their characteristics are presented in Table 2.3.

Rosin fluxes, as the table indicates, are mixtures of isomeric acids including abietic acid. Generally, they are the least corrosive of the flux types in use. Activators, which have traditionally been halide compounds, are used to increase the wetting ability of the flux. Only rosin (R) and mildly activated flux (RMA) are approved for military use. Nonactivated rosin

Table 2.3

Characteristics of Commonly Used Fluxes

Flux	Common Reference	Composition	Approved By Military?	Solubility[a]
Rosin	R	Abietic acid and other isomeric acids.	Yes	cs, ws
Mildly activated rosin	RMA	Abietic acid and other isomeric acids; low conc. of amine hydrochloride activators.	Yes	cs, ws
Activated rosin	RA	Abietic acid and other isomeric acids; medium conc. of amine hydrochloride activators.	No	cs, ws
Super activated rosin	RSA	Abietic acid and other isomeric acids; high conc. of amine hydrochloride activators.	No	cs, ws
Organic acid	OA	Abietic acid and other isomeric acids; halide or non-halide activators.	No	W
Synthetically activated	SA	Alkyl acid phosphates; halide activators.	No	cs
Resin	Resin	Chemically synthesized rosin.	No	W
Low solids	Low solids	Rosin flux with 2 to 5 percent solids content.	No	NR

Notes:

a) Removal of flux can be achieved by use of: CS = chlorinated solvent; W = water; WS = water with saponifier; NR = cleaning not required.

Source: Markenstein (1983); Morrison and Wolf (1985).

fluxes (R) are not suitable for PC boards, but only for component manufacture and solderability testing. Super activated rosin fluxes (RSA) are used for difficult solder applications. Organic acid (OA) fluxes are water soluble; they are stronger than rosin flux and can be corrosive. They allow faster soldering rates and result in fewer reject boards. Synthetically activated (SA) fluxes provide the same strong fluxing action as organic acid fluxes, but are removed with solvents instead of water. They are not as corrosive as organic acid fluxes. Although resin flux is a derivative of rosin flux, it has a significantly different structure and is water soluble. Low solid fluxes, which require little or no cleaning, typically consist of 2 to 5 percent solids compared to 15 to 35 percent solids in regular flux.

After soldering, flux residue is not the only contaminant that needs to be removed from the PC board. Nonpolar or semipolar contaminants may include greases, oils, rosin, and waxes. These are generally composed of long-chain hydrocarbons. Polar contaminants may consist of rosin flux activators and their residues, sodium chloride, and soldering, plating, and etching salts. Particulate contaminants such as dust and machining, drilling, and punching fragments may also have to be removed.

In the literature, there is much discussion about the solubility of abietic acid (a major component of rosin flux) in various solvents. The halogenated solvents, TCE, PERC, and METH are especially good at dissolving abietic acid, a nonpolar contaminant. Alcohols such as methanol, ethanol, and isopropanol, which are polar, are not good dissolvers of the acid. The CFC-113/alcohol azeotropes are not especially good at dissolving the acid primarily because CFC-113 is a very gentle, nonaggressive solvent. The TCA azeotrope with alcohol is somewhat better because of the more aggressive solvency of TCA Polar contaminants, including salts, can be effectively removed by aqueous cleaners and alcohols.

Another significant factor that influences the choice of solvent is compatibility with the substrate. Although CFC-113 is not a particularly good solvent for removing abietic acid, it is compatible with virtually all materials of construction for PC boards. When it is combined with alcohol in an azeotrope; it is a very good compromise solvent. In Morrison and Wolf (1985), a variety of solvents were evaluated for their ability to dissolve polar (represented by water) and nonpolar (represented by n-hexadecane, a long-chain hydrocarbon) contaminants, their evaporation rate (which represents speed in taking the board to the next assembly step), and their wettability (a factor based on density, viscosity, and surface tension of the solvent). The CFC-113/alcohol azeotropes ranked highest when evaluated according to these parameters. Only certain solvents are presently allowed for use as defluxants under military

Table 2.4

Solvents and Cleaners Allowed Under Military Specifications

Solvent or Cleaner	Notes
Ethyl Alcohol	--
Isopropyl Alcohol	--
Ethyl Alcohol	Can only be used as a constituent of a blended solvent.
Butyl Alcohol, Secondary	Can only be used as a constituent of blended solvent.
TCA	TCA with nitromethane stabilizer may be used if mixtures are preblended by supplier.
Solvent Petroleum Distillate (Stoddard)	Shall be used only as a constituent of an already blended solvent.
Reagent Water (Type II)	--
Detergent cleaners and Saponifiers	As approved by the Government Contracting Officer prior to use.

Source: DOD-STD-2000-1B.

specifications that govern cleaning. Table 2.4 lists the solvents allowed for defluxing under DOD 2000. They include various alcohols, TCA, CFC-113, and combinations of alcohols and solvents. Aqueous cleaners can be used only with permission of the contract officer. The use of water soluble (organic acid) flux is not permitted under the specification.

Depending on the type of flux to be removed and the defluxing agent selected, board cleaning may be performed by cold cleaning or vapor degreasing. In cold cleaning, equipment can range from shallow trays into which boards are placed by hand up to automated systems where the boards exit from the solder wave and are conveyed through an in-line cleaner consisting of a series of baths. In such automated systems, cleaning can be enhanced by the use of rotating brushes, spray nozzles, or ultrasonics. In vapor cleaning systems, the operation of PC board defluxers is identical to batch or conveyorized in-line vapor degreasers. The solvent vapor condenses on the cool PC assembly and flushes away the contaminants. While all five halogenated solvents are used for defluxing boards, the two most widely used are CFC-113 followed by TCA

After defluxing, the final step is usually the application of a protective coating to the board. Widely used coating types include epoxy, polyurethane, silicone, and polystyrene. The application of a protective coating is important since it has been repeatedly demonstrated that unprotected boards exposed to severe environments will fail because of moisture penetration, large decreases in insulation properties, electrical shorting, or corrosion (Licari, 1981). Use of coatings also allow designers to lay out boards with narrower traces and closer spacing since the potential for arcing and shorting out due to contamination is reduced.

Precision Cleaning

Precision cleaning of parts made of metal, plastic, ceramic, or glass that are sensitive to particulate contamination are cleaned with CFC-113 or TCA Commercial and military gyroscope gimbal assemblies, hydraulic control systems, and medical equipment are examples of items that require precision cleaning. Computer systems employ magnetic storage devices called disk drives for information storage. Because of extremely small tolerance requirements placed on various components in the drive and other considerations, stringent cleanliness requirements are necessary during assembly. Drive failure can occur if contamination is not controlled at the submicron level. CFC-113 is the solvent generally used to achieve this level of cleanliness. The assemblies are repeatedly immersed in ultrasonic tanks containing pure or blended CFC-113. CFC-113 is also used to dry precision mechanical parts (Wolf et al., 1988). These applications are discussed in detail in the companion Technical Support Document on parts cleaning.

In-Situ Generation of Etchants

As mentioned earlier, CFC-113 and TCA are used to generate etchants. CFC-113 is combined with hydrogen gas at high temperature to produce a mixture of hydrogen chloride (HCl) and hydrogen fluoride (HF). The acid vapor comes in contact with the semiconductor where it etches areas of the wafer that have not been protected. One source indicates that approximately 500,000 pounds or 220 MT of CFC-113 are used in production of etchant gases (SRI, 1985). The same source also places the amount of TCA used to produce HCI etchant gas at 220 MT.

While many semiconductor manufacturers use traditional plasma etching techniques where gaseous HCl and HF are purchased and used directly, there are several advantages to using halogenated solvent to generate etchant gas. First, handling of the solvents is safer than handling HCl and HF gas directly. Gaseous delivery systems operate at high pressure and are subject to leakage. Since HCl and especially HF are toxic, extensive toxic gas leakage monitoring systems may be required. Another advantage is that the purity of the HCl or HF may be greater or at least more consistent with use of solvents. In-situ generation of etchants is expected to see increased used since many regulatory agencies are placing greater and greater restrictions on the storage, handling, and use of compressed gases.

Sources of Release

There is considerable uncertainty regarding the quantification of sources of release from the semiconductor manufacturing industry. Very little detailed emission data on semiconductor fabrication and assembly processes is available given the highly competitive and quite varied nature of the business. To estimate sources of release, the solvent loss profile for the two electronic manufacturing plants visited by SRRP staff and reported on in Section 2.5 was assumed for the industry. Overall emissions from these operations were estimated to be 53 percent to air and 47 percent to land (i.e., solid waste). Table 2.5 presents the solvent use/loss profile for the semiconductor manufacturing industry along with the other industrial sectors of the electronics industry.

A similar situation also exists for PC board fabrication, PC board assembly, and critical cleaning. For PC board operations, the six plant surveys reported on in Section 2.5 were used to construct a profile. Overall, 51 percent of solvent use was emitted to the atmosphere or discharged with the industrial wastewater and 49 percent ended up as solid waste. Since wastewater discharge is small, air emissions are taken to be 50 percent and wastewater discharges are one percent.

While many PC board operations are conducted with open top and conveyorized in-line degreasers, the profile given above is different from the one presented in the Technical Support Document on parts cleaning. In that report, the air emission profiles ranged from 78 percent for an open top degreaser up to 85 percent for an in-line conveyorized unit. Differences in the industry profiles for similar equipment are believed to be due to the need for the electronics industry to maintain a much higher solvent purity level. This triggers the need for more frequent change-outs of solvent and hence more solid waste.

Table 2.5

Solvent Use/Loss Profile for the Electronics Industry

Industry and Operations	Media (a)	1988 Solvent Use (Thousand Metric Tons)					Total
		TCE	PERC	METH	TCA	CFC-113	
Semiconductor Production	Input	2.5	0.8	1.8	1.4	4.4	10.9
Fabrication & Assembly	A(43%)	1.1	0.3	0.8	0.6	1.9	4.7
Fabrication & Assembly	S(57%)	1.4	0.5	1.0	0.8	2.5	6.2
PC Board Fabrication	Input	0.0	0.0	13.8	8.0	0.0	21.8
Develop & Strip Photoresist	A(50%)	0.0	0.0	6.9	4.0	0.0	10.9
Develop & Strip Photoresist	S(49%)	0.0	0.0	6.8	3.9	0.0	10.7
Develop & Strip Photoresist	W(1%)	0.0	0.0	0.1	0.1	0.0	0.2
PC Board Fabrication	Input	0.0	0.0	0.0	0.0	4.8	4.8
Clean & Dry Boards	A(50%)	0.0	0.0	0.0	0.0	2.4	2.4
Clean & Dry Boards	S(49%)	0.0	0.0	0.0	0.0	2.4	2.4
Clean & Dry Boards	W(1%)	0.0	0.0	0.0	0.0	0.0	0.0
PC Board Assembly	Input	0.5	0.5	0.7	6.6	25.7	34.0
Defluxing	A(50%)	0.3	0.3	0.4	3.3	12.9	17.0
Defluxing	S(49%)	0.2	0.2	0.3	3.2	12.6	16.7
Defluxing	W(1%)	0.0	0.0	0.0	0.1	0.3	0.3
Critical Cleaning	Input	0.0	0.0	0.0	0.0	4.8	4.8
Degreasing	A(64%)	0.0	0.0	0.0	0.0	3.1	3.1
Degreasing	S(36%)	0.0	0.0	0.0	0.0	1.7	1.7
Etchant Generation	Input	0.0	0.0	0.0	0.2	0.2	0.4
In-Situ Use	A(0%)	0.0	0.0	0.0	0.0	0.0	0.0
Total Use / Loss	Input	3.0	1.3	16.3	16.2	39.9	76.7
Emission	Air	1.3	0.6	8.0	7.9	20.2	38.1
Emission	Solid	1.7	0.7	8.1	8.0	19.2	37.6
Emission	Water	0.0	0.0	0.1	0.1	0.3	0.6

Source: CMR (1989); D'Ruiz (1991); SRRP staff; and industry sources. Data shown above excludes solvent used in general parts cleaning.

Notes:

a) Percent shown represents amount of solvent used lost to air (A), water (W), or as solid (S) waste. Amount of recycled solvent used is assumed to be minor and is not included in the above estimates of solvent use (amounts represent virgin consumption only).

For critical cleaning operations, the overall profile from the parts cleaning document is assumed: 64 percent air and 36 percent solid waste. While it might be expected that the percent solid waste would be higher to keep in line with the need for maintaining a higher level of solvent purity, this profile closely matches the profile for the plant visited by SRRP staff that performed critical cleaning. At that facility, 32 percent of all solvent used was emitted as solid waste. The profile for in-situ generation of etchants is taken to be zero percent for all media since this use results in the thermal destruction of the solvent.

2.5 SITE SURVEYS

Over the course of this study, SRRP staff visited six PC board operations, two semiconductor manufacturers, and two critical cleaning operations. Plants 1 through 3 are aerospace plants engaged in PC board fabrication and assembly; plants 4 through 6 are commercial plants. Plants 7 and 8 are engaged in electronics assembly only. Plants 9 and 10 are engaged in precision cleaning. Table 2.6 presents the results of the visits to these plants.

All six of the PC board plants employ a CFC-113/alcohol blend for defluxing the boards after assembly. Only one of the plants, Plant 4, uses a TCA blend. Plant 2 uses a CFC-113 blend for defluxing boards produced for the government and water for commercial boards. None of the aerospace plants use recycled solvent while all three commercial plants do.

The six surveyed plants represent a wide range of solvent usage, from about 5 MT to 240 MT per year. For the three aerospace plants, solid waste accounts for 49 to 72 percent of total solvent use. This suggests that the balance, 28 to 51 percent, is emitted to the atmosphere or discharged with the industrial wastewater. In contrast, solid waste generation at the commercial plants accounts for 26 to 40 percent of total CFC-113 use. In this case, atmospheric emissions and solvents discharged with the industrial wastewater account for a larger fraction of the losses, 60 to 74 percent of total use. The reason for this is that the aerospace plants must maintain a higher degree of cleanliness and, hence, empty their degreasers when the contamination level reaches 5 percent. As a percentage of total use, they generate more waste than the commercial plants which allow their degreasers to reach 20 percent contamination before emptying.

In the semiconductor industry, two assembly plants were visited. The first one, Plant 7, produces hybrid microelectronic circuits for the military, space, and medical industries. The firm uses TCA to clean grease and oil from metal and ceramics and CFC-113 as a defluxant after tin leads have been soldered to the components. The firm also uses a small amount of METH as a maskant stripper and PERC as a component of a photoresist stripper. The plant uses no recycled solvent. Plant 8 uses a combination of TCA, CFC-113, and alcohol for flux removal, recycled CFC-113 as a general cleaner, and precision grade CFC-113 for critical cleaning. A minor amount of TCA is also used for general cleaning.

Table 2.6

Summary of Surveyed Facilities

Plant	Solvent(s)	Annual Solvent Use (kg)	Annual Waste Generation (kg)	Contamination Level (Percent)	Mil Spec	Use Recycled Solvent
1	CFC-113 CFC-113/ethanol	12,700	7,600	5	Yes	No
2	CFC-113/methanol Water sequence	11,700	8,400	NA	Yes	No
3	CFC-113/methanol CFC-113/ethanol	238,800	118,000	< 5	Yes	No
4	CFC-113/methanol	4,800	1,900	20	No	Yes
	TCA/isopropyl alcohol	1,900	1,100	NA	No	NA
5	CFC-113/methanol	12,500	3,200	20	No	Yes
6	CFC-113/methanol Also uses water	7,100	2,600	20	Yes[a]	Yes
7	TCA	15,100	8,230	NA	--	No
	CFC-113	10,660	5,910	NA	--	No
8	TCA/CFC-113/alcohol	3,400	1,090	NA	--	No
	CFC-113	7,900	2,570	NA	--	Yes
	TCA	270	80	NA	--	No
	CFC-113 (precision grade)	2,600	860	NA	--	No
9	CFC-113	15,800	4,900	NA	--	No
	TCA	21,000	9,900	NA	--	Yes
	CFC-113/METH	28,900	6,000	NA	--	No

NA Is not available.

a) This manufacturer meets a government specification that requires use of a certain solvent.

Plant 9 does critical cleaning of automotive capacitors and linear transducers. The linear transducers are tested with virgin CFC-113. The plant also uses recycled TCA to clean oils and large particles from diaphragms and a combination of CFC-113 and METH to clean fingerprints and machining residues from parts. Plant 10, which is not shown in Table 2.6, precision cleans electro-optical components including casting, o-rings, and optics. The plant removes greases, oils, and fatty acids from parts which require a very high level of cleanliness. They have been testing a cleaning system that employs supercritical carbon dioxide which they find to be an excellent solvent with good penetrability. A production unit will be put into operation shortly.

2.6 REGULATORY TRENDS

Several of the halogenated solvents have, for some time, been associated with human carcinogenesis. As ozone depleters of the stratospheric ozone layer, CFC-113 and TCA contribute to enhanced ultraviolet radiation at the earth's surface, with resulting increases in skin cancers. A consensus has emerged that these substances can pose major problems when they are released into the environment, and that significantly reducing their use can consequently reduce the health and environmental threats associated with them. Table 2.7 summarizes the health and environmental characteristics of the five halogenated solvents.

Under mandates to curb emissions, the most internationally significant is the Montreal Protocol, signed by nations producing and using the bulk of ozone-depleting chlorofluorocarbons (CFCs), as well as TCA Under the Protocol, to which the United States is a signator, both CFC-113 and TCA production are to be phased out, CFC-113 by the end of the century and TCA by 2005. During the second renegotiation to be held in November 1992, it is anticipated that the phase-out schedule may be accelerated. The phase-out of CFC-113 may be moved ahead to 1995 and TCA to 1997 (Morehouse, 1991).

The 1990 amendments to the Federal Clean Air Act point toward strict regulations of METH, PERC, TCE, TCA, and other halogenated solvents identified as toxic air pollutants. Under the emergency provisions and accelerated rulemaking provisions of the Clean Air Act several environmental organizations have petitioned the EPA to phase out production of CFC-113 by January 1,1995, and HCFCs by January 1,2000 (Morehouse, 1991).

In California, METH and PERC were recently identified as toxic air contaminants. As a result of this determination, METH and PERC use and emissions will be strictly controlled

Table 2.7

Health and Environmental Characteristics of Halogenated Solvents

Solvent	OSHA PEL (ppm)	Known Carcinogen (California)	Photochemical Smog Precursor		Toxic Air Contaminant		Ozone Depletion ODP Factor[c]	Montreal Protocol	Drinking Water RCRA Waste[d]	MCL (mg/L)	
			EPA	SCAQMD	EPA	CARB				EPA	California
TCE	50	Yes[b]	Yes	Yes	Yes	Yes	–	No	F001/F002	–	0.005
PERC	25	Yes[b]	Yes	Yes	Yes	Yes	–	No	F001/F002	–	0.005
METH	500[a]	Yes[b]	Exempt	Exempt	Yes	Yes	–	No	F001/F002	–	–
TCA	350	–	Exempt	Exempt	Yes	Yes	0.1	Yes	F001/F002	0.2	0.2
CFC-113	1,000	–	Exempt	Exempt	Yes	No	0.8	Yes	F001/F002	–	–

Source:

SRRP staff review of various issues of the Federal Register and other regulatory documents.

Notes:

[a] California OSHA PEL for METH is 50.

[b] 26 CCR Section 22-12000.

[c] The Ozone Depletion Factor (ODP) is a measure of the ozone depletion potential of a chemical that depends on its atmospheric lifetime and the amount of chlorine it contains. Values are relative to those of CFC-11 and CFC-12 which have defined ODPs of 1.0.

[d] The solvents are RCRA-listed hazardous waste (F001 through F002) which are banned from land disposal.

Abbreviations:

CARB - California Air Resources Board
MCL - Maximum Concentration Limit
OSHA - Occupational Safety and Health Administration
PEL - Permissible Exposure Level
RCRA - Resource Conservation and Recovery Act
SCAQMD - South Coast Air Quality Management District

throughout the state. The California Air Resources Board (CARB) is in the process of developing regulations that are likely to severely curtail METH use in California. Similar regulations for PERC are likely to follow.

METH, PERC, and TCE are listed by the State of California as known carcinogens. Under the state's landmark toxic control law, passed by the voters in 1986 and commonly known as Proposition 65, any business that exposes people to a listed chemical must give clear and reasonable warning to the individuals exposed. In addition, businesses may not discharge a listed chemical into any source or potential source of drinking water. Exceptions to both requirements exist if the business can show that the amount in question was within "no significant risk" levels (currently defined as 50 micrograms per day for METH, 14 micrograms per day for PERC, and 60 micrograms per day for TCE).

Provisions of Title III of the Superfund Amendments and Reauthorization Act (SARA) have resulted in public pressure on users of air toxics, including halogenated solvents. By mandating a national toxic chemical emissions inventory and delineating a mechanism for public disclosure of all toxic and hazardous chemicals in use by industry, SARA Title III is providing both a database on which to build source reduction programs and effective stimuli for generators to minimize their inclusion in this publicly scrutinized database.

The Federal Pollution Prevention Act of 1990 increases EPA visibility in source reduction activities and provides increased resources to state programs aimed at source reduction. EPA's new 33-50 cooperative government-industry program calls for a voluntary emission reduction of 33 percent in 17 toxic and hazardous chemicals by the end of 1992 and 50 percent by 1995. Two of the five major halogenated solvents, TCA and TCE, are targeted in the 33-50 effort.

2.7 INDUSTRY TRENDS

The electronics industry is constantly changing because of the competitive nature of the business. Several trends in this industry will affect the use of solvents in the future. In this subsection, technological trends in semiconductor fabrication, PC board fabrication, and critical cleaning applications are discussed.

As mentioned earlier, more than 90 percent of the semiconductors produced today are crystalline silicon-based. Research is underway to investigate the use of gallium arsenide, amorphous silicon, indium phosphide, and many other compounds as base materials. Their use may result in higher densities, faster switching speeds, higher power handling capabilities, lower costs, and a wide range of other benefits Although the use of these materials may increase in the future, it is not likely to affect the usage of solvent significantly.

In PC board fabrication, three types of photoresist are in common use: solvent, aqueous, and semi-aqueous. The solvent-based resist is developed with TCA and stripped off with METH. Aqueous and semi-aqueous photoresists are developed and stripped off without the use of halogenated solvents. There has been a clear trend in recent years toward these non-solvent resists. One source estimated that 25 percent of the market was held by solvent photoresist in 1985 (SRI, 1985). Other sources indicate that the market share has dropped to 15 percent and that the market will bottom out at 5 percent within the next five or six years. The only firms to be using solvent-based resists in the next 5 to 10 years are expected to be small job shops whose operations are based entirely on solvent use or who cannot afford the capital investment for new equipment.

Military specifications that required the use of solvent-based resists resulted in the investments made in existing equipment (SRI, 1985). Military specifications have since been changed, and when equipment is replaced, it is replaced with semi-aqueous systems. Developing and stripping semi-aqueous resist is reported to be less expensive than developing and stripping solvent resist. The semi-aqueous process is now the most widely used method.

Another movement that affects the-design and production of PC boards is surface mount technology (SMT). Surface mounted devices (SMDS) are small and have no thru-hole connector leads. Because holes in the boards are not needed with these devices, components may be more densely packed. When SMT is used, there can be a reduction of as much as 40 percent in the size of the PC board. Indeed, the smaller devices have lower component-to-board clearances; they are in the rage of 2 to 10 mils (SMT, 1987). The movement toward SMT means that solvents used in defluxing the assembled PC boards must be able to penetrate smaller crevices. Some industry representatives claim that there has been a movement back to solvents and away from aqueous defluxing systems because they do not provide adequate flux removal from under the SMDs. In the area of cleaning and defluxing non-SMD boards, one source predicts that 90 percent of all cleaning will be performed with aqueous cleaners in the near future (D'Ruiz, 1991).

Because of the expected phase-out of CFC-113 and TCA, an Industry/DOD/EPA working group has been convened to investigate the use of alternative defluxing agents. While the military and government sectors account for 12.2 percent of the PC board market, their impact on the industry may be understated due to the wide-spread adoption of government standards. One source suggests that as much as 40 to 50 percent of the CFC-113 used in electronics is driven by military specifications and that the specification has become a de facto world standard (Naegele, 1989). In March, 1988, the group met to determine ways to evaluate alternative cleaning materials and implement them into manufacturing facilities as quickly as possible (Johnson and Bergman, undated).

The planned program was divided into three phases. The first phase involves benchmark testing to verify the protocols and to establish a baseline using standard printed board assemblies defluxed with a blend of CFC-113, methanol, and nitromethane. In Phase 2, alternative cleaning media are to be tested at a number of facilities- If these alternatives test favorably, the results will be submitted to the DOD to be considered for addition to the appropriate military specifications. In Phase 3, more extensive testing will be conducted along with testing of alternative fluxes and cleaning processes. The specific project requirement and testing protocols have been published by the Institute for Interconnecting and Packaging Circuitry (IPC, 1988; IPC, 1991).

In the area of critical cleaning, industry is actively investigating the use of supercritical carbon dioxide cleaning. The solvency of supercritical carbon dioxide, as well as its low surface tension and low viscosity suggest that it can provide a high level of cleaning. Its low surface tension might also make it a viable method for defluxing SMD circuit boards. To research and promote the technology, an inter-agency/industry task force has been established (JAAST, 1991)

3.0 SOURCE REDUCTION OPPORTUNITIES

In this section, the source reduction options that apply to each of the major activities and operations conducted by the electronics industry are discussed. Printed circuit board assembly is the largest consumer of halogenated solvents and is extensively discussed. Major options to reduce or avoid the use of solvent include use of "no clean" or low solid fluxes, aqueous based defluxing, and many of the options regarding modification to degreaser design that were discussed in the Technical Support Document on parts cleaning.

Printed circuit board fabrication, the second largest consumer of halogenated solvent, is not discussed in detail since there have been and there continue to be strong economic driving forces away from the use of solvents. Since the alteration of military specifications to allow for the use of semi-aqueous resists, the market share of solvent based resists has declined by two-thirds. The discussion of options for the other operations is also brief due to their lesser importance with regard to overall solvent use and the fact that many of the options that apply have been covered in detail in the parts cleaning document. A summary of options investigated is presented in Table 3.1.

3.1 PRINTED CIRCUIT BOARD ASSEMBLY

CFC-113 and TCA are the primary solvents used for removing the flux from PC boards after components have been soldered to them. Major ways to reduce or avoid their use include use of no clean or low solid fluxes, use of alternative defluxing agents, recovery and recycling of solvent vapors, and recycling of waste solvent. As discussed in Section 2.7, a joint industry and government task force is actively investigating alternative defluxing agents. Source reduction options that would reduce or eliminate the use of CFC-113 and TCA in this application are presented below.

1) Do Not Deflux Boards

In certain sectors, it may be acceptable to skip the defluxing step and not clean the board. While this would lower the reliability of the board, a fair question would be to ask just how reliable does the board need to be. Boards used in toys or short-lived equipment may not need the same level of reliability as would military or avionic equipment. While it is not expected that this option could be widely adopted, there are most likely many cases where it could be employed.

Table 3.1

Summary of Source Reduction Options Investigated

Option	Advantages	Disadvantages
P.C. Board Assembly		
1. Do Not Deflux	Avoids or reduces the use of CFC-113 and TCA.	Boards prone to failure. Only applicable to non-critical, short lived applications.
2. No Flux Soldering	Soldering under a nitrogen atmosphere prevents the formation of oxides on the board. Use of flux and defluxing solvents not required.	New technology requiring new equipment and precise process control.
3. Low Solids Flux	No bridging of surface mounted components or circuit traces. Small amounts of residue may reduce or eliminate defluxing requirements.	Flux must be applied uniformly and with precise control. Not currently allowed under military specifications.
4. Least Hazardous Defluxing Agent		
4A. Aqueous Cleaners	Use of water good for removal of acid flux and ionic soils. Detergent required for removal of rosin flux.	Water demineralization and wastewater treatment system required. Increased water and energy use depending on bath temperature. Acidic wash may be required to prevent tin and lead hydroxide deposits on board. May not be suitable for surface mounted boards.
4B. Alcohols	Effective at removal of polar compounds. Often used in blends with CFC-113.	Not effective on non-polar compounds. Danger due to flammability.
4C. Terpenes (d-limonene)	Effective at removing abietic acid, a major component of rosin flux. Solvent extracted from waste orange peels and is biodegradable. Actively being researched as a CFC-113 substitute..	Pure d-limonene is flammable when sprayed and must be used in explosion proof equipment. Solvent is photochemically reactive and has a citrus odor. Not currently allowed by military specifications.
4D. Other Hydrocarbons	Eliminates use of CFC-113 and TCA.	No information available regarding their performance, composition, or health effects.

Table 3.1

Summary of Source Reduction Options Investigated (continued)

Option	Advantages	Disadvantages
4E. HCFCs and CFC-113 Blends	Reduces use of CFC-113 and ozone depletion potential. Conversion could be simple drop-in replacement.	HCFCs will not be widely available. CFCs will be phased-out by year 2000 or sooner.
5. Improved Equipment and Operating Practices	Many options are easy to implement, low cost, and can achieve reductions of 25 to 75 percent depending on degree of implementation. See parts cleaning document for details.	Need for modifications to equipment and/or changes in existing procedures. Some options may increase worker exposure.
6. Recovery and Reuse of Solvent Vapors		
6A. Carbon Adsorption	Well established technology, can reduce emissions from open top degreasers by 65 percent. Recovered solvent can often be reused following drying and particulate filtration.	Expensive, especially if high Ni alloy equipment is required. Need for source of steam. Potential problem with wastewater disposal.
6B. Polymeric Adsorption	Able to handle humid airstreams. Polymer is easier to regenerate, has longer lifetime, and does not exhibit catalytic effects or degradation of halogenated solvent as does carbon.	No commercial systems in operation in the United States. No information available regarding application to P.C. board defluxing.
6C. Brayton Cycle Heat Pump	Achieves high recovery efficiencies and is being investigated as a means of regenerating carbon bed adsorbers. Decoupled system appears to be cost-effective for small scale users.	New technology that is being field tested. Coupled system is cost prohibitive for most operations.
6D. Membrane Separation	Simple operation, no secondary waste streams.	Does not appear to be suitable for high volume, low concentration waste streams.
6E. Cryosolve Process	High recovery efficiency, few moving parts to break or maintain. Similar process now available by U.S. supplier. System reported to be low cost.	Requires source of liquid nitrogen.

Table 3.1

Summary of Source Reduction Options Investigated (continued)

Option	Advantages	Disadvantages
7. Recycling of Waste Solvent		
7A. Filtration and Microfiltration	Equipment widely available. Can extend solvent life and provide for a higher level of cleaning. Methods widely applied in the electronics industry.	Need to replace filter cartridges, increased costs for pumping. Does not remove soluble oils and greases.
7B. Vapor Degreaser Boil-Down	Can recover 60 to 80 percent of the solvent. Requires no additional equipment.	Exposure of heating coils can lead to decomposition of solvent. Increase in oil content can make waste difficult to remove from degreaser.
7C. On-Site Recycling	Process stills provide continuous cleaning of solvent. Batch stills provide maximum recovery. Recoveries range from 60 to 95 percent.	Need for on-site equipment and routine monitoring of acid acceptance valve. Recovered solvent may not be suitable for reuse without additional filtering, dehydration, and replenishing stabilizer.
7D. Off-Site Recycling	No capital investment required. May provide a source of revenue to facility. Most, if not all solvent waste is currently managed by off-site reclamation services.	Dirty solvent is of low value if high in oil/solid content and if facility will not buy back recycled solvent. Purity of solvent may not meet required specifications.
P.C. Board Fabrication		
1. Aqueous/Semi-aqueous Resist	Eliminates use of TCA and METH, lower costs. Industry will continue move away from solvent based resist as older equipment is retired.	Requires replacement of existing equipment. May not be allowed by all specifications.
2. Other Options	See P.C. board assembly options 6, 7, and 8 above and the parts cleaning document.	See P.C. board assembly options 6, 7, and 8 above and the parts cleaning document.

Table 3.1

Summary of Source Reduction Options Investigated (continued)

Option	Advantages	Disadvantages
Semiconductor Fabrication and Assembly		
1. Carbon Dioxide Snow	Equipment is low cost and easy to operate ("snow" guns). Eliminates use of solvent and results in minimal waste.	Limited to particulate removal only. High pressures can cause substrate damage. Static build-up can be a problem and damage static sensitive devices.
2. UV Light and Ozone	Can be used to remove organic contaminants and sterilize equipment.	Experimental technology, Will require worker protection from UV light and ozone exposure.
3. Laser Cleaning	System can be tuned to remove a given contaminant. Method results in no solid waste generation.	Method is experimental and highly dependent on the differences in contaminants and substrate.
4. Laser Marking	Eliminates need for testing identification markings with CFC-113 and METH.	Can cause damage to case or substrate.
Critical Cleaning		
1. Aqueous Cleaning and Drying	Very good at removing water soluble oils and particulates. Method uses long standing technology. System may be more cost effective than CFC-113 drying.	Poor removal of many organic contaminants. Method requires ultra pure water to avoid spotting. Complex shapes are difficult to dry.
2. Other Options	See P.C. board assembly options 6,7, and 8 above and the parts cleaning document.	See P.C. board assembly options 6, 7, and 8 above and the parts cleaning document.

2) Use of No Flux Soldering

Northern Telecom and Motorola are investigating a new technology called inert gas soldering to solder throughhole and surface mount boards. The process applies activators to the board using ultrasonic injection into a nitrogen controlled atmosphere. The activators are organic acids such as formic and abietic acid. Because the activation and soldering process occurs in an oxygen free environment, no oxides form on the boards. Therefore, the soldered boards do not have to be cleaned. Two firms, one Belgian and the other German, are marketing the units which are priced at around $250,000.

3) Use of Low Solids Flux

Flux is generally composed of 15 to 35 percent solids. Low solids fluxes with only 2 to 5 percent solids are being developed and adopted by various users (Lea, 1988; Deram, 1988). An advantage of these fluxes is that solder does not bridge over densely packed surface mounted components and that the small amounts of residue left on the board often does not require defluxing. Many suppliers of “no clean” fluxes claim that the reliability of the boards is equal to those soldered with regular flux and cleaned with solvent.

To leave no residue, the flux must be very dilute and relatively inactive. All metal surfaces must be clean and in a very solderable condition. With no-clean flux, there is virtually no tolerance for solderability or process control problems (Bemier, 1988). While the use of no-clean flux requires much more attention to process control, this increased attention may reveal potential problems that otherwise would not be detected. One manufacturer of flux indicates that the high solids in regular fluxes sometimes mask solderability problems which only became apparent when low solid no-clean fluxes are used.

In one study, AT&T reported on its testing of low solids fluxes (Guth, 1989). The conclusions of the study were that excessive low solids flux residue left on the boards can be detrimental. To prevent excessive build-up of residue, careful process control and monitoring were essential. The flux must be applied uniformly with precise control and must be performed in a closed system to maintain flux composition- Otherwise, the solvent will evaporate and alter the flux composition. AT&T has developed a low solids fluxer that meets these requirements. The fluxer employs an ultrasonic spray for flux dispersal.

In addition to the need for precision application equipment, many of the old formulations contained ionizing acids are activators which were not allowed under military specifications. Today, however, no-clean fluxes are available that contain no halide activators (Deram, 1988). With improvements in the no-clean flux technology, it is likely that their use under military specifications will be re-evaluated. In discussions with SRRP staff, one facility reported that it had experienced significant savings by going to no-clean flux though it was not able to quantify the amount of savings.

4) Use the Least Hazardous Defluxing Agent

The following sections discuss substitute defluxing agents. While it is difficult, if not impossible, to assign absolute values to the hazard of any given material or method, they can be ranked in relative terms. The first level of materials would be aqueous cleaners followed by alcohols, terpenes, and others. The final level would be HCFC replacement solvents and CFC blends.

Use of Aqueous Cleaners

Water can be used to deflux PC boards in two distinct ways. First, water can be employed to remove organic acid flux which is water soluble. Second, water can be used to remove rosin fluxes if saponifiers or detergent additives are employed. Table 2.4 shows, however, that water with saponifiers can only be used with permission of the Government Contracting Officer in military applications. Table 2.3 shows that organic acid flux is not allowed by military specifications.

In the first option, deionized and filtered water is used for organic acid flux removal. A three stage process is generally required: washing, rinsing, and drying. A small amount of saponifier (typically monoethanolamine) is commonly added to the water in the wash stage to improve defluxing. The saponifier reacts with the removed oil, grease, and rosin to form a water soluble soap. The pH of the solution is generally in the range of 10.5 to 12. In the rinse stage, the most effective method is to use a high pressure spray to insure removal of the flux. Drying is accomplished with a hot air knife.

A potential disadvantage of the water/organic acid flux combination is that a highly acidic wash may be required to avoid tin and lead hydroxide deposition on the boards. Tin and lead hydroxide residues left on the boards can lead to insulation failure. When impurities are not completely cleaned from the boards, they can lead to corrosion or allow electromigration (Morrison and Wolf, 1985).

With the second option, use of saponifiers or detergents to remove rosin flux, the same sequence of wash, rinse, and dry is employed. In this case, the cleaning solution emulsifies the nonpolar soils and saponifies the organic components (primarily abietic acid) of rosin flux. The soap produced in the saponifying reaction can carry over to the water rinse and antifoaming agents must be employed to prevent foaming. A hot air knife is also used to remove rinse water and dry the boards.

As in the first option, the use of water can lead to corrosion which will result in the formation of insoluble tin and lead hydroxides on the boards. The rosin flux may not be completely saponified and residues may be left on the board. This residue may lead to subsequent insulation failure. A third difficulty is that alkaline soaps tend to be difficult to rinse. Rinsing is not as much of a problem with the first option since organic acid flux is water soluble.

One barrier to the use of either water system is that the effluents released from the process may exceed local or federal regulations for copper, lead, pH, or Biological Oxygen Demand. Firms that manufacture PC boards fall into the electroplating category (40 CFR Part 413) if they are old sources or the metal finishing category (40 CFR 433) if they are new sources. If the firms do not fabricate the boards but only assemble them, they are subject only to local sewer regulations (USEPA, 1984).

In the work performed by Januk, et al. (1983) six detergent cleaning solutions used for defluxing were analyzed for pH and concentrations of lead and copper. Lead concentrations ranged from 0.3 to 2.1 milligrams per liter (mg/l), copper concentrations ranged from 0.11 to 1.7 mg/l, and pH values ranged from 10 to 11. Compared to EPA pretreatment standards, lead levels exceeded the EPA standard of 0.6 mg/l in three of the six cases. Copper levels were not exceeded, but all six samples exceeded the pH limits of 6 to 9. Treatment to reduce the level of lead and neutralization of the effluent would be required.

Another barrier to the use of aqueous defluxing arises with the movement toward surface mount technology. In choosing a good defluxing agent, two main characteristics are important. First, the defluxing agent must have the capability to wet the board and penetrate under the surface mounted components. Second, it must have the ability to dissolve the flux and its residue. Water and aqueous defluxing agents tend to perform poorly on surface mounted devices because the high contact angle of water prevents it from providing good wettabililty. Many users claim that problems with water cleaning arise when the spacing between components and the board is less than 10 mils. Other users believe that high pressure water cleaning systems can effectively clean, even in cases where the spacing between the component and board is less than 10 mils.

High pressure sprays can, to some extent, improve the ability of water to clean under surface mounted devices. The high pressure jets of water must be used at low spray impingement angles. The impingement angle for surface mounted assemblies can vary from 10 degrees to 40 degrees with an average of about 25 degrees. The water jets must impinge at a very low angle to the board so that the water can penetrate under the components that are spaced close to the board (Ellis, 1987). High pressure air knives installed between the wash and rinse steps can also facilitate water cleaning (Keeler, 1987).

Use of Alcohols

Pure alcohols such as methyl alcohol, ethyl alcohol, and isopropyl alcohol are very good at removing polar compounds. Pure alcohols, however, are not good at removing nonpolar contaminants such as grease and flux residue that remain on the board. Table 2.4 lists and describes a number of solvents that are called out under the military specification. As indicated, methyl alcohol can be used for defluxing PC boards only if it is a constituent of a blend. In contrast, ethyl and isopropyl alcohol can be used neat. Other solvents that might be considered include acetone, methyl ethyl ketone, or mineral spirits. All are photochemically reactive and only mineral spirits is permitted under military specification. Defluxing equipment for use with alcohol and non-halogenated solvents is available in Europe. It must be explosion proof and be fitted with fire protection devices. Some equipment uses nitrogen gas purging for fire protection.

Use of Terpenes

Terpenes, or more specifically d-limonene, is a biodegradable solvent derived from orange peels. Petroferm, Inc., of Femandia, Florida, markets Bioact EC-7 which has received much attention as a cleaning product for removing flux residues from printed wiring assemblies. Bioact EC-7 is a blend of d-limonene and surfactant. Surfactant is used for the removal of ionic contaminants and to facilitate emulsification of d-hmonene so that it can be rinsed off the board with water (d-limonene is relatively insoluble in water).

As previously discussed, the most commonly used rosin flux is composed primarily of abietic acid and related substances. Since the structure of d-limonene is similar to that of abietic acid, formulations containing a significant fraction of d-limonene should be expected to be good at removing the abietic acid component of flux from PC boards. Indeed, test data indicates that d-limonene is one of the best solvents for removing abietic acid (Cabelka and Archer, 1987; Hayes, undated).

For removing non-abietic acid flux components and other contaminants, other sources suggest that d-limonene is not so good as CFC-113/methyl alcohol. In particular, d-limonene does not compare favorably with CFC blends at removing the “white or tan residues” which may arise from outside the soldering or cleaning processes. These residues may be due to improperly cured solder mask which reacts with soldering or cleaning materials. They may also arise from PC board overheating. Analysis of the residues identifies them as baked-on rosin, abietic acid salts, or tin and lead halide salts (Wolff, 1988).

Testing by Wolff indicated that CFC-113/methyl alcohol was better at removing ionic contamination from boards than terpenes. Military specifications require an ionic contamination level no greater than 21 micrograms of sodium chloride equivalent per square inch. In more recent testing by Hayes (1990), Bioact EC-7 was shown to achieve lower ionic contaminant levels than CFC-113/methanol blends. It is not known if the testing performed by Wolff was conducted with pure d-limonene or if the boards were rinsed after defluxing.

In the process recommended by Petroferm, the printed wiring board is either immersed in the cleaner which is at room temperature or sprayed with it. The d-limonene dissolves the flux and the cleaner which contains surfactant is then rinsed from the board with water. The water wash should, in principle, dissolve the polar contaminants and leave a clean surface. The final step is to dry the boards with hot air. In summary, then, the boards are washed, sent through an air knife to remove excess solvent, rinsed with water, sent through an air knife again, and finally air dried.

Equipment designed to deflux circuit boards with terpene formulations is now commercially available (Attalla, 1990). Batch equipment typically consists of a small dishwasher unit that spins the boards while spraying them with the terpene defluxant. To prevent fire, the unit is blanketed with either nitrogen or carbon dioxide. After defluxing, the boards are removed and placed into a similarly designed rinse unit. Rinsing is then followed by drying the boards in a batch oven. Each defluxing cycle can handle 64 boards or assemblies and can handle up to 3,000 boards per day. In-line conveyorized systems are also available.

In spite of their proven ability to deflux boards, there are several potential disadvantages or limitations to the use of terpenes. First, they are not currently allowed under military specification. As Table 2.4 indicates, they are not called out under DoD-STD-2000-1B. As mentioned earlier, there is an ongoing effort to change and revise these military specifications but it is not known if terpenes will be approved or how long the revision process will take.

Another problem with terpenes may be flammability. Pure terpenes are rated as combustible liquids by the National Fire Protection Association (NFPA). The flash points of most high content d-limonene cleaners is on the order of 120°F. Because of their combustible nature, these solvents are appropriate only for use at room temperature. Depending on the terpene content of any remaining waste, spent cleaners might also be classified as hazardous waste. This would require expensive disposal. However, because of their high BTU value, a preferred method of spent terpene disposal would be as a fuel additive in a fuel blending program provided that heavy metal content (especially lead and copper) were at acceptable levels. Recycling of the terpene using vacuum distillation may be viable for large scale applications.

Use of terpene based defluxers will also add an organics load to the wastewater pre-treatment plant or municipal treatment works. In principle, when the board is dipped in terpene, all of the flux should dissolve into the bath. In practice, terpene cleaner and dissolved flux will be dragged into the water rinse. Testing performed by AT&T indicates that the rinse water released to the sewer has high biological oxygen demand (BOD). The water may also contain copper and lead leached from the board. Removal of these metals might be required before the water could be discharged.

Another limitation to the use of terpenes is that allowable workplace exposure levels, PELs, have not been set by OSHA. Terpenes are skin and eye irritants and must be handled properly. In a National Toxicology Program study, d-limonene was found to form renal tumors in male rats but not in female rats or in male or female mice (NTP, 1990). Subsequent investigators have reported that this effect is male rat specific and that the scientific database demonstrates that the tumorigenic activity in male rats is not relevant to humans (Flamm and Lehman-McKeeman, 1991). In fact, d-limonene has been used for years as a food additive and is considered “generally recognized as safe” (GRAS) by the Food and Drug Administration (21 CFR 182.60). As with any chemical, however, workers should be trained to exercise caution and to avoid contact by always using proper protective gear.

Other Hydrocarbons

Researchers in several user firms are developing and patenting various higher molecular weight hydrocarbon solvents to replace CFC-113 and TCA In general, such solvents, if used for defluxing PC boards, will require an aqueous rinse. One of these solvents has been developed and patented by Boeing. Another, developed by Martin Marietta, is being evaluated to replace TCA solvents for defluxing surface mounted devices on PC boards (Hall and Katz, 1989). DuPont has also announced the introduction of a new hydrocarbon solvent to be used in semi-aqueous applications (Dishart and Wolff, 1990). The composition of these materials is proprietary.

Use of HCFCs and CFC Blends

According to Wolf (1991) CFC producers are no longer actively investigating the use of HCFCs as replacement for cleaning. HCFC-123 has been found to cause tumors in male rats and DuPont plans to sell the solvent only to pre-approved users. Users must demonstrate that they are capable of containing the solvent and not allow a concentration greater than 10 ppm to exist in the workplace. So far, only 3 users have been approved. In side-by-side tests conducted by Rockwell, losses of HCFC-141b were shown to be 2.67 times greater than those of CFC-113 in an identical vapor degreaser. Allied has indicated that they will not be offering HCFC-141b for sale as a cleaning solvent.

Many solvents are blends of one of the halogenated solvents with one or more components. Increased use of these solvents in place of the neat halogenated solvents would reduce total use of the solvents. CFC-113 is commonly blended with other substances because, alone, it is a rather gentle solvent. CFC113 azeotropes of methanol and ethanol are widely used for defluxing. The percent composition of these azeotropes is 94 percent CFC-113 and six percent methanol, 96 percent CFC-113 and four percent ethanol. To reduce CFC-113 use, mixtures of CFC-113 with higher concentrations of alcohols could be used A strong disadvantage of this option would be that the mixture would not be an azeotrope. This could lead to the bath becoming richer in the less volatile component, the alcohol, which eventually would render the solution flammable and present a fire hazard.

DuPont has announced the introduction of a new CFC-113 based solvent. It contains 69 percent CFC-113, 25 percent trans-1,2-dichloroethylene, and six percent methanol (Wolff, 1988). The second component, dichloroethylene, is more toxic than CFC-113 and the PEL of the blend is about 740 ppm. Trans-1,2-dichloroethylene has not been tested in a smog chamber to assess its photochemical reactivity. Although its structure suggests it would be extremely reactive, experimental data show it to be much less reactive than other halogenated species (Archer and Simpson, 1977). This implies that the mixture may not be photochemically reactive. This solvent will probably not be adopted on a wide scale and its use is not presently allowed under military specifications.

5) Improved Equipment and Operating Practices

Equipment for use with CFC-113 has generally been designed to minimize solvent losses because of the expense of CFC-113 based solvents compared to other solvents. For users with older equipment and for users of TCA in less tight equipment, there are a variety of equipment modification options that can reduce solvent loss. Many of these are described in detail in the Technical Support Document on parts cleaning. Therefore, only a few of the options are briefly discussed below.

In-line defluxers used by many firms are relatively emission-tight. In contrast, emission levels can be quite high in open top vapor degreasers which are also used by many firms to deflux boards. Ways to reduce emissions include increasing freeboard height, installation of roll top lids, installation of refrigerated freeboard chillers, and automation of the parts handling system. Improved operating practices can also be used to reduce emissions. These include leaving the part in the degreaser until solvent condensation ceases, covering equipment when not in use, avoiding use of sprays above the vapor level, and segregating wastes to promote recycling. Adoption of these measures can reduce air emissions by 50 to 75 percent.

6) Recovery and Reuse of Solvent Vapors

Recovery and reuse technologies for halogenated solvent vapors have been available and practiced for many years. The most common method is carbon adsorption with steam regeneration. Newer methods include polymeric adsorption, Brayton cycle heat pump regeneration, membrane separation, and direct condensation. Before undertaking a detailed emission control study for a given site or operation, the reader may be interested to know that a computerized emission control cost model has been developed for use in screening studies (Engleman, 1991). The model includes 11 control technologies, 25 solvents, and is currently in the process of being validated. A discussion of each method listed above is given in the following sections.

Carbon Adsorption

Carbon adsorption can be used to recover solvent emissions from a vapor degreaser used for defluxing circuit boards. It can also be used on other solvent emission sources provided that the emissions can be readily captured. In a carbon bed system, the solvent is adsorbed using activated carbon. Once the bed is saturated, a second bed may be placed on-line and the saturated bed heated and desorbed. Common desorbing agents include steam, hot air (common with solvents that will subsequently be burned or cornbusted), and hot nitrogen or other inert gas (used in polymer adsorption and the BCHP process, described below).

The amount of steam required for desorbing a bed is commonly set at four pounds per pound of solvent to be desorbed. From the bed, steam and desorbed solvent are routed to a water cooled or refrigerated condenser and then to a decanter for phase separation- The recovered solvent may then be passed through a desiccant dryer for removal of trace water and a cartridge filter for removal of small particulates carried over from the carbon bed. The water phase, containing trace amounts of halogenated solvent, may be steam stripped or passed through a carbon cartridge filter before being discharged to the sewer or treatment plant. The desorbed or regenerated bed is placed back on-line when the second bed becomes saturated and needs to be desorbed.

Proper design, operation, and maintenance of the equipment are critical to the successful operation of the carbon bed system. Examples of design errors and operational problems often encountered include: selection and use of carbon that does not meet design specifications, excessive corrosion due to improper choice of construction materials, use of poorly designed and/or maintained dampers which do not open and close properly and allow solvent vapors to bypass the bed, improper timing of the desorption cycle so that beds are either over-steamed (waste of energy) or under-steamed (decreased bed capacity), and installation of faulty and unreliable emission monitoring controls and sensors.

All five of the halogenated solvents studied in this report can be recovered using carbon adsorption, but METH and particularly TCA require equipment to be constructed of high nickel alloys because of the slight hydrolysis that occurs during the steam desorption cycle.

TCA is very susceptible to hydrolysis and recovery equipment for TCA is often constructed of Hastelloy C. The fabrication of Hastelloy C equipment can cost two to three times as much as equipment fabricated from mild steel.

Carbon adsorption has a relatively high capital and operating cost and requires the use of steam which may not be available. Water pollution problems also may result from chemicals contained in the recovered water stream. Water soluble stabilizers removed during steam desorption will be present in the water and may enter the sewer system unless handled as a hazardous waste or treated. When attempting to recover the types of blends or azeotropes of CFC-113 or TCA commonly used in defluxing, the alcohol component will remain in the water phase. Some halogenated solvent may also remain in the steam condensate but the amount tends to be small.

Polymeric Adsorption (PA)

Polymeric adsorption is a new process for solvent recovery and purification, developed by Nobel Industries in Sweden. The process is based on adsorption of solvent onto specially developed macro-porous polymer particles, using fluidized bed technology. The polymers have been optimized for use as adsorbents; they consist of crosslinked styrene divinyl benzene. According to the manufacturer, advantages of polymer adsorption over carbon include the ability to handle humid airstreams, ease of polymer regeneration, long lifetime, and absence of catalytic effects on halogenated solvents.

In the PA process, solvent is adsorbed by the polymer particles as the solvent laden air passes through the adsorption bed. The flow of air causes the polymer bed to fluidize and behave like a liquid. Heavy, solvent laden polymer particles drop to the bottom of the bed while the lighter unladen particles remain at the top. The solvent laden particles are continuously removed from the bottom of the bed, regenerated, and fed back to the top of the adsorption bed. In the desorber or regenerator, the solvent laden polymer is heated with a hot inert gas such as nitrogen which causes the solvent to desorb. The solvent and hot gas are then routed to a condenser where the solvent is condensed and collected while the inert gas is reheated and returned to the desorber. The desorbed polymer is returned to the adsorption bed. The PA process is attractive because it has a few moving parts and energy consumption is low.

According to the manufacturer, the PA process is well-suited for continuous emission airflows of 300 to 100,000 scfm and solvent concentration of 0.005 to 0.1 pounds per 1,000 cubic feet. It is especially well-suited for recovery of water soluble solvents such as alcohols from humid air and recovery of halogenated solvents that oxidize and degrade in warm humid air. This process is also recommended for the recovery of solvents with low boiling points (105°F); however, the incoming airstream temperature should be kept below 90°F. A pilot test unit and full scale unit are currently operating in Sweden.

Brayton Cycle Heat Pump (BCHP)

The Department of Energy (DOE) has been supporting the development of the BCHP in conjunction with 3M and Garrett Air Research since 1978. The technique uses a reverse Brayton refrigeration cycle to condense solvent vapor to liquid. The process cools the incoming gas stream to a very low temperature (as low as -298°F), and condenses the solvent for collection. This process has been viewed with having very limited application potential and most of the work on BCHP technology has focused on its use as a means of regenerating carbon adsorption systems.

Most of the current research work underway focuses on the use of carbon adsorption with coupled or decoupled Brayton cycle regeneration (Scheiling, 1991; and Marr, 1991). The systems being investigated are identical to conventional carbon bed adsorption systems during the adsorption cycle. Once saturated, the beds are then regenerated using the BCHP process. Hot, inert gas (typically nitrogen) passes through the adsorbent bed and desorbs the solvent. The solvent laden gas is then cooled, compressed, cooled again, and then sent through the compressor side of the BCHP (a free-spindle turbo unit). The gas stream is further cooled in an interchanger and enters the expander side of the BCHP where it is cooled to as low a -80°F. The remaining solvent condenses and is recovered for reuse while the inert gas is reheated and used for regeneration.

To prevent ice formation, water must be eliminated from the regeneration gas. Use of either drying steps or appropriate water rejecting adsorbents can eliminate this problem. The BCHP process avoids the use of steam for regeneration and, thereby, does not produce a wastewater stream and eliminates the problem of water soluble stabilizer depletion from the solvent. This method has been demonstrated at 3M for solvent recovery from a commercial size magnetic tape manufacturing facility (Nucon, 1989). A demonstration program using a decoupled BCHP regenerator (the carbon bed remain on-site and a transportable BCHP system is routinely brought on-site to regenerate the beds) is currently being set-up in the Southern California area by Southern California Edison (Mar-r, 1991).

Membrane Separation

Synthetic membranes have been used to separate aqueous and gaseous mixtures and to recover hydrogen from petrochemical and chemical production purge gas streams. Since membranes can be tailor fitted to a given mass separation task, they tend to be suitable for separations that are difficult to achieve by other methods. Semi-permeable composite membranes have been used to separate organic solvents from air. The membrane modules, which are made by coating a tough, relatively open, microporous support membrane with a very thin dense film, allow a large membrane surface area to be packed into a small volume. The support membrane provides mechanical strength and the thin dense coating performs the separation. Organic solvents are preferentially drawn through the membrane by a vacuum pump and the solvent is condensed and removed as a liquid. The manufacturer of these systems claims that comparison to carbon adsorption shows that the membrane process is more cost-effective if the solvent concentration is relatively high (0.5 percent or higher), and the airstream volume low, less than 1,000 scfm (Wijmans et al., undated). Capital costs for a membrane system are in the range of $400 to $1,000 dollars per scfm of airflow and operating costs range from $0.5 to $1.00 dollar per 1,000 scfm treated (MTRI, undated).

Cryosolv Process

The Cryosolv Process developed by Meisser Griesheim, a German company, is a method for purifying air containing high solvent content and can handle up to 1,000 m^3 or 35,000 ft3 per hour (Meisser, 1988). The process is a low temperature condensation process, which allows for the direct reuse of recovered solvent. The process uses liquid nitrogen as a cooling agent, and it is believed that the process involves the direct contact of the liquid nitrogen with the solvent laden airstream. Condensation temperatures range from -100°C (-150°F) to -140°C (-220°F). The system has been demonstrated on a coating line in West Germany. Liquid Carbonic also offers a similar process for sale in the United States (Liquid Carbonic, 1989).

7) Recycling of Waste Solvent

There are several methods of reducing the use of virgin halogenated solvent by recycling contaminated solvent. The techniques evaluated below include filtration and microfiltration, on-site recycling, and off-site recycling.

Filtration and Microfiltration

This process removes insoluble solid particulate matter from a fluid by entrapment, and is a useful method for extending the life of a cold cleaning bath or removing metal fines and sludge from a vapor degreaser sump. While filtration does not remove soluble contaminants such as dissolved oils or fluxes from the solvent, it can be used to remove solid dirt and greases before they have a chance to dissolve in the solvent. This can be quite effective on cold cleaning baths since the low temperature of the solvent prevents the rapid dissolution of removed soil and grease. Many mechanical agitation systems such as jet spray pump around units are equipped with solvent filtration devices. The major types of filters used are bag filters and cartridge filters.

Microfiltration systems are filtration technologies that can remove oil, soil, and grease to a much finer degree than standard filtration. These techniques are also being investigated for their ability to remove emulsified oil and grease from aqueous cleaning solutions. Many filter users have reported longer solvent life, higher efficiency and product quality, and low manpower costs associated with operation and maintenance of their cleaning equipment.

Typically, most vapor degreasers are equipped with a 5 or 10 micron filter for removal of particulates. The smaller particles that are not removed accumulate in the sump and eventually contaminate the solvent vapor and hence the assemblies being cleaned. The use of a microfiltration system can remove particulates down to less than 0.1 microns in size. This minimizes the potential for particulate contamination of the solvent vapor and can remove water, acids, organic soils, and inorganic soils from the solvent. Microfiltration systems are usually connected to the rinse sump during the day, and in a shutdown, are switched to the boiling sump to ensure particulate free solvent in both sumps for the next run.

On-Site Recycling

On-site recycling is becoming more and more popular as a way of reducing virgin solvent use and reducing the disposal of halogenated solvent. According to Dow (undated), 64 percent of their large scale vapor degreaser customers were performing on-site solvent recycling in 1987. This was up from 52 percent in 1984. The performance of on-site recycling can reduce a facility’s purchase of virgin solvent by 20 percent. Waste from an on-site solvent recycling operation is often sent off-site for additional solvent recovery or use in a cement kiln fuel blending program. Since off-site recyclers pay for recovered solvent value and charge for sludge disposal, many on-site recyclers have found that the most economical level of on-site recovery is to recover solvent to the point where the solvent value in the waste equals the disposal charge for the sludge. This way, on-site recyclers achieve maximum value for the solvent they recover while maintaining a zero cost way of managing their wastes off-site. Details of these arrangements are highly site specific.

On-site recycling equipment for halogenated solvents falls into one of three categories: 1) process stills, 2) batch stills, and 3) semiportable ministills. Process stills are used in conjunction with vapor degreasers to provide continuous cleaning of the solvent. Dirty solvent from the sump of the degreaser is pumped to the still for processing and then returned to the degreaser's clean solvent storage tank. Solvent recovery with a process still typically ranges from 60 to 80 percent. Dow reports that 62 percent of those facilities that recycle on-site do so with process stills. An advantage to process stills over batch stills is that the degreaser does not have to be shut down while the solvent is being processed. Another advantage is that the level of contamination in the degreaser stays at a steady low level. Process stills may also be used for recycling solvent from cold cleaning operations provided that the quantity of dirty solvent to be recycled is large enough and is generated at a relatively constant rate.

Batch distillation is performed whenever the degreaser requires cleaning - anywhere from once per week to once per month or longer. Batch distillation is also commonly used to recycle solvent from cold cleaning operations. To be recycled, dirty solvent is pumped into the still, heated and condensed, and then placed in drums or storage tanks for return to its point of use. Batch stills are typically capable of much higher solvent recovery rates than process stills, usually around 70 to 95 percent. The reason for this is that waste from a process still must often be pumped out into drums while many batch stills are designed with liner bags that are then used to lift the waste out of the unit. Since the waste does not have to be pumped out, the viscosity of the waste is less of an issue and higher solvent recovery can be practiced. According to Dow (undated), 36 percent of the facilities that recycle their vapor degreaser waste do so with batch stills. The use of batch mini-stills is not common with vapor degreasing but they are widely used in maintenance parts cleaning.

If the boiling point of the solvent is high (greater than 200°F as with PERC), distillation can be performed under vacuum to minimize thermal decomposition- Another technique is to inject live steam into the solvent which allows the solvent to boil at a lower temperature. The condensate of water and solvent is then phase separated by gravity in a decanter. Steam injection should not be used when the solvent contains water soluble inhibitors or a water soluble component such as alcohol. The use of steam sparging can also result in increased air emissions if the sparging and condensing equipment is not designed and operated properly.

Off-Site Recycling

For generators who are not able to either economically or technically install and operate on-site recycling equipment, off-site reclamation may be a viable option- The off-site recycler, under a contractual agreement, picks up the generator's contaminated solvent, recycles it, and delivers the purified solvent back to the generator. If the generator does not want the recycled solvent back, then he receives a lesser credit for the solvent and the recycler sells the solvent to another user. The sludges that result from the off-site reclamation operation contain small concentrations of halogenated solvent and are usually blended with nonhalogenated solvent waste and sold as fuel to cement kilns. The production of cement requires a source of chlorine and the use of halogenated solvent suits this need well.

Since the 1986 land disposal ban on halogenated solvents was enacted, off-site reclamation has gained widespread use because of the high cost of other available options such as thermal destruction. While the economics of solvent reclamation are favorable, many users question the quality of recycled solvent and, hence, are reluctant to use it. Many users are prevented from using recycled solvents because of military specifications based on high purity virgin solvent specifications. The reluctance to use recycled solvents is justified to some extent since various contaminants may be found in some recycled materials and no two reclamation firms follow the same quality control standards.

The specification for TCA (Mil-T-81533A) requires a maximum water content of 100 parts per million (ppm). While some recyclers who use staged molecular sieve dryers can meet this requirement, many others cannot. Recyclers operating molecular sieves can typically produce solvent with 25 to 50 ppm moisture. High moisture levels in TCA can be dangerous because the solvent tends to be unstable and is subject to hydrolysis or acid formation. The moisture content specified for CFC-113 (Mil-C-81302D) is 10 ppm.

The other military specification requirement that recycled solvent does not commonly meet is the "other halogenated constituent" limit. The limit for TCA is 0.5 percent by volume. Generally, recycled TCA contains one to two percent METH and CFC-113. In recycled CFC-113, common contaminants are TCA and METH. Today, most reclaimers perform detailed analysis on each batch of solvent and supply a fairly high purity solvent. Work is currently underway to revise the Mil-spec procedures and allow the use of recycled solvent (Morehouse, 1991).

3.2 PRINTED CIRCUIT BOARD FABRICATION

As discussed in Section 2.7, the current market share for solvent-based photoresist is estimated to be 15 percent. This share is expected to bottom out at 5 percent within the next five or six years and remain there. Given that there already exists a major driving force toward the elimination of solvent-based photoresist use, the decline in halogenated solvent use for photoresist developing and stripping will also continue. In addition to product substitution, many of the options discussed in the Technical Support Document on parts cleaning could be used to reduce emissions from facilities still using solvent-based resist.

One new technique being investigated as a means of eliminating the use of METH for stripping is abrasive blasting. Alpheus Cleaning Technologies is investigating the use of low pressure carbon dioxide pellets for resist stripping (Alpheus, 1992). Test work in the area of PC board defluxing showed that the use of high pressures resulted in some damage. Also, static charge build-up was observed which could lead to damage of static-sensitive parts. By reducing blast pressure and using more of a carbon dioxide snow than pellets, defluxing of the boards was achieved, but with mixed results. In the resist stripping applications, static charge is not an issue and the results have been more positive. Use of carbon dioxide snow for cleaning semiconductor wafers has been reported on by Hoenig (1985).

In addition to carbon dioxide snow, the use of wheat starch blasting for removal of photoresist has been reported (Larson, 1991). The substrate material consisted of vapor deposited copper on a cloth laminate with very low solvent resistance. The use of wheat starch blasting at low pressure removed the resist and did not result in substrate damage. Wheat starch blasting is mainly being investigated as a means of paint stripping and is discussed in more detail in the companion Technical Support Document on paint stripping.

3.3 SEMICONDUCTOR FABRICATION AND ASSEMBLY

Most, if not all, of the solvent-using operations conducted during semiconductor fabrication and assembly are identical to processes employed during general parts cleaning. The major difference would be for the need to maintain critical cleanliness of the solvent batch which would trigger the need for more frequent replacement of the bath. Rather than repeat all of the options discussed in the companion Technical Support Document on parts cleaning, only those new cleaning technologies that relate directly to semiconductor fabrication and assembly are discussed below.

1) Use of Carbon Dioxide Snow

A number of firms have investigated the use of carbon dioxide snow to remove particulate contaminants from wafer surfaces (Hoenig, 1985). In this process, liquid carbon dioxide from a cylinder is fed into a syphon tube and flashed to form carbon dioxide “snow.” The snow particles knock particulates free from the surface of the wafer and then sublime. A syphon tube “snow gun” costs approximately $400 (Hoenig, undated). Several aerospace and electronics firms have also experimented with this method for cleaning optics and disk heads. A limitation of this option is that it only removes particulate contamination and is effective at removing organic contaminants. Alpheus (1992) reported that static charge generation is a problem with carbon dioxide snow cleaning. The current status of this option is unknown.

2) Use of Ultraviolet Light and Ozone

Researchers have been examining this method for removing organic contamination for more than 15 years (Sowell et al., 1973; Vig and LeBus, 1976; McClintock et al., 1982; Zafonte and Chin, 1984). It may ultimately be used to clean organic contaminants from semiconductors and disk heads, to remove solder flux, and to clean bearings that cannot be degreased. This method relies on the combination of Ultraviolet *(W)* light from a low pressure mercury lamp and ozone to oxidize hydrocarbon contaminants to carbon dioxide and water (Zafonte and Chin, 1984).

While the method is effective at removing organic contaminants, inorganic residues would have to be cleaned with alternative techniques. Another disadvantage of the method is that it may be corrosive to some metals and may attack some plastic materials. Workers would be required to wear goggles to protect their eyes from *W* exposure, and the low PEL of ozone (0.1 ppm) would require high ventilation rates. Given these limitations and disadvantages, it is unlikely that this option would be implemented on a wide scale.

3) Use of Laser Cleaning

Laser cleaning has been practiced for some years in the restoration and preservation of historical artifacts (Doxstader, updated). The advantage of the laser technique is that by tuning the frequency of the laser, organic contaminants can be effectively removed or burned off while minimizing damage to the substrate. A disadvantage of this technique is that the characteristics of both the contaminant and substrate must be known so that the optimal absorption frequency can be chosen. This technique is still in the early research stage.

4) Use of Laser Marking

As previously discussed, a blend of CFC-113 and METH is often used for mark permanency testing. One viable alternative would be to use a laser to mark or scribe the case of the integrated circuit. Laser marking can also be used to mark the substrate, provided it does not damage or interfere with the operation of the circuit. No other information regarding process specifics or the viability of this option is available.

3.4 OTHER CRITICAL CLEANING APPLICATIONS

For this study, other critical cleaning applications are defined as non-PC board, non-semiconductor cleaning operations. As Table 2.1 indicates, these operations primarily involve the use of CFC-113. For the most part, critical cleaning operations are similar in nature to general parts cleaning and the same options apply (see the companion Technical Support Document on parts cleaning for discussion). One option, use of demineralized water, is discussed below because it specifically deals with critical cleaning in the electronics industry.

Most of the following information was derived from a meeting that was held to bring together major users of CFC-113 in mechanical cleaning operations (UCLA, 1988). According to the presentation by IBM, ultra-pure water can be an effective cleaning media for removing aqueous based machine cutting oils and ionic salt contaminants. IBM has been very successful at using hot deionized water to clean and dry aluminum disk drives. IBM produces rigid magnetic media disks for direct access storage devices. The manufacturing process involves flattening, smoothing, and rounding a stamped aluminum blank using a range of machining, grinding, and polishing operations. The next step is to clean and dry this prepared disk substrate so that a magnetic coating can be applied. The substrates are cleaned with an aqueous cleaner and then sprayed with deionized water. The first spray is an ambient rinse followed by a second spray maintained at 160°F to 190°F.

The new drying system that replaced the CFC-113 displacement system relies on the hot deionized water spray and an air tunnel supplied with HEPA filtered air to effect “finish” drying. Flash drying is effective when the parts being dried are of simple geometry so that they are well drained and exceed a given weight to surface area ratio. For most flat metal plates, flash drying can be effective if the thickness of the part exceeds one-tenth of an inch (Pinkerton, 1984). After drying, the air tunnel is designed to drop the temperature of the parts down to room temperature by the time they reach the end of the line.

IBM claims that this system works well but should be considered cautiously in certain respects. First, flat surfaces are easier to dry using the technique than more complex surfaces. Second, disks are better dried than are the fixture. Third, the quality of the water must be very high. A typical specification would be that resistance be greater than 16 megohms, ionic contamination be less than 1 part per billion, and that total organic carbon be less than 25 ppb. Benefits, according to IBM, are that it avoids the use of any halogenated solvent, that it employs no new or experimental technology, and that the equipment is readily available. IBM claims that the new system is more cost-effective than the CFC-113 drying system.

IBM also evaluated three parts cleaning processes for other disk-drive components. These systems included CFC-113 combined with ultrasonics, water combined with ultrasonics, and a water spray system. These systems were compared for their ability to clean and remove particulates, organic contaminants, ionic contaminants, and moisture residue. The water cleaning processes worked better than the CFC-113 process for removing ionic contaminants but were not so effective at removing organic contaminants. The CFC-113 system also dried parts two to three times faster than the water based systems but moisture residue was effectively removed by all processes (Ko, 1989).

4.0 ANALYSIS OF SOURCE REDUCTION OPTIONS

The primary defluxing of fabricated PC boards is the largest user of CFC-113 in the electronics industry. Approximately 26,000 MT of CFC-113 are used each year in this application. Aqueous defluxing or defluxing with terpenes may be adopted by many facilities as the use and availability of CFC-113 is phased-out, provided that these methods are proven effective and military specifications are changed. Until phase-out and replacement occur, options involving the conservation of CFC-113 can be pursued. To determine the economic viability of conservation measures, given the short time frame in which industry will be able to recover their investments in implementing these measures, economic analysis is presented below for installation of a carbon bed unit on an existing system and the replacement of the existing equipment with "low emission" equipment.

Both analyses are for a hypothetical facility employing the use of a medium sized conveyorized in-line defluxer. Since phase-out of CFC-113 will occur in 1997, capital expenses are annualized over a 5 year period as opposed to the more typical 10 to 15 year period. Readers interested in the application of carbon adsorption to a medium sized open-top degreaser and the conversion to aqueous cleaning should consult the companion Technical Support Document on parts cleaning.

The analysis is based on emission factors and operating conditions that mimic a "typical" operation. Given that no such "typical" facility exists and that every operation is unique, the main value of the analysis is in presenting the derivation of the estimates as opposed to the final economic results. To this end, all of the assumptions used in this analysis are presented in the following sections. The results of the analysis are summarized in Table 4.1.

Annual operating costs for the existing defluxer are estimated to be $190,910. Installation of a carbon bed system reduces the operating cost of the defluxer to $185,740 but adds its own operating cost of $35,490. Combined with the annualized capital and installation costs, overall operating costs will increase to $221,230. Based on an incremental increase of $30,320 and a reduction in CFC-113 emissions of 15.2 tons per year, the effectiveness of this option is $1,990 dollars per ton. The cost effectiveness for a new defluxer would be $1,660 per ton. If CFC use was not phased-out in 5 years and the equipment could be used for 10 years, then the cost effectiveness of the carbon system would be $1,140 per ton and the new defluxer would result in savings of $720 per ton or $10,170 per year.

Table 4.1

Summary of Costs for Carbon Bed and New Defluxing System

Cost Item	Existing Defluxer	Carbon Control System			New Defluxer
		Defluxer	Carbon Bed	Total	
Equipment & Installation					
Carbon Bed System	NA	NA	$72,000	$72,000	NA
Low Emission Defluxer	NA	NA	NA	NA	$175,000
Installation	NA	NA	$50,400	$50,400	$157,500
Equipment Modification	NA	NA	$6,000	$6,000	NA
Total Capital Cost ($)	NA	NA	$128,400	$128,400	$332,500
Annualized Equipment (a)	NA	NA	$33,900	$33,900	$87,780
Operating Expenses					
Heating	$1,350	$1,350	$990	$2,340	$4,120
Conveying	$720	$720	NA	$720	$720
Pumping & Filtering	NA	NA	NA	NA	$2,700
Ventilation	$540	$540	$810	$1,350	NA
Cooling Water	$520	$520	$120	$640	NA
Cold Trap Chiller	NA	NA	NA	NA	$1,080
Solvent Purchase	$187,200	$187,200	NA	$187,200	$120,000
Emission Fees	$6,080	$910	$260	$1,170	$1,520
Waste Disposal	($11,100)	($11,100)	($10,250)	($21,350)	($11,100)
Operating Labor	NA	NA	$5,000	$5,000	NA
Maintenance, Materials	$1,600	$1,600	$2,160	$3,760	$3,500
Maintenance, Labor	$4,000	$4,000	$2,500	$6,500	$4,000
Total O&M Cost ($/year)	$190,910	$185,740	$1,590	$187,330	$126,540
Total Annual Cost ($/yr)	$190,910	$185,740	$35,490	$221,230	$214,320
Incremental Cost ($/year)	NA	NA	NA	$30,320	$23,410
CFC Emissions (tpy)	18.8	2.8	0.8	3.6	4.7
CFC Emission Reduction (tpy)	NA	NA	NA	15.2	14.1
Effectiveness ($/Ton)	NA	NA	NA	$1,990	$1,660

Notes:

a) Annualized equipment cost is based on a service life of 5 years and 10 percent interest. The capital recovery factor (CRF) is 0.264.

b) Summaries of the operating conditions and process parameters associated with the costs shown above are presented in Table 4.2.

An advantage of the new equipment option over the carbon bed option is that residual waste streams (the recovered solvent and condensed steam) are not produced. The choice between carbon bed and new defluxer heavily rests on the ability of a facility to reuse the recovered solvent. When solvent can be reused, the carbon bed system can achieve sizable reduction in solvent use/loss, but does so at a much greater capital expense. Given the very limited time period in which these options could be adopted and the subsequent need to phase-out the use of CFC by 1997, it is unlikely that either of these options will be implemented on a wide scale. It is more likely that facilities will invest their capital in researching and implementing non-CFC technologies and bypass these interim measures.

4.1 THE EXISTING FACILITY

A hypothetical facility currently operates a 10 year old medium-sized in-line CFC defluxer that consists of a 60 gallon boiling liquid sump, a 40 gallon warm liquid sump, and a 15 gallon vapor sump. The CFC used is a blend of 95 percent CFC-113 and 5 percent alcohol. The maximum heat input rate is 80,000 British Thermal Units (BTUs) per hour and the cooling water flow is 100 gallons per hour. These values are based on data presented in ASM (1982). A summation of all operating assumptions used in this analysis is presented in Table 4.2 along with those for the carbon bed system and new “low emissions” system.

Summary of Operational Parameters

The facility operates 16 hrs/day, 5 day/wk, 50 wks/yr, and defluxes 10,000 circuit boards per day. The amount of flux removed is taken to be 0.6 gallons per 10,000 ft2 of circuit board (Hayes, undated). Since each board is assumed to be 1 ft^2, the build-up of flux in the unit is 0.6 gal/day. The average heat input rate for defluxing the boards is taken to be 45,000 BTU/hr. Energy use for the conveyor system is 3 HP or 2 kw. Ventilation requirements are 2 HP or 1.5 kw and the defluxer is only ventilated while operating. The facility pays $0.09 per kw-hr and $6.50 per million BTUs. Heat is supplied by a small gas fired boiler and electricity is used for motive force.

Since the facility produces boards for a military product, the solvent must be replaced when the level of contamination in the boiling sump reaches 5 percent by volume. The warm liquid and vapor sump receive clean distillate and do not require replacement on a routine basis. Based on a flux loading of 0.6 gallons per day, it takes 5 days for the boiling sump to reach 5 percent contamination (60 gallons of CFC x 0.05/0.6 gal/day of flux). The clean-out schedule

Table 4.2

Summary of Operational Parameters for the Carbon Bed System and Low Emission Defluxer

Item	Parameter	Cost
Operation	16 hrs/day, 250 days/yr	---
PC Boards	10,000 per day	---
Existing Defluxer		
Heating (Start-up)	80,000 Btus/hr, 1hr/day	$6.50/1,000,000 Btus
Heating	50,000 Btus/hr, 15 hrs/day	$6.50/1,000,000 Btus
Conveying	2 kw-hr, 8 hrs/day	$0.09 per kw-hr
Ventilation	1.5 kw-hr, 15 hrs/day	$0.09 per kw-hr
Cooling Water	100 gal/hr, 16 hrs/day	$1.30/1,000 gallons
Solvent Purchase	5,850 gallons per year	$32 per gallon
Emission Fees	19 tons per year	$0.16 per pound
Waste Disposal	3,000 gallons per year	$3.70 per gallon credit
Maintenance, Matl.	2% of capital ($80,000)	---
Maintenance, Labor	1 hr/wk testing	$20 per hour
Maintenance, Labor	3 hrs/wk clean-out	$20 per hour
Carbon Bed System		
Heating (Regeneration)	38,000 Btus/hr, 16 hrs/day	$6.50/1,000,000 Btus
Ventilation	2.25 kw-hr, 16 hrs/day	$0.09 per kw-hr
Cooling Water	23 gal/hr, 16 hrs/day	$1.30/1,000 gallons
Emission Fees	3.6 tons per year (total)	$0.16 per pound
Waste Disposal (Filters)	incl. in maint. matl.	---
Waste Disposal (Solvent)	2,330 gal/yr	$4.40 per gallon credit
Operating Labor	1 hr/day	$20 per hour
Maintenance, Matl.	3% of capital ($72,000)	---
Maintenance, Labor	0.5 hrs/day	$20 per hour
Low Emission Defluxer		
Heating (Start-up)	18 kw, 1hr/day	$6.50/1,000,000 Btus
Heating	11 kw, 15 hrs/day	$6.50/1,000,000 Btus
Conveying	2 kw-hr, 16 hrs/day	$0.09 per kw-hr
Pumping & Filtering	7.5 kw-hr, 16 hrs/day	$0.09 per kw-hr
Ventilation	not required	$0.09 per kw-hr
Cooling Water	not required	$1.30/1,000 gallons
Chiller	3 kw, 16 hrs/day	$0.09 per kw-hr
Solvent Purchase	3,750 gallons per year	$32 per gallon
Emission Fees	4.7 tons per year	$0.16 per pound
Waste Disposal	3,000 gallons per year	$3.70 per gallon credit
Maintenance, Matl.	2% of capital ($175,000)	---
Maintenance, Labor	1 hr/wk testing	$20 per hour
Maintenance, Labor	3 hrs/wk clean-out	$20 per hour

is once per week. Boil-back of the unit cannot be practiced because it will expose the heating coils in the sump and the use of recycled solvent is not allowed. Therefore, the annual amount of waste generated will be 150 gallons of flux and 2,850 gallons of solvent. Air emissions are equal to solid waste generation of 12 gallons per day.

Overall, the unit requires the purchase of 5,850 gallons of solvent per year at a delivered cost of $14.50 per gallon. This cost will escalate due to increases in ozone depletion taxes and shrinking supply. In 1992, a tax of $1.34 per pound or $17.50 per gallon will be applied to the selling price. For this analysis, a constant price of $32 per gallon is assumed. Because CFC-113 is a valuable solvent, dirty solvent can be sold to a recycler. At present, the facility receives $2 per gallon of solvent recovered and pays $1.25 per gallon of sludge handled. If the recycler generates a sludge containing 5 gallons of flux and 5 gallons of solvent per 100 gallons of dirty solvent processed, then the facility will receive a credit of $1.68 per gallon of waste. Assuming a similar increase in the value of this waste as in the cost of virgin solvent, the credit is assumed to be $3.70 per gallon. In terms of relative economics, the value assigned to this credit is minor compared to the expense of the solvent.

Being located in the South Coast Air Quality Management District, the plant may also pay emission fees. The emission fee for CFC-113 is $0.16 per pound emitted. For the supply of water used for cooling, the facility is charged approximately $0.15 per 1,000 gallons. Sewer fees cost $1.15 per 1,000 gallons.

The cost for maintenance supplies is difficult to determine but, assuming that the capital cost for a similar sized defluxer is $80,000 and that annual maintenance materials represent two percent of capital, then $1,600 should be a reasonable estimate. Maintenance for the system consists of three hours every week for clean-out, solvent replacement, and waste handling for reclamation. Additional labor consists of one hour per week for solvent testing. The fully burdened labor rate for all workers involved is $20 per hour. A summary of the costs associated with the existing unit was presented in Table 4.1. As shown, the cost of operating the defluxer is $190,910 per year.

4.2 INSTALLATION OF CARBON ADSORPTION

To control emissions, the facility is considering installing a dual-bed carbon bed adsorption system with steam regeneration. The carbon system will be operated whenever the defluxer is in operation and will be designed for a one hour regeneration cycle. Recovered solvent cannot be reused on-site but will be sold to an off-site recycler. A summary of the operational parameters used in analyzing the carbon bed option was presented in Table 4.2 along with information regarding the existing defluxer.

A major determining factor in the efficiency of any air emission control system is capture efficiency. To increase capture efficiency and hence recovery, a vented tunnel will be installed on the end of the defluxer. This tunnel will capture vapors emitted from the exit end of the defluxer and will also provide for a slightly longer drying time. The capture efficiency of the tunnel extension is taken to be 85 percent and the efficiency of the carbon bed system is 95 percent. The overall control efficiency for the system is 81 percent.

The size of the carbon bed system is mainly dictated by the amount of CFC vented to the unit. Based on a capture efficiency of 85 percent, an adsorption value of 0.08 pounds of CFC per pound of carbon, a one hour adsorption cycle, and a safety factor of two, the system will require 200 pounds of carbon per bed.

Steam requirements for the system are based on four pounds of steam per pound of CFC adsorbed. Approximately 32 pounds per hour of steam will be required to desorb the bed. Steam will be provided by a small gas-fired steam generator that is included with the carbon system. Cooling water requirements are based on six pounds of water per pound of steam used. This equates to a flow of 23 gph. The installation of the carbon bed system will require the inclusion of a three HP (2.25 kw-hr) blower at the tunnel extension in addition to the existing ventilation blowers.

As a result of the steaming process, 128,000 pounds of water and 30,280 pounds of CFC will be condensed each year. The solubility of CFC-113 in water is 0.028 pounds per 100 pounds of water and the amount of CFC discharged in the water amounts to 36 pounds per year. Water soluble alcohols used in the defluxing formulation would also be present in the water stream. While the water could be steam stripped, steam stripping would consume additional energy, result in air emissions if not controlled, and would be ineffective at removing the water soluble contaminants. To remove these contaminants from the wastewater before discharge, a small water phase carbon canister will be installed. The cannister will be replaced and disposed of on a routine basis. The recovered CFC will be sold to an off-site recycler for additional processing. The value for this solvent is taken to be $4.40 per gallon since it will be relatively clean.

To determine the cost of the carbon bed system, correlations presented by Vatavuk and Neveril (1983) were used. One correlation estimates the cost of a fully packaged dual bed adsorber system including blower, controls, and steam regenerator as $10,000 plus $721 times the weight of carbon raised to the 0.0481 power. For a 400 pound system, the capital cost is estimated to be $22,870. This price is for a carbon steel unit purchased in 1977. To obtain an estimate for 1991, the Marshall & Swift equipment price index was used to factor up the price. The M&S index was 505 for 1977 and 935 for 1991. This increases the price to $42,340. Next, the facility decides that the use of carbon steel may result in contamination of the recovered solvent and instead selects 304 stainless steel. This increases the price by 70 percent up to $72,000.

Installation costs are highly variable and dependent on existing site conditions. To determine the full installation cost of this system, a factor of ten percent for tax and freight, 30 percent for direct cost such as site preparation, electrical and plumbing hook-ups, insulation work, etc., and 30 percent for indirect costs such as permitting, start-up assistance, engineering fees, etc., is assumed. This places the total installed cost for the system at $122,400. For the tunnel extension, an additional installed cost of $6,000 is assumed. This brings the total installed cost up to $128,400.

Material supply costs for the system are taken to be three percent of the capital cost for the carbon bed system alone or $2,160 per year. This would include the cost associated with change-out and disposal of the water phase carbon and one time change-out of the carbon bed after five years. Operator requirements are taken to be one hour per day and 0.5 hours per day for maintenance activities.

A summary of the costs for this option were presented in Table 4.1. As shown, annual operating costs for the existing defluxer are estimated to be $190,910. Installation of a tunnel extension and carbon bed system increases overall operating costs to $221,230. Annualization was based on an equipment life of 5 years to account for the phase out of CFC-113. Based on an incremental increase of $430,320 and a reduction in CFC emission of 15.2 tons per year, the effectiveness of this option is $1,990 dollars per ton.

If the equipment can be operated for 10 years instead of 5, then the incremental costs for this option would increase to $17,350 per year and the cost effectiveness would be $1,140 per ton. If the facility has on-site use for the solvent, perhaps in a non-military application, then the option would save the facility $77,820 in avoided solvent purchases and the overall savings for installing a carbon bed would be $47,500 per year. Therefore, installation of a carbon bed system can pay for itself provided the recovered solvent can be reused on-site.

43 LOW EMISSION EQUIPMENT

Under this scenario, the facility considers investing the money it would spend for a carbon bed system in a new “low emission” defluxer. The unit is a fully enclosed conveyorized system that subjects the boards to three spray cleaning steps and a hot vapor rinse. To control emissions, the boards must pass through a liquid seal both before and after the spray cleaning steps. To control emissions from the hot vapor rinse, the unit is equipped with a below freezing condenser at the exit port.

Given the presence of the liquid seals on the spray cleaning system and the inclusion of the subfreezing condenser on the vapor rinse, air emissions are small and the unit need not be ventilated for worker protection (proper ventilation would still be required outside of the system). For this analysis, control of air emissions is assumed to be 75 percent. Such equipment has a capital cost in the range of $150,000 to $175,000. Assuming a capital cost of $175,000 and an installation factor of 1.9 to account for extensive renovation inside the facility, the total capital cost would be $332,500. Based on an interest rate of 10 percent and an equipment usage life of 5 years, the annual capital charges amount to $87,780.

The unit contains 260 gallons of solvent (120 gallons in the first seal tank, 80 gallons in the second seal tank, and 60 gallons in the boiling sump) and requires a maximum of 18 kw for heating. The average heating load is assumed to be 11 kw. Cooling by means of a refrigerated condenser requires 5 HP (3 kw). Power for the spray pumps and filters is taken to be 10 HP (7.5 kw). Conveyor loads are the same as for the existing defluxer.

According to the vendor, solvent reductions can be expected to be 75 percent compared to the existing defluxer. This amounts to a reduction in solvent use/loss of 2,100 gallons. For waste disposal, the unit will generate 60 gallons per week of contaminated solvent. As with the existing defluxer, the facility will receive a credit of $3.70 per gallon. Maintenance labor will amount to three hours per week for system clean-out and one hour per week for solvent testing. Maintenance materials are taken to be two percent of capital. The economics for this option were presented in Table 4.1.

As shown, direct operating and maintenance costs for the new defluxer amount to $126,540. This is $64,370 dollars per year less than the existing degreaser. However, inclusion of the annualized capital costs of $87,780 increased the overall annual cost to $214,320. This resulted in an incremental cost increase of $23,410. Given a reduction of 14.1 tons per year in CFC emissions, the effectiveness of this option is $1,660 per ton. If the equipment can be annualized over a 10 year time period, annual savings of $10,170 would result. Depending on the non-CFC technology selected for future use, it is possible that the new defluxer could continue to be used. This would also result in favorable economics. Equipment salvage value has not been accounted for in this analysis.

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5.0 ESTIMATION OF SOURCE REDUCTION POTENTIAL

A standardized methodology was devised to determine ranges of source reduction potential for each option and industry. The use of ranges, as opposed to fixed values, was deemed more appropriate since the surveys conducted in this study, and from which the range estimates are derived, were limited both in geographic range and number (a fuller discussion of limitations is presented in the Summary Report for the Technical Support documents). The results of this exercise are presented in Section 5.1 followed by the discussion of methodology in Section 5.2.

5.1 QUANTIFICATION

To quantify potential source reduction, each option discussed in Section 3 was assigned a range of effectiveness and implementation potential in accordance with the methodology discussed in Section 5.2. The top one or two methods for each impacted medium were then combined and the media reductions combined to yield reductions for a given operation (i.e., wafer fabrication, PC board fabrication, PC board assembly, and critical cleaning). Operation reductions were then combined to yield an overall reduction for the industry. Since only the top one or two options were selected, as opposed to selecting all options, the estimated reductions are viewed as being conservative. The results of this exercise are presented in Table 5.1.

For the electronics wafer fabrication and assembly operations, PC board fabrication, and critical cleaning operations, viable source reduction options include proper use of solvent and the selection of the least hazardous cleaning medium. Since solvent use varies widely in the operations studied, it was deemed acceptable to assign the overall reduction values from the reduction analysis presented in the Technical Support Document on parts cleaning rather than try to identify specific source reduction techniques and project reductions.

Three specific measures in the area of PC board fabrication and assembly that could and will be implemented by the electronics industry include use of aqueous or semi-aqueous photoresist, use of no flux soldering, and use of low solids or no-clean flux. These measures have already been implemented at several major facilities and the trend should continue over time. Combined with reductions in the area of parts cleaning, overall reductions range from 21 to 54 percent short-term, 48 to 74 percent medium-term, and 63 to 85 percent long-term.

Table 5.1

Source Reduction Potentials for the Electronics Industry

	Source Reduction Method	Media	Effectiveness (%)		Implementation Potential						Source Reduction Potential					
					Short(%)		Medium(%)		Long(%)		Short(%)		Medium(%)		Long(%)	
			Low	High	Low	High	Low	High	Low	High	Low	High	Low	High	Low	High
	Electronics - Wafer Fab. and Assembly															
	1. Use of CO2 Snow Gun	A/S	100	100	0	20	0	20	0	20	0	20	0	20	0	20
	2. UV Ozonation of Contaminants	A/S	100	100	0	20	0	20	20	40	0	20	0	20	20	40
	3. Laser Cleaning	A/S	100	100	0	0	0	20	0	20	0	0	0	20	0	20
	4. Laser Marking	A/S	100	100	0	0	0	20	0	20	0	0	0	20	0	20
>	5. Measures Discussed in Parts Cleaning	A/S	--	--	--	--	--	--	--	--	27	56	47	72	47	72
	Reduction Potential for Method 5	A/S									27	56	47	72	47	72
	Electronics - PC Board Fabrication															
>	1. Aqueous/Semi-Aqueous Photoresist	A/S/W	60	80	40	60	60	80	80	100	24	48	36	64	48	80
>	2. Measures Discussed in Parts Cleaning	A/S/W	--	--	--	--	--	--	--	--	27	56	47	72	47	72
	3. Carbon Dioxide Pellet Blasting	A/S/W	100	100	0	20	0	20	0	20	0	20	0	20	0	20
	Reduction Potential for Methods 1 & 2	A/S/W									45	77	66	90	72	94
	Electronics - PC Board Assembly															
	1. Do Not Deflux Boards	A/S/W	100	100	0	0	0	20	0	20	0	0	0	20	0	20
>	2. No Flux Soldering	A/S/W	100	100	0	20	20	40	40	60	0	20	20	40	40	60
>	3. Low Solids (No Clean) Flux	A/S/W	100	100	0	20	20	40	40	60	0	20	20	40	40	60
	4A. Aqueous Cleaning	A/S/W	100	100	20	40	40	60	40	60	20	40	40	60	40	60
	4B. Pure Alcohols	A/S/W	100	100	0	20	0	20	0	20	0	20	0	20	0	20
	4C. Terpenes & Surfactants	A/S/W	100	100	20	40	40	60	40	60	20	40	40	60	40	60
	4D. Other Hydrocarbon Solvents	A/S/W	100	100	0	20	0	20	0	20	0	20	0	20	0	20
	4E. HCFCs & CFC Blends	A/S/W	0	0	0	20	0	20	0	20	0	0	0	0	0	0
	5. Improved Equipment & Op. Practices	Air	60	80	20	40	20	40	20	40	12	32	12	32	12	32
	6. Solvent Vapor Recovery / Reuse	Air	60	80	20	40	20	40	20	40	12	32	12	32	12	32
	7. Waste Solvent Recovery / Reuse	Solid	60	80	40	60	40	60	40	60	24	48	24	48	24	48
	Reduction Potential for Methods 2 & 3	A/S/W									0	36	36	64	64	84
	Electronics - Critical Cleaning															
>	1. Measures Discussed in Parts Cleaning	A/S	--	--	--	--	--	--	--	--	27	56	47	72	47	72
	Reduction Potential for Method 1	A/S									27	56	47	72	47	72
	Electronics Overall Reduction Potential		Weighing factors (see note below).								21	54	48	74	63	85

Note: Weighing factors for overall reduction are 10.9/76.7 (semiconductor production), 26.6/76.7 (PC board fabrication), 34.0/76.7 (PC board assembly), and 4.8/76.7 (critical cleaning). Weighing factors for air, solid, and water not required since selected measures apply to all media.

Given that many other viable methods exists for reducing or eliminating the use of halogenated solvents, these estimates are considered to be conservative. Viable short-term options include vapor control and solvent waste recycling. Medium and longer term options include the use of aqueous and or terpene-based cleaning. According to data from CMR (1989 and 1992), the electronics industry reduced its use of METH by 70 percent and TCA by 44 percent from the baseline year 1988 to 1991. While specific data was not available, CFC-113 use by all industry has declined by 58 percent and the electronics industry is known to have made sizeable reductions. However, given the broad spectrum of operations involved in the electronics industry, there most likely will be some areas where the reduction or elimination of halogenated solvent use will be much more difficult than the above estimates imply.

5.2 METHODOLOGY

The methodology used to estimate nationwide source reduction potential is comprised of the following major steps: assign source reduction effectiveness ranges to each option, assign implementation potential ranges to each option, compute the range of source reduction potential for each impacted medium and then compute the range of source reduction potential for the industry. Definitions and examples are provided in the following sections.

Source Reduction Effectiveness

Source Reduction Effectiveness (SRE) measures the pure technical effectiveness of a source reduction option for a unit operation,- i.e., the extent to which the use of the target substance can be reduced by application of a given source reduction option in an industrial process or operation at a typical facility. The ranges of SRE used in this study were:

Reduction	Range [percent)
None	0
Small	O-20
Moderate	20-40
Medium	40-60
High	60-80
Very High	80-100
Full Elimination	100

For example, the use of water in place of halogenated solvent would be assigned an SRE of 100 percent since halogenated solvent use is fully eliminated. Likewise the substitution of one halogenated solvent with another would be assigned an SRE of zero percent because the option does not reduce halogenated solvent use. The assignment of SRE ranges ignored the effect on non-technical constraints on reducing source reduction potential.

Implementation Potential

The Implementation Potential (IP) is a percentage range estimate of the extent to which a particular source reduction option could be implemented on an industrywide scale, taking into consideration many technical and nontechnical constraints. The ranges used for IP were identical to those used for SRE above. To account for time effects, IP ranges were determined for short-term (0 to 5 years), mid-term (5 to 10 years), and long-term (10 to 20 years) periods of time.

Estimating the IP for each source reduction option is a complex task, involving the meshing of environmental, technical, and socioeconomic variables into workable scenarios. Since this study has generally looked at source reduction technologies which have been demonstrated to work in the field, then from a technical standpoint alone the IP of most options studied is relatively high. Technology, however, is only one component. Other environmental and socioeconomic variables prominent in determining IP are:

- extent of current use
- economic considerations
- time
- customer attitudes
- regulatory compliance
- management capabilities and commitment
- information and training resources
- monitoring and maintenance capabilities

Extent of Current Use

Implementation potential for a given source reduction alternative depends on the extent to which this alternative has been implemented in the studied industry. For example, easy and accessible techniques such as improved maintenance or operator training have largely been implemented, especially by larger, more sophisticated firms. Hence, the implementation potential ratings for these alternatives would be lower, because a fraction of facilities where they can still be applied is probably small.

Economic Considerations

A contemplated source reduction project often finds itself as only one of many competitors for available capital. As with other activities requiring capital expenditures, two basic economic considerations govern source reduction: availability of capital, and the potential return on investment. Capital availability varies considerably among halogenated solvent users, with smaller operations generally at a disadvantage. To account for this effect, low cost measures were rated higher than high cost measures.

Time

Time can markedly change feasibility and potential of source reduction measures. Technologies can move from novel to standard; what may be considered economically infeasible today may be judged cost-effective tomorrow. Generally, well established technologies have been given a higher short-term IP rating than the emerging ones.

Customer Attitudes

If a service or a product developed through source reduction methods is less marketable than one from standard practices, the source reduction option will likely fail. Customer attitudes are an important influence in source reduction. SRRP staff research found that rigid customer specifications, particularly military specifications, pose significant source reduction barriers in many industries. These barriers tend to keep the IP rating for measures involving material or process changes low.

Regulatory Compliance

Complexities in meeting regulatory requirements for end-of-pipe pollution control generally spur source reduction. Both technological complexities in achieving specific emission reductions, and administrative complexities in obtaining required permits and approvals (e.g., obtaining of air permits), influence the rating of the implementation potential of source reduction measures.

Management Capabilities and Commitment

Successful implementation of source reduction depends on: a) the management level at which it is actively endorsed, and b) the technical and administrative capability of that management in regard to implementation. Source reduction usually requires a reorientation of management perceptions and priorities away from traditional environmental management approaches, and toward pollution prevention. Some of the common barriers to such reorientation can be expressed by the following viewpoints:

- We already invested in an expensive treatment system. Why reduce?
- We will not be the first to try this out. Let others do it; then we will see.
- Product quality will definitely be affected by substitutions. We will not do anything until we have to.

The rating of IP must consider management’s resistance to change. In deriving the rating, higher scores were assigned to industries where process and product changes are frequent than to more static industries.

Information and Training Resources

The best source reduction technologies available, supported by top management, can fail if sufficient information and training for effective implementation, running and monitoring are not available to managers who must direct source reduction efforts and to line employees who must make them work, and adapt them to changing conditions. Information and training needs in the constantly evolving source reduction field are many. They range from simple instruction manuals to sophisticated databases. In general, the greater the requirement for information and training resources, the lower the IP rating.

Monitoring and Maintenance Capabilities

Unless source reduction programs are carefully monitored, they can rapidly become suboptimal, posing a number of technical, economic, and other problems. Similarly, without proper maintenance geared specifically to source reduction goals, source reduction measures can falter. For small firms, the need for extensive monitoring and maintenance will lower an option’s IP rating.

Source Reduction Potential

The Source Reduction Potential (SRP) for each implementation time frame was calculated as the product of Source Reduction Effectiveness and Implementation Potential. As an example, an SRE of 20 to 40 percent and an IP of 60 to 80 percent would yield an SRP of 12 to 32 percent. The assignment of short-term, medium-term, and long-term IPs was done to account for reductions in constraints over time. While it could be argued that short-term, medium term, and long-term SRE values should have been assigned to account for technical improvements over time, the added complexity and the movement away from a conservative stance did not appear warranted.

After calculation of individual SRPs, the top one or two options for each impacted medium were selected from among the non-solvent based alternatives. While the use of hydrocarbon solvents in place of halogenated solvents could achieve sizable reductions in halogenated solvent use, these options were not viewed as true source reduction since the overall environmental benefit is unclear. Also excluded were options that could pose major impacts on other media (i.e., air versus water). In general, most selected options dealt with the use of similar products with less solvent content, more efficient use of products, and recycling/reuse of solvent vapors and waste. The SRP for an impacted medium was calculated as follows:

$$SRP_{medium} = SRP_1 + SRP_2\,(100 - SRP_1)/lOO$$

where $SRI_{1,2}$ are the two leading calculated source reduction potentials for each medium. SRP_{medium} is the combined range of source reduction.

It should be noted that selection of one or two top ranking options in calculating an SRP for an impacted medium is arbitrary. If there are 10 source reduction methods available, and there are appropriate driving forces, then it is likely that more than two will be implemented; in which case the reduction in halogenated solvent use will exceed the estimate. Therefore, this technique provides a conservative estimation of SRP.

Overall Source Reduction Potential

Once the SRPs for each impacted medium have been determined, the overall SRP for each industrial sector (e.g., formulator and user) and the industry as a whole, are determined. The SRP for each industrial sector is determined by the following formula:

$$SRP_{sector} = (W_{air}/W_{total}) \times SRP_{air} + (W_{solid}/W_{total}) \times SRP_{solid} + (W_{water}/W_{total}) \times SRP_{water}$$

Where W_{air}, W_{solid}, and W_{water} is the weight of halogenated solvent released into the environment from an environmental sector. The industry-wide SRP is then determined by weighting each SRP sector by the ratio of solvent released from that sector by the total amount of solvent used by the industry.

6.0 REFERENCES

Allied-Signal, "Allied-Signal Develops New Solvents to Replace Ozone Depletion Chlorofluorocarbons," March 7,1989 (Allied-Signal, 1989).

Allied-Signal "The CBL-18R Circuit Board Defluxer from Baron Blakeslee," brochure (Allied-Signal, undated).

Alpheus. Video presentation of the CO_2 Cleanblast System and personal communications with Alpheus Cleaning Technologies Corp. staff. Rancho Cucamonga, CA, 1992 (Alpheus, 1992).

Archer, W.L. and Simpson, E-L., "Chemical Profile of Polychloroethanes and Polychloroalkenes," Ind. Eng. Chem., Vol. 16, #2,1977, p-153 (Archer and Simpson, 1977).

Attalla, G., "Designing Cleaning Equipment for the Terpene Alternative," Surface Mount Technology, p.43, December 1988 (Attalla, 1988).

Attalla, G. "In-Line Semi-Aqueous Cleaning," Proceedings of the National Electronic Packaging and Production Conference, NEPCON West, February 26 to March 1, 1990 (Attalla, 1990).

AT&T, G.M. Wenger and Munie, G-C., "Defluxing Using Terpene Hydrocarbon Solvents," IPC Technology Review, P-17, November, 1988 (AT&T, 1988).

Bell, J., "Goodbye to the Circuit Board," New Scientist, p.42,4 July 1985 (Bell, 1985).

Bemier, D., "Understanding and Controls Necessary for Wave Soldering Reliability--Part 1," Electronic Manufacturing, July 1988 (Bemier, 1988).

Cabelka, T-D. and Archer, W., "Critical Fee Energy in Wetting: The Key to Maximum Effectiveness in SMA Cleaning," Surface Mount Technology, p-18, December 1987 (Cabelka and Archer, 1987).

CMR. Chemical Marketing Reporter, "CFC Alternative Aimed at Use in Electronics," January 1988 (CMR, 1988a).

CMR. Chemical Marketing Reporter, "Fluorocarbon Replacement Could Be Big Terpene User," February 1,1988 (CMR, 1988b).

CMR. Chemical Marketing Reporter, "Production Profiles for TCE, TCA, PERC, and METH," January 23, January 30, February 6, and February 20,1989 (CMR, 1989).

DD-STD-2000-lB, "Military Standard, Soldering Technology, High Quality/High Reliability," 10 June 1986.

Davis, G.A, Piasecki, B., and Mueller, M-J., "Waste Reduction Strategies for the Printed Circuit Board Industry," Cal-Tech Management Associates, October 1987 (Davis et al., 1987).

Deram, B., "Technical Considerations for Use of No-Clean Fluxes, "Kester Solder, September 1988 (Deram, 1988).

Dishart, K and Wolff, M. “Advantages and Process Options of Hydrocarbon Based Formulations in Semi-aqueous Cleaning,” Proceedings of the National Electronic Packaging and Production Conference, NEPCON West, February 26 to March 1, 1990 (Dishart and Wolff, 1990).

Dow Chemical Company, “Waste Minimization for Chlorinated Solvent Users, “Form No. lOO-6371-88-SAI (Dow, undated).

Dow Chemical Company, “Solvent Update - Carbon Adsorption for Solvent Vapor Emission Control,” Vol. 3, No. 2, June 1989 (Dow, 1989).

Dow Chemical, “Prelete Defluxer, High Performance Solvent for Post-Solder Electronic Assembly Cleaning,” (Dow, undated).

Doxstader, R., “High Intensity Light Surface Preparation,” A&R Industries, Oceanside, CA (Doxstader, undated).

D’Ruiz, Carl D., “Aqueous Cleaning as an Alternative to CFC and Chlorinated Solvent-Based Cleaning,” Noyes Publications, Park Ridge, NJ, 1991 (D’Ruiz, 1991).

DuPont, “Riston Photopolymer Film Resist Image Transfer systems, “1988 (DuPont 1988).

DuPont Chemical Company, Freon Products Bulletin Numbers FS-27, FS-21, FST-I-IA, FST-11, and S-16 (DuPont, undated).

Elliott, D. A, Cleaning Alternatives for the 199Os,” 12th Annual Electronics Manufacturing Seminar, China Lake, CA, February 1988 (Elliott, 1988).

Ellis, B-N., “Aqueous Cleaning of Surface Mounted Assemblies,” Brazing and Soldering, #12, Spring 1987 (Ellis, 1987).

Engleman, V., Science Applications International Corporation, “Evaluation of VOC Control Options,” Second Annual International Workshop on Solvent Substitution held at Phoenix, AZ, Dec 10 -13,199l. Managed by Weapons Complex Monitor Forums (Engleman, 1991).

Flamm, W. and Leham-McKeeman, L. “The Human Relevance of the Renal Tumor-Inducing Potential of d-Limoriene in Male Rats: Implications of Risk Assessment,” Regulatory Toxicology and Pharmacology, 13,70-86,199l (Flamm and Lehman-McKeeman, 1991).

Foecke, Terry L., “Waste Minimization in the Electronics Products Industries,” Journal of the Air Pollution Control Association, Vol. 38, No. 3, P-283, March 1988 (Foecke, 1988).

Guth L., “Low Solids Flux Technology for Solder Assembly of Circuit Packs,” AT&T, May 1989 (Guth, 1989).

Hall, L-E., and Katz, O.A, “Productivity Improvements Through the Effective Implementation of Waste Minimization Technology, Martin Marietta, 1989 (Hall & Katz, 1989).

Hayes, M-E., ‘“High Performance Cleaning with Terpene/Surfactant Mixtures,” Petroferm Inc. (Hughes, undated).

Hayes, M. “Advances and Acceptance of Electronic Assembly Cleaning with Terpenes,” Proceedings of the National Electronic Packaging and Production Conference, NEPCON West, February 26 to March 1,199O (Hayes, 1990).

Heingard, Christer, “POLYADFB - A New Process for VOC Control and Solvent Recovery,” Proceedings from Air and Waste Management Association Annual Meeting, June 1989 (Heinegard, 1989).

Hoenig, AS., “The Application of Dry Ice to the Removal of Particulates fro Optical Apparatus, Spacecraft, Semiconductor Wafers, and Equipment Used in Contaminant Free Manufacturing Processes,” University of Arizona, September 1985 (Hoenig, 1985).

Hoenig, S.A, “Sno Gun,” brochure (Hoenig, undated).

IPC. “Cleaning and Cleanliness Testing Program - A Joint Industry/Military/EPA Program to Evaluate Alternatives to Chlorofluorocarbons (CFCs) for Printed Circuit Assembly Cleaning,” IPC-CP-61. Published by the Institute for Interconnecting and Packaging Circuitry. Lincolnwood, IL November 30,1988 (IPC, 1988).

IPC. “Cleaning and Cleanliness Protocol to Evaluate Alternatives to Chlorofluorocarbons (CFCs) for Printed Circuit Assembly Cleaning,” IPC-CP-61. Published by the Institute for Interconnecting and Packaging Circuitry- Lincolnwood, IL February 1991 (IPC, 1991).

JAAST. Joint Association for the Advancement of Supercritical Technology, Mission Statement. Dr. D.L. Hjeresen, Director. Los Alamos National Lab (JAAST, 1991).

Johnson, K. and Bergman, D., “Ad Hoc EPA/DOD/IPC Solvents Working Group: CFC EMPF Test Results” (Johnson & Bergman, undated).

Keeler, R., “Post-Solder Cleaning Meets its Match in SMT Geometry,” Electronic Packaging and Production, p-86, January 1987 (Keeler, 1987).

Kenyon, W-G., “New Ways to Select and Use Defluxing Solvents,” DuPont, Technical Report RP-7 (Kenyon, undated).

Kirk Othmer Encyclopedia of Chemical Technologies. “Solvent Recovery,” Vol. 21, 1979 (Kirk Othmer, 1979).

Ko, M., “Comparison of Freon with Water Cleaning Processes for Disk-Drive Parts,” IBM Corporation, 1989 (Ko, 1989).

Laird Merino Corporation, Product Literature on Solvent Filterate System, Fountain Valley, CA (Laird, undated).

Larson, N., Boeing Defense and Space Group, “1991 Perspectives on Wheat Starch Paint Stripping,” Second Annual International-Workshop on Solvent Substitution held at Phoenix, AZ, Dec. 10 -13,199l. Managed by Weapons Complex Monitor Forums (Larson, 1991).

Lea, C., “Restrictions on the Use of Chlorofluorocarbons for Cleaning Soldered PCBs, “Circuit World, Vol, 14, No. 4, p.4, 1988 (Lea, 1988).

Licari, J. “Plastic Coatings for Electronics,” Published by Robert E. Krieger Publishing Company, Inc. Malabar, FL, 1981 (Licari, 1981).

Liquid Carbonic. Product Literature on Liquid Carbonic's Environmental Vapor Recovery System. Form 6898,1989 (Liquid Carbonic, 1989).

Markenstein, H., "Solder Flux Developments Expand Choices," Electronic Packaging and Production, p. 39, April 1983 (Markenstein, 1983).

Marr, A., Southern California Edison, "A Utility's VOC Recovery Program," Second Annual International Workshop on Solvent Substitution held at Phoenix AZ, Dec 10 -13, 1991. Managed by Weapons Complex Monitor Forums (Mar-r, 1991).

Mauzerall, Denise, "Aqueous Cleaning -- an Economic Alternative to the Use of Chlorinated and Chlorofluorocarbon (CFC) Solvent in the Electronic and Metal Cleaning Industries," ICF Corporation, Proceedings from the Third Hazardous Materials Management Conference/West. November 1987 (Mauzerall, 1987).

McClintock, J. A, Wilson, R-A, and Byer, N-E., "W-Ozone Cleaning of GaAs for MBE," J. Vac. Sci. Tehnol, Vol. 20, No. 2, February 1982, p-241 (McClintock et al., 1982).

Meisser Griesheim, "Focus on Gas - Clean Air from Exhaust Air: Condensation of Solvents by Means of the Cryosolv Process." May 1988 (Meisser, 1988).

Morehouse, Maj. Tom. HQ USAFKEW "Update on the Montreal Protocol and the Air Force Pollution Prevention Program." Second Annual International Workshop on Solvent Substitution held at Phoenix, AZ, Dee l0- 13, 1991. Managed by Weapons Complex Monitor Forums (Morehouse, 1991).

Morrison, P. and Wolf, K, "Substitution Analysis: A Case Study of Solvents, "Journal of Hazardous Materials, Vol 10, p.189,1985 (Morrison and Wolf, 1985).

MTRI. Membrane Technology and Research, Inc., Vapor Separator Systems Product Literature, (MTRI, undated).

Naegels, T., "To Fix the Sky," Electronics, April 1989, p. 93 (Naegels, 1989).

NTP. National Toxicology Program, "Toxicology and Carcinogenesis Studies of d-Limonene in F344/N Rats and B6C3Fl Mice (Gavage Studies)," NTP Technical Report 347, U.S. Dept. of Health and Human Services, National Institutes of Health, Bethesda, MD, 1990 (NTP, 1990).

Nucon International, Product Literature on Braysorb Process (Nucon, undated).

Paul, H. et al., "Removal of Organic Vapors from Air by Selective Membrane Permeation." Daimler Benz AG, Stuttgart, West Germany, 1988 (Paul et al., 1988).

Pedco Environmental Inc., "Industrial Process Profiles for Environmental Use: Chapter 30. The Electronics Component Manufacturing Industry," EPA-600-283-033 (Pedco, undated).

Petroferm, Inc., Product Literature on BIOACT DG-1, EC-7 and FA terpene cleaners, (Petroferm, undated).

Pinkerton, H-L., "Drying Practices and Equipment," in Electroplating Engineering Handbook, 4th ed., Edited by L. Durney. Published by Van Nostrand Reinhold Company, 1984 (Pinkerton, 1984).

Pound, R., “Solvents Flush Solder Flux from Tight Spaces Electronic Packaging and Production,” p-58, August 1984 (Pound, 1984).

Russo, J-F. and Fischer, MS., “Closed-Loop Water Recycling for PWB Aqueous Cleaners, ” Separation Technologists, Inc., March 8,1989 (Russo & Fischer, 1989).

Sanger, D. and Johnson, IS., “A Study of Solvent and Aqueous Cleaning of Fluxes,” Naval Weapons Center, China Lake, CA, February 1983 (Sanger and Johnson, 1983).

SMT Forum, “High Pressure Spray and Ultrasonic Cleaning for Surface Mounted Assemblies,” Surface Mount Technology, p. 12, December 1987 (SMT, 1987).

Sowell, R.R., Cuthrell, R-E., Mattox, D.M., and Bland, R.D., “Surface Cleaning by Ultraviolet Radiation, “J. Vat. Sci Technol, Vol.. 11, No. 1 Jan/Feb 1974, p. 474 (Sowell et al., 1974).

SRI. B. Waterhouse and A. Miller “Integrated Solvents Analysis: Electronics Industry Uses,” Stanford Research Institute, July 1985 (SRI, 1985).

UCLA, “Proceedings of Workshop on Replacing CFC-113 in Critical Mechanical Cleaning Applications,” Engineering Research Center, November 1988 (UCLA, 1988).

USDC. County Business Patterns, U.S. Department of Commerce, Bureau of Census, 1986 (USDC, 1986a).

USDC. County Business Patterns, California, U.S. Department of Commerce, Bureau of Census, 1986 (USDC, 1986b).

USDOE, U.S. Department of Energy, “Brayton Cycle Heat Pumps for Solvent Recovery and Recycling,” (USDOE, undated).

USEPA, “Assessment of Chlorinated Solvent Usage and Control Costs in Metal Cleaning and Electronics Cleaning - Draft Report,” Contract No. 02128-318, Office of Pesticides and Toxic Substances, March 1988 (USEPA, 1988a).

USEPA, “Summary and Presentations, Industry/EPA Meeting on Aqueous Cleaning, ” Office of Air and Radiation/Office of Toxic Substances, August 31,1988 (USEPA, 1988b).

USEPA “Guidance Manual for Electroplating and Metal Finishing Pretreatment Standards,” U.S. Environmental Protection Agency, February 1984 (USEPA, 1984).

Van Zant, Peter, “Microchip Fabrication, A Practical Guide to Semiconductor Processing,” Semiconductor Services, San Jose, CA, 1986 (Van Zant 1986).

Vig, J.F. and LeBus, J-W., “W/Ozone Cleaning of Surfaces, IEEE Transactions on Parts, Hybrids and Packaging,” Vol. PHP-12, No. 4, December 1976, p-365 (Vig and LeBus, 1976).

Wijmans, J.G. et al., “Removal of Volatile Organic Compounds from Air Streams Using a Membrane System,” MTRI, (Wijmans et al. undated).

Wolf, K, Institute for Research and Technical Assistance. “HCFC’s: Are They Still Viable in Solvent Applications?,‘I Second Annual International Workshop on Solvent Substitution held at Phoenix AZ, Dee 10 -13, 1991. Managed by Weapons Complex Monitor Forums (Wolf, 1991).

Wolff, M.C., “A Novel Environmentally Acceptable Fluorosolvent - Properties and Performance Data,” Presented at Nepcon West, 1988 (Wolff, 1988).

Zafonte, L. and Chin, R., “W/Ozone Cleaning for Organics Removal on Silicon Wafers,” SPIE, Vol. 470, Optical Microlithography 111: Technology for the Next Decade, 1984, p. 164 (Zafonte and Chin, 1984).