



ELECTRONICS, DEGREASING AND DRY CLEANING SOLVENTS TECHNICAL OPTIONS REPORT

**PURSUANT TO ARTICLE (6) OF THE MONTREAL PROTOCOL
ON SUBSTANCES THAT DEplete THE OZONE LAYER
UNDER THE AUSPICES OF THE
UNITED NATIONS ENVIRONMENT PROGRAMME**

JUNE 30, 1989

**ELECTRONICS CLEANING, DEGREASING,
AND DRY CLEANING
SOLVENTS TECHNICAL OPTIONS REPORT
SUMMARY REPORT**

**UNEP SOLVENTS
TECHNICAL OPTIONS COMMITTEE**

<u>COMMITTEE MEMBER</u>	<u>AFFILIATION</u>	<u>COUNTRY</u>
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Mr. Leo Lambert	Digital Equipment Corp.	USA

ALTERNATES

Dr. Ruth Anderson	AT&T	USA
Dr. John Fisher	AT&T	USA
Mr. Shigeo Matsui	Toshiba Corporation	Japan

ORGANIZATION OF THE SIX TECHNOLOGY REPORTS

Pursuant to Article 6 of The Montreal Protocol on Substances that Deplete the Ozone Layer four panels of international experts have completed Scientific, Environmental Effects, Economic, and Technology Reports. This Report is one of six volumes on technology. There is a Technology Review Panel Report, chaired by Victor Buxton (on the behalf of Canada) and Dr. Stephen O. Andersen (on the behalf of the United States of America) which is a summary of five detailed Technical Options Reports. The five technical reports are: Refrigeration, Air Conditioning and Heat Pumps, chaired by Dr. Lambert Kuijpers (The Netherlands); Flexible and Rigid Foams, chaired by Ms. Jean Lupinacci (USA); Aerosols, Sterilants and Miscellaneous Uses of CFCs, chaired by Mrs. Ingrid Kokeritz (Sweden); Halon Fire Extinguishing Agents, chaired by Mr. Gary Taylor (Canada); and Electronics Cleaning, Degreasing and Dry Cleaning Solvents, chaired by Dr. Stephen O. Andersen (USA). For further information please contact Technology Panel Chairman Victor Buxton, Environment Canada (phone 819-997-1640).

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DISCLAIMER

The expert judgments reported here are not necessarily those of the companies and organizations that employ the committee members, the countries that nominated them to the committee, or the United Nations Environment Programme. The conclusions reported in this document were developed by consensus. Committee members do not endorse the cleaning performance, worker safety, or environmental acceptability of any of the technical options discussed. Every cleaning operation requires consideration of worker safety, proper disposal of contaminants, and waste products generated from cleaning processes. Moreover, as work on CFC substitutes continues, including additional toxicity testing, more information on health and safety issues of the alternatives will become available for use in selecting among alternatives to the solvents discussed in this document.

GLOSSARY

Acute toxicity	The short-term toxicity of a product in a single dose. Can be divided into oral, cutaneous and respiratory toxicities.
Adsorption	Not to be confused with absorption. Adsorption is a surface phenomenon which some products can exhibit, whereby they can form a physicochemical bond with many substances.
Aerosol spray	A means of atomising liquids by propelling them from a pressurised container by a soluble gas. Apart from the fact that CFC gases can be used as the propellant, CFC-113 mixtures may be the propelled liquid.
Alcohols	A series of hydrocarbon derivatives with at least one hydrogen atom replaced by an -OH group. The simplest alcohols (methanol, ethanol, n-propanol, and isopropanol) are good solvents for some organic soils, notably rosin, but are flammable and can form explosive mixtures with air: their use requires caution and well-designed equipment.
Aqueous cleaning	Cleaning parts with water to which may be added suitable detergents, saponifiers or other additives.
Azeotrope	A mixture of chemicals is azeotropic if the vapour composition is identical to that of the liquid phase. This means that the distillate of an azeotrope is theoretically identical to the solvents from which it is distilled. In practice, the presence of contaminants in the solvent slightly upsets the azeotropy.
Biodegradable	Products in waste water are classed as biodegradable if they can be easily broken down or digested by, for example, sewage treatment.
BOD	An abbreviation for biochemical oxygen demand.
Carbon tetrachloride	A chlorocarbon solvent with a high ODP (about 1.1). It is also considered toxic and a probable human carcinogenic (classified as a B2 carcinogen by US EPA). Its use is strictly regulated in most countries and is used primarily as a base material for the production of other chemicals.

CFC	An abbreviation for chlorofluorocarbon.
CFC-112	1,1,2,2-tetrachloro-1,2-difluoroethane.
CFC-113	A common designation for the most popular CFC solvent, 1,1,2-trichloro-1,2,2-trifluoroethane, with an ODP of approximately 0.8.
CFC-113a	An isomer of CFC-113; 1,1,1-trichloro-2,2,2-trifluoroethane.
Chlorocarbon	An organic chemical composed of chlorine and carbon, e.g., carbon tetrachloride.
Chelation	Chelation is the solubilisation of a metal salt by forming a chemical complex or sequestering. One way of doing this is with ethylenediaminetetraacetic acid (EDTA) salts which have a multi-dentate spiral ligand form that can surround metallic and other ions.
Chlorofluorocarbon	An organic chemical composed of chlorine, fluorine and carbon atoms, usually characterised by high stability contributing to a high ODP.
Chronic toxicity	The long-term toxicity of a product in small, repeated doses. Chronic toxicity can often take many years to determine.
COD	An abbreviation for chemical oxygen demand.
Conformal coating	A protective material applied in a thin, uniform layer to all surfaces of a printed wiring assembly including components.
Defluxing	The removal of flux residues after a soldering operation. Defluxing is a part of most high-reliability electronics production.
Detergent	A product designed to render, for example, oils and greases soluble in water, usually made from synthetic surfactants.
Dry cleaning	A common term for cleaning garments in organic solvents, as opposed to water.
Cleaning of electronics assemblies and circuitry	See defluxing.

Fatty acids	The principal part of many vegetable and animal oils and greases, also known as carboxylic acids which embrace a wider definition. These are common contaminants for which solvents are used in their removal. They are also used to activate fluxes.
Flux	An essential chemical employed in the soldering process to facilitate the production of a solder joint. It is usually a liquid or solid material, frequently based on rosin (colophony).
Greenhouse effect	A thermodynamic effect whereby energy absorbed at the earth's surface, which is normally able to radiate back out to space in the form of long-wave infrared radiation, is retained by gases in the atmosphere, causing a rise in temperature. The gases in question are partially natural, but man-made pollution is thought to increasingly contribute to the effect. The same CFCs that cause ozone depletion are known to be "greenhouse gases", with a single CFC molecule having the same estimated effect as 10,000 carbon dioxide molecules.
Halons	Fire-extinguishing agents with high ODPs.
HCFC	An abbreviation for hydrochlorofluorocarbon.
HFC	An abbreviation for hydrofluorocarbon.
Hydrocarbon	An organic chemical composed only of hydrogen and carbon. Gaseous or volatile hydrocarbons are flammable.
Hydrocarbon derivative	An organic hydrocarbon whose molecule has been modified by adding atoms other than hydrogen and carbon, e.g., alcohols.
Hydrocarbon/surfactant blend	A mixture of low-volatile hydrocarbon solvents with surfactants, allowing the use of a two-phase cleaning process. The first phase is solvent cleaning in the blend and the second phase is water cleaning to remove the residues of the blend and any other water-soluble soils. The surfactant ensures the water-solubility of the otherwise insoluble hydrocarbon. Terpenes are often used in this application.
Hydrochlorocarbon	An organic chemical composed of hydrogen, chlorine and carbon, e.g., trichloroethylene.

Hydrochlorofluorocarbon	An organic chemical composed of hydrogen, chlorine, fluorine and carbon atoms. These chemicals are less stable than pure CFCs, thereby having generally lower ODPs.
IARC	An abbreviation for International Agency for Research on Cancer.
Inert gas soldering	A soldering process done in a relatively oxygen-free atmosphere. The process greatly reduces oxidation of the solder, so that less flux is required, thereby easing or eliminating the need for cleaning.
Isopropanol	See alcohols.
Leaded surface mount component	A surface mount component (SMC) whose external connection consists of formed leads.
Leadless surface mount component	A surface mount component (SMC) whose external connection consists of metallized terminations that are an integral part of the component body.
Low-solids flux	A flux which contains little solid matter, thereby easing or eliminating the need for cleaning. See no-clean flux.
MEA	An abbreviation for monoethanolamine.
Metal cleaning	General cleaning or degreasing of metallic components or assemblies, without specific quality requirements or with low ones.
Methyl chloroform	See 1,1,1-trichloroethane.
Monoethanolamine	A saponifier capable of eliminating rosin fluxes and fatty acids. Also abbreviated to MEA.
No-clean flux	A flux whose residues do not have to be removed from an electronics assembly, therefore, no cleaning is necessary. This type of flux is usually characterised by low quantities of residues.
ODP	An abbreviation for ozone depletion potential.
Organic acid (OA) flux	See water-soluble flux.

Ozone

A gas formed when oxygen is ionised by, for example, the action of ultraviolet light or a strong electric field. It has the property of blocking the passage of dangerous wavelengths of ultraviolet light. Whereas it is a desirable gas in the stratosphere, it is toxic to living organisms at ground level (see volatile organic compound).

Ozone depletion

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

Ozone depletion potential

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

Ozone layer

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

PCB

An abbreviation for printed circuit board.

Pentafluoropropanol

A fluorinated alcohol.

Perchloroethylene

A perhalogenated chlorocarbon solvent used extensively in industrial degreasing and for dry cleaning.

Perhalogenation	An organic molecule is perhalogenated if all the parent hydrogen atoms in a hydrocarbon are replaced with halogen atoms (astatine, bromine, chlorine, fluorine or iodine). For example, carbon tetrachloride (CCl_4) is perchlorinated methane (CH_4). Chloroform (CHCl_3) is an example of a simple chlorinated methane, where only three of the hydrogen atoms have been replaced.
Photoresist	A photomechanical product, in the form of a liquid or a laminated dry film, used in the manufacture of printed circuits. Certain types require the use of large quantities of ozone-depleting hydrochlorocarbon solvents, mostly 1,1,1-trichloroethane and methylene chloride, for their processing.
Precision cleaning	Cleaning of high-precision mechanical parts and electronic sensory devices, as opposed to general metal cleaning. This is usually done under controlled atmospheres, notably in "clean-rooms" with low particulate contamination.
Printed circuit	A printed circuit is an electronic component designed for interconnecting the other components. It usually consists of a metallic conductor pattern on an organic insulating substrate. After fabrication, it is known as a printed circuit board (PCB); after assembly where components are added, it is known as a printed wiring assembly (PWA).
PWA	An abbreviation for printed wiring assembly.
Reflow soldering	A method of electronics soldering commonly used with surface mount technology, whereby a paste formed of solder powder and flux suspended in an organic vehicle is melted by the application of external heat.
Rosin	A solid resin obtained from pine trees which, in a pure form and usually with additives, is frequently used as a flux.
Rosin flux	A flux whose main constituent is rosin. There are several categories of rosin flux, often designated by the codes R (pure rosin), RMA (rosin, mild activation), RA (rosin, activated usually with free chloride ions), RSA (rosin, super activated), SA (synthetic resin, activated).

Saponifier	A chemical designed to react with organic fatty acids, such as rosin, some oils and greases etc., in order to form a water-soluble soap. This is a solvent-free method of defluxing and degreasing many parts. Saponifiers are usually alkaline and may be mineral (based on sodium hydroxide or potassium hydroxide) or organic (based on water solutions of monoethanolamine).
SMC	An abbreviation for surface mount component.
SMD	An abbreviation for surface mount device.
Solvent	Although not a strictly correct definition, in this context a product (aqueous or organic) designed to clean a component or assembly by dissolving the contaminants present on its surface.
Solvent containment	Means of preventing or reducing the emission of CFC or other solvents into the environment. This technique usually involves improving the design of the equipment in which the solvent is used and preventing losses.
Surface mount technology (SMT)	A technique of assembling SMDs or SMCs on the surface of PCBs and PWAs, as opposed to wiring them through holes. Surface mount technology offers a number of important advantages, but also some disadvantages, such as difficulty in defluxing under certain types of SMD.
Surface mount component (device)	A component (device) capable of being attached to a PCB by surface mount technology. The device may be either leaded or leadless.
Surfactant	A product designed to reduce the surface tension of water. Also referred to as tensio-active agents/tensides. Detergents are made up principally from surfactants.
Terpene	Any of many homocyclic hydrocarbons with the empirical formula $C_{10}H_{16}$, characteristic odour. Turpentine is mainly a mixture of terpenes. See hydrocarbon/surfactant blends.
1,1,1-trichloroethane	A hydrochlorocarbon solvent with an estimated ODP of between 0.1 and 0.16. Also known as methyl chloroform.

Vapour phase cleaning A cleaning process, usually with CFC-113 solvent or hydrochlorocarbon solvents, where the final rinse of the parts being cleaned is achieved by condensing solvent vapours on the parts.

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

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

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

UNEP SOLVENTS TECHNICAL OPTIONS COMMITTEE REPORT

EXECUTIVE SUMMARY

The Montreal Protocol on Substances that Deplete the Ozone Layer restricts the production and consumption of some ozone-depleting chemicals. Chlorofluorocarbon 1,1,2-trichloro-1,2,2-trifluoroethane, commonly referred to as CFC-113, is one of these chemicals. CFC-113 is used widely as a solvent to clean electronics assemblies, delicate instruments and surfaces (defined as precision cleaning applications in this report), and metal parts and surfaces. CFC-113 also is one of the solvents used to clean clothes and other fabrics and materials by the dry cleaning industry. This report discusses the solvent uses of CFC-113 and the feasibility of replacing CFC-113 with alternative cleaning agents or processes to reduce and eventually eliminate the need for CFC-113.

This report also addresses the potential use of 1,1,1-trichloroethane¹ and carbon tetrachloride as substitutes for CFC-113. While technically feasible as a substitute for CFC-113, the use of 1,1,1-trichloroethane already contributes significantly to atmospheric chlorine levels. While this report identifies and evaluates the technical potential of 1,1,1-trichloroethane as a CFC-113 substitute, it also notes the market uncertainty over the international acceptability of 1,1,1-trichloroethane (e.g., whether this chemical will be added to the Montreal Protocol to protect the ozone layer).

¹ 1,1,1-Trichloroethane is also referred to as methyl chloroform, TCA, and CH_3CCl_3 .

Because of toxicity and ozone depletion concerns, carbon tetrachloride is not considered an acceptable substitute for CFC-113.

Feasibility of a CFC-113 Phaseout

This report is organised according to the major industry application areas which use CFC-113, 1,1,1-trichloroethane, and carbon tetrachloride as cleaning solvents. For each application area, the UNEP Solvents Review Committee examined the extent of CFC-113 and 1,1,1-trichloroethane use, alternatives, environmental aspects associated with the alternatives, and the extent to which the alternatives can replace CFC-113 and 1,1,1-trichloroethane in solvent cleaning worldwide. The UNEP Solvents Technical Options Committee's consensus is that all CFC-113 use in solvent applications can be phased out by, or before, the year 2000.

Table ES-1 presents the earliest technically feasible reduction schedule for CFC-113 use as a solvent. A complete phaseout of the use of CFC-113 is technically feasible by or before the year 2000. This phaseout would require a combination of options including rationalized cleaning for performance, not cosmetic purpose; no-clean and low-clean solutions such as controlled atmosphere soldering and low solid flux; containment, recovery, and recycle; aqueous and hydrocarbon/ surfactant blends; alcohol and petroleum solvents; new HCFC solvents; chlorinated solvents and CFC blends (while available). This phaseout depends upon prompt world-wide response by user and supplier industries, adequate capital, engineering skills, access to accurate information and availability of new technologies.

Industries have already tested the new alternatives but this information is not yet publicly available. Cooperative efforts could quickly verify the performance and economy of new technologies to provide the basis of choices

Table ES-1. TECHNICALLY FEASIBLE REDUCTION SCHEDULE

1989/1990	CFC Consumption
1989/1990	50-60%
1991/1992	30-50%
1993/1994	20-40%
1995/1996	10-30%
1997/1998	5-20%
1999/2000	0-10%
2001	0%

NOTE: This schedule assumes that:

- there will be a prompt response by governments, producers and users to the requirements of the protocol;
- adequate engineering skills and information is available to develop application process to evaluate alternatives and to obtain market and regulatory approvals for the use of selected alternatives; and
- adequate capital resources are available to evaluate and procure alternatives and that necessary equipment is commercially available.

that maintain or improve product quality and durability, preserve capital investment, and are cost effective. Large companies have announced their intentions to lead the phaseout and to share the information they gain through rapid innovation. Small companies will wait for proven technologies that will be made available from their suppliers. There is a substantial opportunity to speed this process by coordinating the needs of small users and the producers of technical options. This would capture economies of scale.

There is no single substitute for all uses of CFC-113. However, every solvent use area has one or more available alternative(s) which can be adopted. In electronics cleaning, precision cleaning, and metal cleaning applications, there are a variety of alternative solvents and processes available that offer cleaning performance equal to, or better than, CFC-113 and that have equivalent net costs. With the freeze on production and subsequent reduction of CFC availability in the Montreal Protocol signatory countries, the price of CFC-113 will increase. This higher price will, consequently, increase the number of alternative solvents and technologies that are cost competitive with CFC-113.

Carbon tetrachloride is technically able to replace CFC-113 in some cleaning applications. However, carbon tetrachloride is toxic and has an ozone depletion potential of 1.1. These concerns make carbon tetrachloride an unacceptable substitute. Furthermore, it is possible that carbon tetrachloride will be added to the list of substances controlled under the Montreal Protocol in 1990. Carbon tetrachloride is not used as a solvent in the United States or Western Europe, because its use is restricted or prohibited as a carcinogen.² It is unlikely, therefore, that carbon

² The U.S. EPA has classified carbon tetrachloride in Category B2 as a "probable human carcinogen."

tetrachloride will be used in these countries in the future. However, carbon tetrachloride is used as a solvent in other parts of the world. The existing use of carbon tetrachloride as a solvent should be reduced and eliminated because of the compound's carcinogenicity and its high ODP. The Committee does not recommend the use of carbon tetrachloride as a substitute for any cleaning applications discussed in this report.

1,1,1-trichloroethane is also a technically viable substitute in some cleaning applications. It has an ODP of 0.10-0.16 and can be an attractive substitute if it is not regulated under the Montreal Protocol or by national and/or regional legislation. It is technically feasible to freeze or substantially reduce the production and use of 1,1,1-trichloroethane without affecting a timely phaseout of CFC-113.

Some of the HCFC products under development have ODPs similar to 1,1,1-trichloroethane and massive future use of them as a general substitute for CFC-113 may reduce the effect of restrictions; they would be better reserved for applications where there is no other technically feasible substitute.

Other potential solvents, including CFC-112 and CFC-113a, currently are not regulated under the Montreal Protocol but have high ozone depletion potential. CFC-112 and CFC-113a are being marketed as substitutes for CFC-113 despite high ODPs. Parties to the Protocol may want to consider specific measures to anticipate and avoid unwanted development of chemical substitutes that are allowed under the Protocol but are as damaging to the ozone layer as controlled substances.

Environmental Risk of Options is Uncertain

This document is primarily a technical and economic assessment of alternatives to replace the use of CFC-113, 1,1,1-trichloroethane, and carbon tetrachloride used as solvents. It is not a risk assessment and therefore

only contains a general description of some of the environmental health and safety issues. The health and environmental effects of these technical options needs further investigation. The UNEP could coordinate and distribute health and environmental studies of the use of cleaning options.

Many of the soils removed by cleaners are themselves toxic. Some commercially available solvents like carbon tetrachloride are generally recognised as toxic while other solvents are suspected but not confirmed as toxic. Other cleaners including aqueous and hydrocarbon/surfactant cleaners may also be hazardous; however, only limited testing of these chemicals has been completed.

Nonetheless, the use of some toxic chemicals is permitted in certain cases by governmental authorities with workplace controls and waste treatment and/or disposal. However, regulatory measures are not available in all locations. In these circumstances it may be prudent to select cleaning options that do not depend on workplace controls and waste treatment.

The carcinogenicity, mutagenicity (genotoxicity), acute, chronic, and developmental toxicity, neurotoxicity, and ecotoxicity of the alternative compounds that could be used in cleaning applications must be evaluated prior to their use. Waste solvent or waste water should be properly treated, disposed of or destroyed to prevent creating new environmental problems in solving concerns about stratospheric ozone depletion.

There are governmental and industry projects underway to study the human health and environmental implications of alternatives and substitutes to CFCs. For example, international manufacturers of new chemical alternatives to CFCs have formed three separate research consortia to conduct toxicity studies on partially-halogenated substitute chemicals (HFCs and HCFCs). The consortia, Program for Alternative Fluorocarbon Toxicity Testing (PAFT-1, -2, and -3) are

developing toxicity profiles on HCFC and HFC substitutes with broad commercial potential. Acute toxicity tests will be completed for the PAFT 1 & 2 chemicals by September 1989. The final analysis of these test results will be issued in January 1990. Long term testing (two-year bioassays for these same chemicals) has begun or will soon begin with results of these tests available by 1992-3. Acute and chronic tests, including the two-year bioassay for both methyl chloroform and carbon tetrachloride, have been available for some time.

There is also a consortium called Alternative Fluorocarbon Environmental Acceptability Study (AFEAS) to estimate ozone depletion potential (ODP); to calculate global warming potential (GWP); to study mechanisms for atmospheric decomposition; and to evaluate the atmospheric decomposition products and their potential health and environmental effects. Individual manufacturers are also undertaking toxicity studies of other potential chemical alternatives.

Alternative Solvents and Processes

Major CFC producers have taken steps to provide users with solvent blends that use less CFC-113 in the formulations. Solvent blends using 1,1,1-trichloroethane also are available which technically can be used as substitutes. Low CFC-113 blends, some HCFC blends and 1,1,1-trichloroethane are uncertain long-term substitutes because CFC-113 may be phased out and 1,1,1-trichloroethane may be regulated in the future. Alternatives such as aqueous cleaning, hydrocarbon/surfactant blends (e.g., terpene-based solvents), other organic solvents and blends (e.g., isopropanol), inert gas solderings, and no-clean alternatives are the ozone-safe CFC-113 alternatives. Some of these in use by many companies in the industry applications are discussed in this report. Others, such as HCFCs with relatively low ODPs, are either under development or undergoing toxicity trials. Table ES-2 is a list

Table ES-2. COMPARISON OF CFC-113 SOLVENT ALTERNATIVES CONSIDERED IN THE REPORT*

Physical Properties	Pentafluoropropanol	Potential CFC-113 Substitutes							Methylene Chloride	CFC-113 ^j
		HCFC-225ca	HCFC-225cb	HCFC-141b/ HCFC-123/ methanol	Carbon Tetrachloride	Isopropanol	1,1,1-Trichloroethane	Trichloroethylene	Perchloroethylene	
Ozone Depleting Potential	0	<0.05 ^{**}	<0.05 ^{**}	0.08	1.1	0	0.15	0	0	0.8 ^{***}
Chemical Formula	CF ₃ CF ₂ CH ₂ OH	CF ₃ CF ₂ CHCl ₂	CClF ₂ CF ₂ CHClF	CH ₃ CCl ₂ F/ CHCl ₂ CF ₃ / CH ₃ OH	CCl ₄	CH ₃ CH ₂ CHOH	CH ₃ CCl ₃	CHClCCl ₂	CCl ₂ CCl ₂	CCl ₂ FCClF ₂
Molecular Weight	150	202.94	202.94	Not Appl.	153.82	60.09	133.5	131.4	165.9	187.38
Boiling Point (°C)	81	51.1	56.1	30-32	76.5	82	72-88	86-88	120-122	47.6
Density (g/cm ³) at 25 °C	1.51	1.55	1.56	1.28	1.59	0.787	1.34	1.46	1.62	1.56
Surface Tension (dyne/cm)	19	16.3	17.7	18.5-19.0	27.0	22.6	25.4	29.3	31.3	17.3
Kauri Butanol Value	36	34	30	N/A	113	N/A	124	130	91	31
Toxicity	Incomplete ⁺	Incomplete ⁺	Incomplete ⁺	Incomplete ⁺	High	Medium	Low	Medium	Medium	Low
Carcinogenicity	Unknown	Unknown	Unknown	Unknown	Yes	No	Inconclusive ^a	See Note ^b	See Note ^c	No
VOC ^e	N/A	N/A	N/A	No	N/A	N/A	No ^f	Yes ^g	Yes ^h	No ⁱ
Flash Point (°C)	None	None	None	None	None	12	None	None	None	None

* Hydrocarbon/surfactant blends, aqueous cleaners, and no clean technologies are considered viable alternatives to CFC-113 in this report. However, because hydrocarbon/surfactant blends and aqueous cleaners have a large number of formulations, they are not included in this particular table. No-clean technologies are processes rather than materials, and also are not included in this table.

** Manufacturer's estimate.

*** Montreal Protocol Value. The UNEP technical assessment lists a probable range of 0.8 to 0.9.

+ Toxicity testing is in progress.

Table ES-2 (Continued)

- a Tests concerning the carcinogenicity of 1,1,1-trichloroethane have proven inconclusive (NTP 1984). Table ES-1 (Continued)
 - b The U.S. EPA (1989b) has not formally classified trichloroethylene in Category B2 as a "probable human carcinogen," while the International Agency for Research on Cancer (IARC) has classified this solvent in Group 3, a substance not classifiable as to its carcinogenicity in humans (HSIA 1989c).
 - c The U.S. EPA (1989a) has not formally classified perchloroethylene in Category B2 as a "probable human carcinogen." IARC has classified perchloroethylene in Group 2B as a substance considered "possibly carcinogenic to humans" (HSIA 1989a).
 - d The U.S. EPA (1989b) has classified methylene chloride in Category B2 as a "probable human carcinogen," while IARC has classified methylene chloride in Group 2B as a substance considered "possibly carcinogenic to humans" (HSIA 1989b).
 - e VOC = Volatile Organic Compound. These are constituents that will evaporate at their temperature of use and which, by a photochemical reaction, will cause atmospheric oxygen to be converted into a potential smog-promoting tropospheric ozone, under unfavourable climatic conditions.
 - f 1,1,1-Trichloroethane is exempt from the U.S. EPA classification of VOCs (HSIA 1987).
 - g Trichloroethylene is regulated in the U.S. as a VOC in many states (HSIA 1989c).
 - h Perchloroethylene is regulated in the U.S. as a VOC in most states (HSIA 1989a).
 - i The U.S. EPA has indicated that methylene chloride may be exempted from regulation as a VOC under state regulations (HSIA 1989b).
 - j In addition to the blends containing over 90 percent CFC-113, CFC manufacturers have also introduced "low" CFC-113 blends containing 60 percent to 70 percent CFC-113. These blends are excellent temporary substitutes.
- Sources: Asahi Glass 1989; Ashland Chemical 1988; Basu and Bonner 1989; Daikin 1989; HSIA 1989a, 1989b, 1989c, 1987; IPC 1987; NTP 1984; Rodgers 1989; and U.S. EPA 1989a, 1989b.

of alternative materials and processes announced to date and their physical/chemical properties, including their ODP values. This list is likely to grow substantially over the next few years. Table ES-3 summarises some of the advantages and disadvantages of the CFC-113 alternatives discussed in this report.

The Committee believes that companies, as a first step, can implement conservation and recovery practices to decrease CFC-113 consumption. Such steps are important while processes and equipment are modified, redesigned, or other production changes are made to eliminate CFC-113 use altogether. They can improve operating practices, install containment features, and recycle solvent to reduce consumption by up to 50 percent. The further addition of activated carbon adsorption will reduce solvent use by 30 to 40 percent. For one company, the payback period on an activated carbon adsorption system is two years. The use of carbon adsorption systems is optimal only at certain minimum concentrations of solvent in the exhaust stream entering the adsorber. If alternative technologies such as aqueous cleaning, alcohol-based cleaning, inert gas (controlled atmosphere) wave soldering, and low solids-no clean fluxes are adopted, then all uses of CFC-113 in the electronics cleaning, precision cleaning, and metal cleaning application areas can be eliminated. In the dry cleaning industry, which accounts for less than five percent of worldwide CFC-113 use, alternative solvents such as white spirits are commercially available and the HFCs and HCFCs currently under development can be a viable CFC-113 alternatives. These new substitutes are likely to be commercially available in the next three to five years. Each alternative dry cleaning chemical will have to be used according to safety precautions concerning flammability and/or toxicity.

Table ES-3. ADVANTAGES AND DISADVANTAGES OF ALTERNATIVES TO CFC-113

Alternative	Advantages	Disadvantages
Chlorinated Solvents		
Methylene Chloride	Effective cleaner	Probable carcinogen ^a Waste disposal
Trichloroethylene	Effective cleaner	Probable carcinogen ^b Waste disposal
Perchloroethylene	Effective cleaner	Probable carcinogen ^c Waste disposal
1,1,1-Trichloroethane	Effective cleaner	Ozone depleting substance Waste disposal
Aqueous Cleaners	Effective cleaner	Waste disposal, Energy consumption
Water only	No additional chemicals	Limited effectiveness
Hydrocarbon/Surfactant Blends ^d	Effective cleaner	Toxicity uncertain Waste disposal, Combustible ^e
Alcohol	Effective cleaner	Flammable ^e Waste Disposal Fiscal concerns ^f
No-Clean Technologies	Less or no residue to be cleaned	Not yet approved for many applications including military
HCFCs	(Under development)	

^a The U.S. EPA (1989b) has classified methylene chloride in Category B2 as a "probable human carcinogen," while the International Agency for Research on Cancer (IARC) has classified methylene chloride in Group 2B as a substance considered "possibly carcinogenic to humans" (HSIA 1989b).

^b The U.S. EPA (1989b) has classified trichloroethylene in Category B2 as a "probable human carcinogen," while the IARC has classified this solvent in Group 3, a substance not classifiable as to its carcinogenicity in humans (HSIA 1989c).

Table ES-3 (continued)

^c The U.S. EPA (1989a) has classified perchloroethylene in Category B2 as a "probable human carcinogen." IARC has classified perchloroethylene in Group 2B as a substance considered "possibly carcinogenic to humans" (HSIA 1989a).

^d This includes solvents based on terpenes.

^e In this report a combustible substance is defined as one which has a flash point under 37.8°C, while a flammable substance is defined as one which has a flash point over 37.8°C.

^f Some countries impose duties on all alcohols, including methanol, propanols and some butanols, as well as ethanol. Other countries require a license for any still capable of distilling alcohols (Ellis 1989c).

Sources: HSIA 1989a, 1989b, 1989c, 1987.
U.S. EPA 1989a, 1989b.

Electronics Cleaning

The electronics industry is the largest worldwide user of CFC-113. An estimated 8.00×10^7 kilograms of CFC-113 were used to remove flux from printed circuit board assemblies³ in 1986, representing 45 percent of worldwide CFC-113 consumption. Removal of fluxes and flux residues after soldering traditionally has been considered essential for high quality electronic assemblies to ensure electrical performance and adhesion of conformal coatings, to facilitate inspection and electrical testing, and to prevent corrosion and electro-migration. CFC-113 solvents mixed with alcohols have been the solvents of choice for electronics cleaning because they effectively remove flux residues without damaging solvent-sensitive components on the printed circuit board assemblies, are nonflammable, and have low toxicity levels.

An estimated 50 percent of current CFC-113 use in the electronics industry results directly or indirectly from military specifications. Industry experts agree that the use of alternative cleaning processes, such as aqueous cleaning, could increase if military specifications allowed manufacturers to meet performance criteria using a choice of flux and cleaning methods. The U.S. military has agreed to change military specifications based on a joint U.S. Department of Defense, U.S. Environmental Protection Agency, and U.S. industry benchmark test program currently in progress. The U.K. Ministry of Defence also has pioneered a new flux standard that will allow elimination of CFC use in U.K. military production. In Europe, two cleaning evaluation programmes are also examining alternative electronics cleaning

³ A wide variety of products are built with printed circuit board assemblies including computers, satellites, avionics, and home entertainment electronics.

processes. A cooperative government/industry cleanliness and reliability evaluation programme of candidate solvents is also being undertaken in Scandinavia. This programme is evaluating aqueous alcohol and derivatives, chlorinated, and terpene-based alternatives.

Alternative solvents that are demonstrated to clean as well as, or better than, the benchmark cleaning performance of CFC-113 will be accepted as candidate materials by the U.S. military for use in manufacturing military electronics equipment. This change is likely to take effect within the next year. Aqueous cleaning, alcohols and HCFC/alcohol blends, hydrocarbon/surfactant blends (including terpene-based formulations), and chlorinated solvents are effective cleaning alternatives.

Other promising cleaning alternatives include hydrocarbon/surfactant blend-based solvents, including terpenes, and low solids fluxes. Hydrocarbon/surfactant blend-based solvents work effectively in close geometry spacings and at room or slightly higher temperatures. These solvents remove both polar and non-polar contaminants, and are noncorrosive. The use of low solids fluxes in some applications may eliminate the need for cleaning altogether.

Precision Cleaning and Displacement

A second major use of CFC-113 as a cleaning solvent is in precision cleaning applications and water displacement/drying. Precision cleaning is used to clean delicate instruments and surfaces such as gyroscopes, computer disk drives, miniature bearings, medical equipment and supplies, and optical components. Aqueous cleaning, alcohols and HCFC/alcohol blends, hydrocarbon/surfactant blends (including terpene-based formulations), and chlorinated solvents are effective alternatives. Many alternative techniques are in the testing stage; as research and development increase in this area, use of alternatives could virtually replace CFC-113 use by, or before, the

year 2000. Alternatives include alcohols and HCFC/alcohol blends, 1,1,1-trichloroethane and other chlorinated solvents, hydrocarbons, aqueous cleaning processes, and biodegradable solvents.

Metal Cleaning

A third major application area is in metal cleaning applications. CFC-113 use in metal cleaning has grown out of concern about the adverse human health effects of some chlorinated solvents, particularly in the U.S. and Japan. Conservation and recovery practices and the use of other chlorinated solvents can reduce CFC-113 use substantially in the short-term. Additional reductions and elimination of CFC-113 use can be achieved by using a variety of aqueous and semi-aqueous cleaners, and hydrocarbon/surfactant blend cleaners.

Dry Cleaning

The dry cleaning industry is a relatively minor CFC-113 user. There are numerous operating and maintenance procedures that can be implemented to reduce use in existing machines. Alternative solvents have been identified and their use on specific fabric types approved in some countries. White spirits, for example, are an alternative to CFC-113 for cleaning most fabrics. These must be used with caution in industrial facilities, however, due to their flammability. CFC-113 use as a dry cleaning solvent can be reduced further by using 1,1,1-trichloroethane and the HCFC substitutes currently under development. Pentafluoropropanol, HCFC-225ca, and HCFC-225cb are promising alternatives for dry cleaning. CFC-113 use in this area also could be reduced by establishing centralised cleaning facilities at which technical and procedural controls on solvent use could be implemented.

Corporate Positions for Protection of the Ozone Layer

Protection of the stratospheric ozone layer has become an important policy objective for companies that now use CFC-113 solvents. These companies are acting out of concern for the environment and in response to economic incentives (e.g., price increases, chemical shortages, and prudent investment criteria) resulting from national and global regulation. These corporate policies confirm that large markets exist for substitutes and alternatives and reinforce the judgment of the Committee that phaseouts are technically and economically feasible. Many of these corporate policies also offer assistance in technology transfer to developing countries.

Several multinational corporations have announced prompt goals to reduce and eliminate CFC and halon use. In January 1988, AT&T announced a goal to reduce solvent use of CFC-113 by 50 percent by 1991. Sharp Corporation forecasts that they will achieve a 40 percent reduction in solvent use from 1988 levels by the end of this year. Table ES-4 presents the Sharp Corporation's CFC phaseout plan. Digital Equipment, Hitachi, Matsushita, NEC, Northern Telecom, Seiko-Epson, Siemens, Toshiba, and other major electronics manufacturers have announced similar policies to reduce the use of CFC-113.

Northern Telecom has established a goal to eliminate CFC-113 and Halon purchases by the end of 1991, and Seiko-Epson has announced their intention to completely phase out all CFC use by 1993. AT&T has a new goal of 1994. In each case, top management was involved in setting this policy. For example, the full board of directors of Seiko-Epson voted on the phaseout policy and appointed a board member who was given primary responsibility to supervise the phaseout.

Table ES-4. MEASURES FOR PHASE OUT OF CFCs: ONE COMPANY'S PLAN

Measures for Phase-Out of CFCs by Manufacturing Group											
	Montreal Protocol Schedule	Target	TV and Video Systems Group CFC-113	Audio Systems CFC-113	Information Systems CFC-113	Integrated Circuits CFC-113	Electronic Components CFC-113	Appliance Systems			
								CFC-11	CFC-12	CFC-113	
1986	Base Year						• Alternatives • Reduce exchange frequency • Improve cleaning conditions • Improve cleaning equipment				
1987	Adoption (Sept.)										
1988			• Re-use waste solvents • Install solvent recovery systems		• Improve cleaning equipment • Non-cleaning technology of circuit boards^a	• Reduce cleaning processes • Alternatives • Aqueous cleaning					• Use alternative substances for wiping
1989	Freeze at '86 Level	20% Reduction		• Non-cleaning technology of circuit boards^a							• Investigate alternatives
1990			• Improve open tray cleaning • Non-cleaning technology of circuit boards	• Improve cleaning equipment • Non-cleaning technology of circuit boards^a	• Non-cleaning technology of circuit boards^a	• Add cooling equipment • Non-cleaning technology^a • Add solvents recovery systems • Improve cleaning equipment • Alternatives • Aqueous cleaning	• Improve cleaning equipment • Adopt new cleaning processes • Reduce exchange frequency • Aqueous cleaning	• Alternatives (50%)			• Alternatives (60%)
1991											
1992											
1993	20% Reduction	50% Reduction									
1994			• Alternatives	• Non-cleaning technology of circuit boards^b • Alternatives	• Non-cleaning technology of circuit boards^b • Alternatives	• Renew equipment • Non-cleaning technology^b • Alternatives • Improve wire bonding machines	• Switch to iso-propyl alcohol • Switch to low solids fluxes • Aqueous cleaning • Alternatives	• Alternatives	• Alternatives		• Alternatives
1995											
1996											
1997											
1998	50% Reduction	Phase-out									
1999											
2000											

^a Partially substituted.^b Fully substituted.

Source: Sharp Corporation 1989.

All the electronics manufacturing companies that met with the Committee are implementing corporate policies to phase out use of CFCs and halons at all their facilities, including facilities in nations not yet party to the Protocol. These policies should reassure developing countries that they will be at the forefront of new technology development and implementation and, furthermore, that corporate financing will be available in their countries.

New corporate and government procurement policies also have begun to discourage purchase of products dependent on CFC-113 use. The U.S. Defense Department, AT&T and Siemens have new policies that set a high priority on ozone layer protection. The U.S. Secretary of Defense has directed U.S. Armed Forces to reduce the use of CFCs and halons as well as to avoid the purchase of products that depend on these chemicals. This policy is primarily in support of environmental protection, but recognizes the strategic importance avoiding dependence on chemicals that may be unavailable or expensive. This policy will be implemented through prompt changes in procurement specifications and through other innovative management practices. Because the military is such an important customer and its procurement standards are industry guidelines, new, ozone-safe solvents should be readily available and easier to use because of this policy change.

AT&T recently notified their international suppliers that ozone layer protection was a top corporate priority. AT&T asked their suppliers to notify them of whether their products were made with CFCs and also to identify their proposed actions to eliminate the use of CFCs. Furthermore, AT&T warned suppliers that soon they may have to provide a Supplier Warranty certifying that products sold to AT&T are not made with and do not contain CFCs, and otherwise conform to government requirements established to comply with the

Montreal Protocol. This bold announcement puts suppliers on notice that future markets will be dominated by companies that do not use CFCs.

Siemens' production facility in Erlangen, Germany is one of the largest of electronic manufacturing plants in the world, producing goods valued at one billion U.S. dollars annually. Siemens made a corporate decision to replace some CFC-113 solvent cleaning with an alcohol solvent. This decision confronted Siemens with the technical necessity that all circuit board components be compatible with alcohol. Siemens notified all suppliers that the parts they furnished must be fully compatible with alcohol. Due to the enormous amount of business Siemens provides, the suppliers responded promptly. As a result, Siemens has sources to supply every component used in their company with materials compatible with alcohol. Not only was this change important to Siemens' strategy, it is also valuable to smaller manufacturers who can now take advantage of Siemens' initiative and buy alcohol-compatible components.

These phaseout policies by large CFC-113 customers who produce vital computer, communication, and defense products serve as an indicator to other companies that CFC-113 alternatives and substitutes are currently available and that the range of alternatives should continue to increase in the future.

Conclusions

In summary, the Committee has drawn the following conclusions regarding the technically feasible reduction of CFC-113 and 1,1,1-trichloroethane, and carbon tetrachloride use by the year 2000:

- CFC-113 use can be phased out by, or before, the year 2000;
- Inevitable price increases in CFC-113 as production drops may create a de facto situation in which CFC-113 becomes economically less desirable and a more rapid phase out of CFC-113 may occur than is currently foreseen;

- Up to 50 percent of current CFC-113 use can be reduced with minimal net cost; for some users of CFC-113, the addition of activated carbon adsorption systems may reduce solvent use by up to a further 30 to 40 percent with a reasonable payback;
- Opportunities exist for improved cleaning and innovation through the use of substitutes for CFC-113;
- No-clean and aqueous processes as well as alcohol and hydrocarbon/surfactant blend substitutes are the most promising alternatives;
- A number of multinational and national electronics manufacturers have announced new corporate policies to promptly phase-out CFC use. These efforts will speed development, verification, and commercialisation of new technology and may reduce costs of phase-out.
- New technology currently under development will help smaller companies successfully switch to CFC-113 cleaning alternatives;
- Ozone-depleting HCFCs under development should be continually monitored if they become commercially available in large quantities so that they are reserved for those applications where their special qualities are essential.
- 1,1,1-Trichloroethane will be an attractive substitute for CFC-113 if it is not regulated as an ozone depleting substance under the Montreal Protocol or by new national and regional regulations;
- Many of the alternatives for CFC-113 also are alternatives to the use of 1,1,1-trichloroethane;
- 1,1,1-Trichloroethane production can be frozen or substantially reduced without affecting a timely phaseout of CFC-113;
- Industry will select alternatives based on the best technology for each application;
- Parties to the Protocol may consider specific measures to anticipate and avoid unwanted development of chemical substitutes that are allowed under the Protocol but are as damaging to the ozone layer as controlled substances. CFC-112 and CFC-113a are two such substances;
- The human health and environmental effects of the alternative compounds that could be used in cleaning applications must be evaluated prior to their use. Waste solvent or waste water should be properly treated, disposed of or destroyed to prevent creating new environmental problems in solving concerns about stratospheric ozone depletion. More evaluation is needed; and

Workplace controls and effective waste treatment and/or disposal services for certain alternatives may not be available in all locations. In these circumstances it may be prudent to select cleaning options that do not depend on workplace controls and waste treatment.

CHAPTER 1
INTRODUCTION
WORLDWIDE CFC-113 USE

1.1 BACKGROUND

In 1981, in response to growing scientific consensus, the United Nations Environment Programme (UNEP) began negotiations to develop a multilateral response to reduce the threat of ozone depletion. These negotiations resulted in the Vienna Convention for the Protection of the Ozone Layer in March 1985. The convention provided a framework for international cooperation in research, monitoring, and information exchange. Further negotiations resulted in the "Montreal Protocol on Substances that Deplete the Ozone Layer." The Montreal Protocol was signed in September 1987 and requires the Parties to control or reduce their use of specific ozone depleting chemicals.

The Protocol sets out a schedule for addressing ozone layer depletion in both the short and long-term. The intent is to control all substances that deplete the ozone layer. In the short-term, the Protocol sets out a reduction schedule to reduce the global consumption and emissions of the five most ozone depleting chlorofluorocarbons (CFCs), and the three most commonly used fire extinguishing agents called halons. These are:

- | | |
|--------------|--|
| • CFC-11 | Trichlorofluoromethane (CCl_3F); |
| • CFC-12 | Dichlorodifluoromethane (CCl_2F_2); |
| • CFC-113 | Trichlorotrifluoroethane ($\text{C}_2\text{Cl}_3\text{F}_3$); |
| • CFC-114 | Dichlorotetrafluoroethane ($\text{C}_2\text{Cl}_2\text{F}_4$); |
| • CFC-115 | Chloropentafluoroethane (C_2ClF_5); |
| • Halon 1211 | Bromochlorodifluoromethane (CBrClF_2); |
| • Halon 1301 | Bromotrifluoromethane (CBrF_3); and |
| • Halon 2402 | Dibromotetrafluoroethane ($\text{C}_2\text{Br}_2\text{F}_4$). |

Table I-1 compares the worldwide consumption and ozone depletion potential of the controlled CFCs. The reduction schedule set out in the Protocol is as follows:

- a freeze in consumption (defined as production plus imports minus exports) at 1986 levels:
 - CFCs starting on July 1, 1989
 - Halons starting on January 1, 1992
- a reduction in consumption of CFCs:
 - 20 percent starting on July 1, 1993
 - 50 percent starting on July 1, 1998

In addition, the Protocol created four international review panels to report on:

- the science (the extent of the threat);
- the anticipated environmental and public health effects of stratospheric ozone depletion;
- the technical viability, in each of the major use sectors, of tightening the requirements of the Montreal Protocol (earliest feasible reduction schedule); and
- the related anticipated economic consequences.

For the technical viability panel, committees were formed to report on the state of technology and the availability of substitutes in the following use areas: solvents, foams, halons, refrigerants, and miscellaneous uses. This report summarizes the work of the Solvents Technical Options Committee.

To provide the widest possible international participation in the review, experts from industry, government, academic institutions, and private consulting firms were identified and invited to participate. Both the Review Panel Chairperson and UNEP staff contacted many countries to encourage their active participation in this review process. Furthermore, the Committee chairperson contacted producers, manufacturers, and trade associations to arrange for additional technical input.

Table I-1. COMPARISON OF WORLDWIDE CONSUMPTION OF CONTROLLED CFCs
AND OZONE DEPLETION POTENTIAL (ODP)

	Worldwide Consumption (kilotons)	Percent of Basket	Relative Total ODP	Percent ODP of Basket	Atmospheric Retention Time (years)
CFC-11	370	35.0	1.00	36.4	75
CFC-12	480	45.4	1.00	47.2	111
CFC-113	178	16.8	0.80	14.0	90
CFC-114	15	1.4	1.00	1.5	*
CFC-115	15	1.4	0.60	0.9	*

* Not available

Source: Montreal Protocol 1987.

This Committee report, Volume I, provides clear and concise technical guidance on what reductions are technically feasible and by what date. Volume II will include technical papers of importance; Volume III will include company and corporation literature on substitutes. This report has undergone extensive peer review and also will be distributed internationally by UNEP.

This report is part of the UNEP review under Article 6 of the Protocol. Article 6 specifically directs Parties (nations that have ratified the Protocol) to assess whether the control measures, as provided for in Article 2 of the Protocol, are sufficient to meet the goals for reducing ozone depletion based on a review of the current state of knowledge on technical, scientific, environmental, and economic issues related to stratospheric ozone protection.

1.2 TERMS OF REFERENCE FOR THE COMMITTEE

The member countries of the Committee included representatives from North American, European, and Japanese governments and companies (see Table I-2). In addition, the Committee had the benefit of advice from a distinguished panel of expert advisors which included representatives of government agencies, chemical producers, and industry associations (see Table I-3) from North America and Europe. Committee meetings were held in the United States, Europe, and Japan to facilitate participation by interested organisations and to enable Committee members to gather information first hand on the potential for substitution of CFC-113 and the progress made to date. The Committee met with a number of companies, trade associations, and government agencies to understand their position on this issue. Corporate participants are listed in Table I-4.

1.3 BASIS FOR COMMITTEE RECOMMENDATIONS TO UNEP AND COMMITTEE POSITION ON 1.1.1-TRICHLOROETHANE AND PARTIALLY HALOGENATED FLUOROCARBONS

The Committee's recommendations to the UNEP are the consensus of the Committee members. New scientific information suggests that ozone is

Table I-2. MEMBER COUNTRIES OF THE UNEP
SOLVENTS TECHNICAL OPTIONS COMMITTEE

Member Countries

Canada
Japan
Sweden
Switzerland
United Kingdom
United States

Table I-3. ORGANISATIONS WHOSE EMPLOYEES SERVE ON THE
UNEP SOLVENTS TECHNICAL OPTIONS COMMITTEE

Member Organisations

AT&T Engineering Research Center
British Aerospace (Dynamics) Ltd.
Digital Equipment Corporation
General Dynamics, Fort Worth Division
ICF Incorporated
Northern Telecom Limited
Protonique S.A.
National Environmental Protection Board
Statens Natarvardsverk - Sweden
Sketchley Plc.
Texas Instruments Inc.
Toshiba Corporation
U.S. Environmental Protection Agency

Table I-4. CORPORATE AND GOVERNMENT PRESENTATIONS IN MEETINGS HELD BY THE
UNEP SOLVENTS TECHNICAL OPTIONS COMMITTEE

Allied-Signal, U.S.A.
Asahi Glass, Japan
British Aerospace, U.K.
British Antarctic Survey, U.K.
Daikin Industries, Japan
Digital Equipment Corporation, Scotland and U.S.A.
DuPont - Mitsui Fluorochemicals Co. Ltd, Japan
Halogenated Solvents Industry Alliance, U.S.A.
Herbert Streckfuss GmbH, F.R.G.
ICI Chemicals and Polymers Ltd., U.K.
KLN Ultraschall GmbH. F.R.G.
Ministry of International Trade and Industry, Japan
NEC, Japan
Northern Telecom Ltd., U.S.A. and Canada
Petroferm Incorporated, U.S.A.
SEHO, F.R.G.
Seiko-Epson, Japan
Sharp Corporation, Japan
Separation Technologists, U.S.A.
Siemens A.G., F.R.G.
Sigma Industries, U.S.A.
Toshiba Corporation, Japan
United States Air Force Engineering Services Center,
Tyndall Air Force Base, U.S.A.

depleting at a faster rate than the scientific community and the Parties to the Protocol had originally anticipated. Future chlorine and bromine concentrations in the upper atmosphere will depend primarily on future emissions of CFCs, halons, and other ozone depleting substances.

In August 1988, the U.S. EPA issued a study entitled "Future Concentrations of Stratospheric Chlorine and Bromine,"¹ which looked at chlorine and bromine levels after the implementation of the restrictions in the Montreal Protocol. The U.S. EPA found that levels of chlorine in the stratosphere would increase from 2.7 to 8 parts per billion (ppb) by 2075, even with the reductions in CFC production called for in the Protocol.

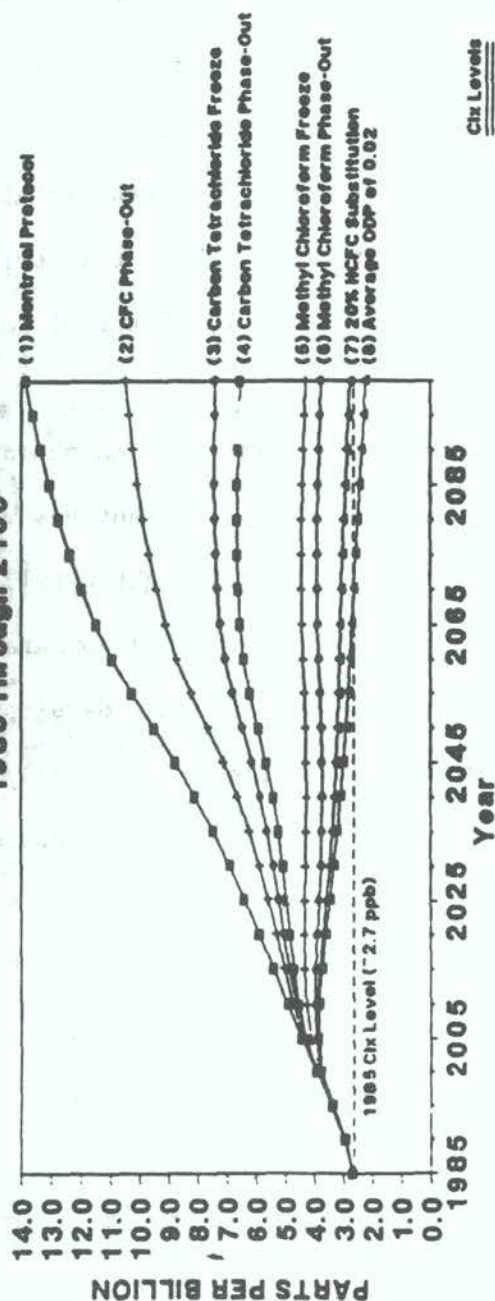
This increase would be caused not only by the allowed use of CFCs and halons under the Protocol, but also by CFC use in countries that are not members of the Protocol and by the growth in the production and use of the non-regulated chemicals such as 1,1,1-trichloroethane² and carbon tetrachloride. Specifically, the study predicted that approximately 45 percent of the total increase in chlorine and bromine would be caused by emissions from the remaining CFCs and halons. An additional 35 percent of the increase in chlorine would occur as the result of 1,1,1-trichloroethane emissions. Furthermore, the U.S. EPA analysis showed that if 1,1,1-trichloroethane use increases as predicted, it would account for over 80 percent of the growth in chlorine levels associated with substances not covered by the Protocol. Figures I-1 summarises the U.S. EPA findings.

¹ Clx Report, U.S. EPA Office of Air and Radiation, 400/1-88/005, August 1988.

² 1,1,1-Trichloroethane is also referred to as methyl chloroform, TCA, and CH_3CCl_3 .

CUMULATIVE REDUCTIONS

TOTAL CIX CONCENTRATIONS 1986 Through 2100



	Cix Levels	
	Max	2076
(1) Montreal Protocol Reductions; No Methyl Chloroform Controls; No Carbon Tetrachloride Controls; HCFCs Capture 50% of What CFC Market Would Have Been Without Protocol	13.9	12.4
(2) 2000 Phase-Out of Fully Halogenated CFCs; No Methyl Chloroform Controls; No Carbon Tetrachloride Controls; HCFCs Capture 50% of What CFC Market Would Have Been Without Protocol	10.8	9.7
(3) 2000 Phase-Out of Fully Halogenated CFCs; No Methyl Chloroform Controls; HCFCs Capture 80% of What CFC Market Would Have Been Without Protocol; Carbon Tetrachloride Freeze	7.6	7.4
(4) 2000 Phase-Out of Fully Halogenated CFCs; No Methyl Chloroform Controls; HCFCs Capture 80% of What CFC Market Would Have Been Without Protocol; Carbon Tetrachloride Phase-Out	6.6	6.6
(5) 2000 Phase-Out of Fully Halogenated CFCs; Methyl Chloroform Freeze; HCFCs Capture 80% of What CFC Market Would Have Been Without Protocol; Carbon Tetrachloride Phase-Out	4.4	4.4
(6) 2000 Phase-Out of Fully Halogenated CFCs; Methyl Chloroform Phase-Out; HCFCs Capture 80% of What CFC Market Would Have Been Without Protocol; Carbon Tetrachloride Phase-Out	4.0	3.9
(7) 2000 Phase-Out of Fully Halogenated CFCs; Methyl Chloroform Phase-Out; HCFCs Capture 20% of What CFC Market Would Have Been Without Protocol; Carbon Tetrachloride Phase-Out	3.9	3.0
(8) 2090 Phase-Out of Fully Halogenated CFCs; Methyl Chloroform Phase-Out 20% of What CFC Market Would Have Been Without Protocol; HCFCs Average An ODP of 0.02; Carbon Tetrachloride Phase-Out	3.9	2.6

Assumptions: o 100% Global Participation e HCFCs Average An ODP of 0.05 (Except Case 8)

Figure I-1. CUMULATIVE REDUCTIONS IN TOTAL CIX CONCENTRATIONS: 1985-2100.
(Source: U.S. EPA 1989. Communication from James Hemby to the UNEP Solvents Technical Options Committee.)

In an update of this report presented at the first meeting of the Protocol Parties held in Helsinki in April, 1989, the U.S. EPA presented an analysis that examined what actions would be required to stabilise chlorine at current atmospheric levels. It showed that a phaseout of CFCs and at least a freeze in 1,1,1-trichloroethane would be required. It is important to note however, that stabilisation would not reverse past ozone depletion. To reverse past ozone depletion that the Ozone Trends Panel reports has already occurred and to return Clx levels in the stratosphere to those that existed prior to the Antarctic ozone hole, even further cuts in 1,1,1-trichloroethane might be required.

These conclusions were significant enough to warrant an examination by the Committee of the technical feasibility of using only alternatives which do not deplete the ozone layer. In the short-term some users might use 1,1,1-trichloroethane and the other low ODP alternatives. Figure I-2 compares the ODP of 1,1,1-trichloroethane, and the new HCFCs currently under development.

Table I-5 presents the Committee consensus on earliest technically feasible reduction schedule for CFC-113 use as a solvent. This schedule indicates that a complete phaseout of the use of CFC-113 is technically feasible by or before the year 2000. This phaseout would require a combination of options including rationalized cleaning for performance, not cosmetic purpose; no-clean and low-clean solutions such as controlled atmosphere soldering and low solid flux; containment, recovery, and recycle; aqueous and hydrocarbon/ surfactant blends; alcohol and petroleum solvents; new HCFC solvents; chlorinated solvents and CFC blends (while available). This phaseout depends upon prompt world-wide response by user and supplier industries, adequate capital, engineering skills, access to accurate information and availability of new technologies.

Figure I-2. Relative Total Ozone Depletion *

Potential of Selected Solvents

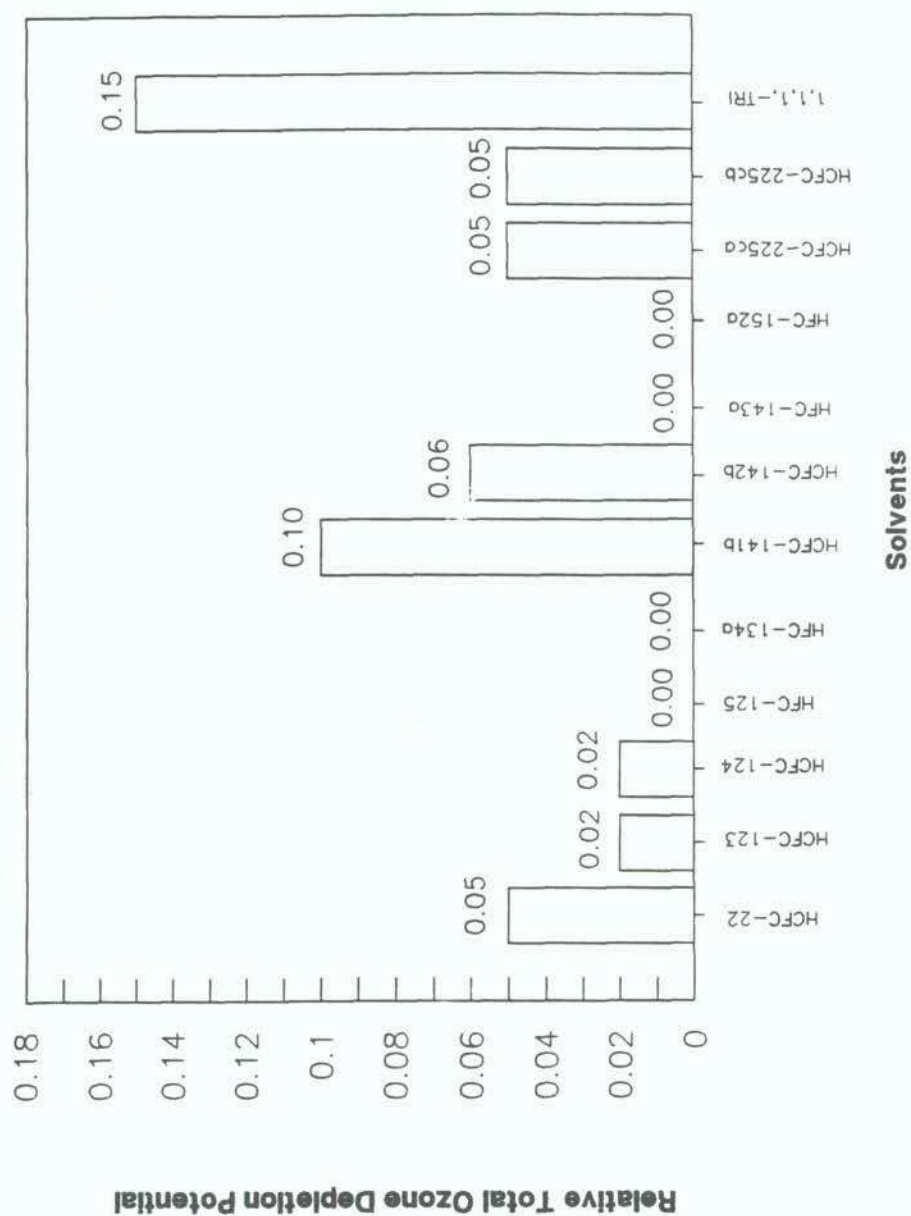


Figure I-2. RELATIVE TOTAL OZONE DEPLETION POTENTIAL OF SELECTED SOLVENTS*

(* Relative to CFC-11 which is set at a value of 1.)

Table I-5. TECHNICALLY FEASIBLE REDUCTION SCHEDULE

1989/1990	CFC Consumption
1989/1990	50-60%
1991/1992	30-50%
1993/1994	20-40%
1995/1996	10-30%
1997/1998	5-20%
1999/2000	0-10%
2001	0%

NOTE: This schedule assumes that:

- their will be a prompt response by governments, producers and users to the requirements of the protocol;
- adequate engineering skills and information is available to develop application process to evaluate alternatives and to obtain market and regulatory approvals for the use of selected alternatives; and
- adequate capital resources are available to evaluate and procure alternatives and that necessary equipment is commercially available.

1.4 CORPORATE POLICY

The Committee met with a number of companies including several multinational corporations in Europe, North America and Japan which have pledged to phase out CFC-113 use in their facilities worldwide. Northern Telecom Ltd. has a goal of 1991, Seiko-Epson and others 1993, AT&T 1994, and none later than the year 2000. Detailed phaseout plans developed by major companies indicate the seriousness of the effort. Top management involvement in all aspects of phaseout efforts can ensure a sustained level of effort towards achieving the goal of CFC-113 phase out by the year 2000.

New corporate and government procurement policies also have begun to discourage purchase of products dependent on CFC-113 use. One of the largest communications companies worldwide recently notified their worldwide suppliers that in the future they may have to certify that the manufacture of their products do not involve the use of CFC-113. Another large and diversified electronics company recently made a corporate decision to switch to alcohol solvents to replace CFC-113 based cleaning in their largest manufacturing facility (one of the largest single location manufacturing plants in the world) and notified their suppliers that all components supplied in the future must be compatible with alcohol. Suppliers responded promptly to the new requirement. This has made it possible not only for this company to eliminate CFC-113 use but also has enabled smaller manufacturers to purchase components compatible with the new alternative alcohol.

These phaseout policies by large CFC-113 customers who produce vital computer, communication, and defense products serve as an indicator to other companies that CFC-113 alternatives and substitutes are currently available and that the range of alternatives should continue to increase in the future.

1.5 ENVIRONMENTAL RISK OF OPTIONS IS UNCERTAIN

This document is primarily a technical and economic assessment of alternatives to replace the use of CFC-113, 1,1,1-trichloroethane, and carbon tetrachloride used as solvents. It is not a risk assessment and therefore only contains a general description of some of the environmental health and safety issues. The health and environmental effects of these technical options needs further investigation. The UNEP could coordinate and distribute health and environmental studies of the use of cleaning options.

Many of the soils removed by cleaners are themselves toxic. Some commercially available solvents like carbon tetrachloride are generally recognised as toxic while other solvents are suspected but not confirmed as toxic. Other cleaners including aqueous and terpene cleaners may also be hazardous, however, only limited testing of these chemicals has been completed.

Nonetheless, the use of some toxic chemicals is permitted in certain cases by governmental authorities with strict workplace controls and effective waste treatment and/or disposal. However, workplace controls and effective waste treatment and/or disposal services are not available in all locations. In these circumstances it may be prudent to select cleaning options that do not depend on workplace controls and waste treatment.

The carcinogenicity, mutagenicity (genotoxicity), acute, chronic, and developmental toxicity, neurotoxicity, and ecotoxicity of the alternative compounds that could be used in cleaning applications must be evaluated prior to their use. Waste solvent or waste water should be properly treated, disposed of or destroyed to prevent creating new environmental problems in solving concerns about stratospheric ozone depletion.

There are governmental and industry projects under way to study the human health and environmental implications of alternatives and substitutes to CFCs. For example, international manufacturers of new chemical alternatives to CFCs have formed three separate research consortia to conduct toxicity studies on partially-halogenated substitute chemicals (HFCs and HCFCs). The consortia, Program for Alternative Fluorocarbon Toxicity Testing (PAFT-1, -2, and -3) are developing toxicity profiles on HCFC and HFC substitutes with broad commercial potential. Acute toxicity tests will be completed for the PAFT 1 & 2 chemicals by September 1989. The final analysis of these test results will be issued in January 1990. Long term testing (2-year bioassays for these same chemicals) has begun or will soon begin with results of these tests available by 1992-3. Acute and chronic tests, including the 2-year bioassay for both methyl chloroform and carbon tetrachloride have been available for some time.

There is also a consortium called Alternative Fluorocarbon Environmental Acceptability Study (AFEAS) to estimate ozone depletion potential (ODP); to calculate global warming potential (GWP); to study mechanisms for atmospheric decomposition; and to evaluate the atmospheric decomposition products and their potential health and environmental effects. Individual manufacturers are also undertaking toxicity studies of other potential chemical alternatives.

CHAPTER 2

ELECTRONICS INDUSTRY APPLICATIONS

2.1 OVERVIEW

Most of the CFC-113 used in the electronics industry is applied to remove flux from electronics assemblies.¹ For purposes of this report, electronics industry applications are defined to include only those products built with printed circuit board assemblies. This definition does not include: (1) CFC-113 use in the memory sector of the electronics industry;² and (2) CFC-113 use in component drying.³

Electronics assemblies are manufactured for a wide array of uses, from toys and home appliances to space and military applications. A partial list of products built with electronics assemblies illustrates the importance and widespread use of these assemblies:

- computers;
- satellites;
- avionic instrumentation;
- military equipment;
- land telecommunications;
- home electronics; and
- radio-TV electronics.

¹ Electronics assemblies include printed circuit board assemblies, hybrid assemblies, and hybrid circuit assemblies. Hybrid assemblies are "micro circuit boards" that combine many types of integrated circuits that are often mounted on a ceramic substrate. These assemblies are mounted on circuit boards and may be as small as a single integrated circuit. A hybrid circuit assembly is a printed circuit board with hybrid circuits mounted on it.

² The cleaning of computer disk drives is considered a precision cleaning application in this report (see Chapter 3).

³ As opposed to printed circuit board assemblies discussed in this chapter. Component drying is discussed briefly in Chapter 6.

The removal of fluxes and flux residues after soldering traditionally has been considered essential for high quality electronic assemblies because this:

- ensures electrical performance;
- ensures adhesion of conformal coating;
- facilitates testing and inspection; and
- prevents corrosion and electro-migration.

Prior to concern about depletion of the ozone layer, CFC-113 solvents mixed with alcohols were the solvents of choice for electronics cleaning applications. These solvents effectively remove flux residues without damaging solvent-sensitive components on electronic assemblies, are nonflammable, and have low toxicity levels.

This chapter provides a summary overview of CFC-113 use in electronics assemblies and examines alternatives for reducing and replacing CFC-113 solvent use. Section 2.2 discusses the major electronic assembly processes, flux types, and defluxing (cleaning) processes in which CFC-113 is used. Section 2.3 describes alternatives for reducing or replacing CFC-113 use, and includes discussions of conservation and recovery practices, alternative solvents, aqueous cleaning, and no-clean alternatives. Section 2.4 evaluates costs of the alternatives. Section 2.5 discusses environmental considerations. Section 2.6 discusses potential global reduction of CFC-113 use in electronics industry applications.

The alternative cleaning solvents, including no-clean alternatives, discussed in this chapter are being used successfully by a wide variety of companies. With the freeze and subsequent reduction of CFC availability in the Montreal Protocol signatory countries, the price of CFC-113 is increasing. For example, price increases of 30 to 35 percent for some users went into effect in early July, 1989. The costs of using alternative solvents will, therefore, become more competitive, especially if the alternatives offer equal

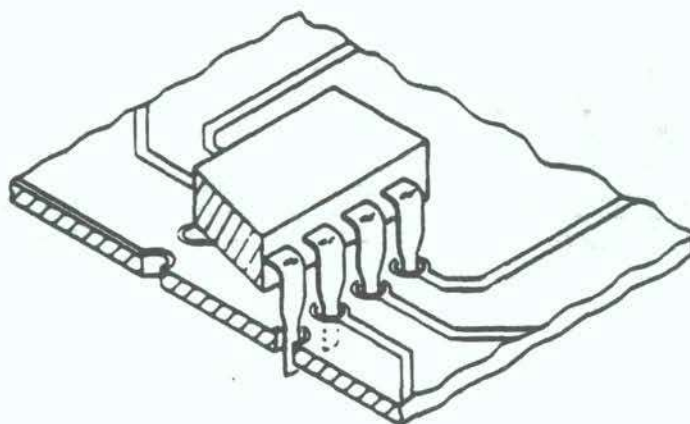
or better cleaning performance and component compatibility. The consensus opinion of the Committee is that use of CFC-113 in electronics industry applications can be eliminated by or before the year 2000.

2.2 CFC-113 USE IN ELECTRONICS ASSEMBLIES

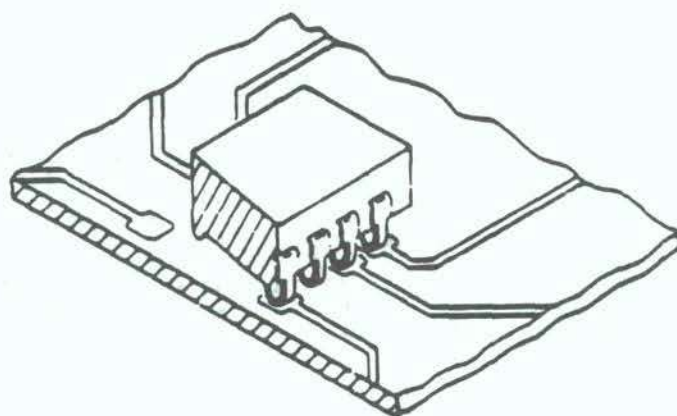
2.2.1 Major Assembly Processes

Electronic components are fluxed and soldered to electronic assemblies and then cleaned to remove flux residue and other contaminants introduced in the production process. The electronic components are attached by through-hole assembly technology or by surface mounted assembly technology. With surface mount technology (SMT), components are attached directly to the board without inserting component leads through holes (see Figure II-1). Without holes, components can be densely packed on the board thereby reducing the size of the board. One major company cites a 40 percent reduction in the size of the printed wiring board over through-hole technology when surface mount technology is used (Mullen 1984).

Boards are soldered in one of two general ways: (1) a molten solder is used to solder and secure the components in the board; or (2) a solid solder (normally in the form of wire solder or small solder spheres in a flux paste matrix) is deposited on the board and later heated. Wave, dip, and drag soldering are examples of the former; hand, condensation reflow, or hot gas soldering are examples of the latter. Wave soldering commonly is used in high volume electronics assembly. Wave-soldered boards are fluxed and passed over a wave or fountain of solder that flows up from the solder bath. This process provides a continuous source of fresh, clean solder. The solder reacts only with the metallic surfaces of the component leads and metallic traces and plated through-holes of the printed circuit boards. Figure II-2 compares the

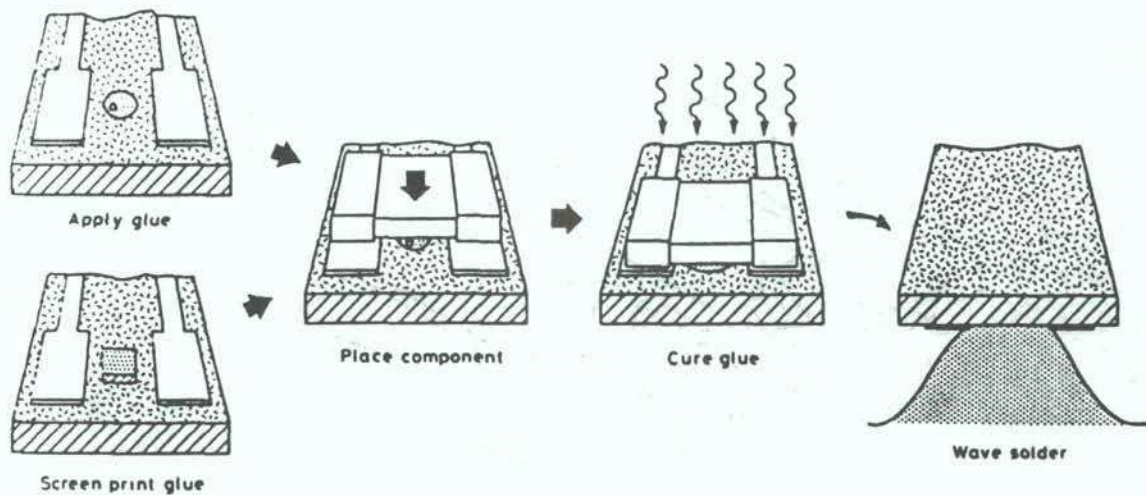


i) DIP Through-hole Component.

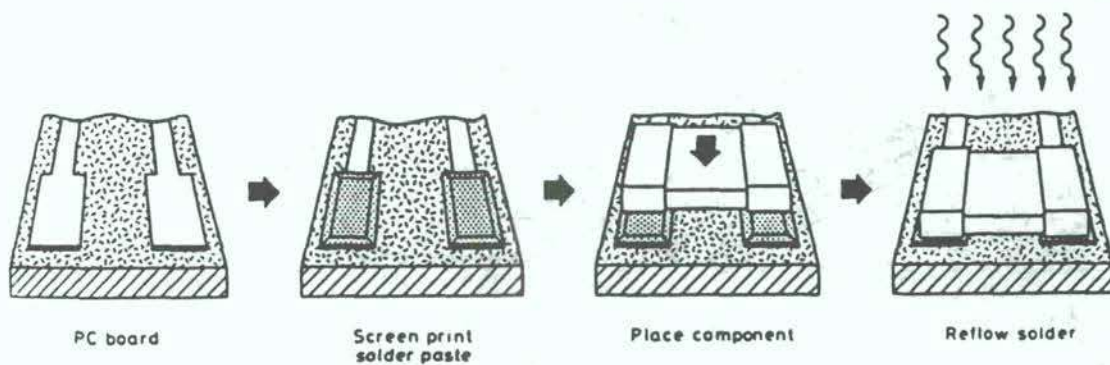


ii) SMC J-lead Surface-Mount Component.

Figure II-1. COMPARISON OF THROUGH-HOLE AND SURFACE MOUNT TECHNOLOGIES.
(Source: Mullen, Jerry. 1984. How to Use Surface Mount Technology. Texas Instruments Publishing Center, Dallas, Texas.)



i) The assembly steps for a wave soldered single-sided surface mount board.



ii) The assembly steps for a reflow soldered single-sided surface mount board.

Figure II-2. COMPARISON OF THE ASSEMBLY STEPS FOR WAVE SOLDERED AND REFLOW SOLDERED SINGLE-SIDED BOARDS. (Source: Lea 1988.)

assembly steps for wave soldered and reflow soldered single-sided boards.

Figure II-3 illustrates surface mounting variations and assembly steps.

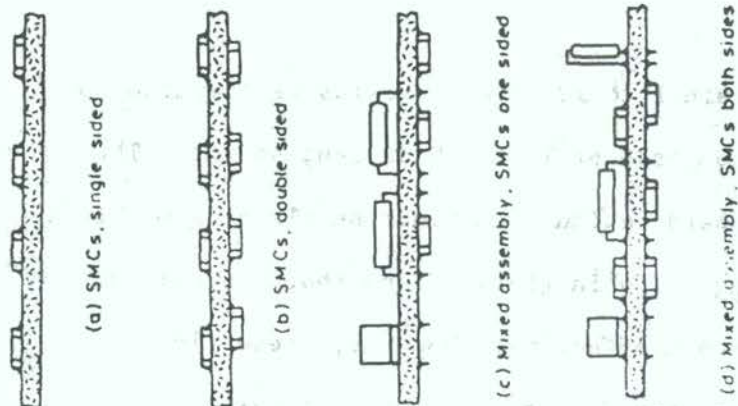
2.2.2 Flux Types

Rosin/resin flux, synthetically activated flux, and water soluble flux (also frequently referred to as organic acid flux) are the major flux types (see Table II-1). In 1986, rosin/resin flux and water soluble flux accounted for the majority of the market (55 percent and 40 percent, respectively) while synthetically-activated flux accounted for five percent (Schneider 1987).

Rosin fluxes meet U.S. military specifications (MIL-F-14256) when properly prepared, have a history of successful use, and do not always need to be removed after fluxing for non-military purposes (Markenstein 1983). Rosin fluxes are a complex mixture of isomeric acids that are classified by the amount of activator present. Activators, generally halides, increase the wetting ability of the solder by removing oxides present on the surfaces to be soldered. While they are the least corrosive and conductive fluxes, rosin fluxes have limited wetting abilities and require a saponifier to be aqueously cleaned (Matisoff 1986).

Low solids rosin fluxes contain 1 to 10 percent solids as compared to standard flux which are usually composed of 15 to 40 percent solids. The small amounts of post-soldering board residue can minimise cleaning problems or eliminate the need for cleaning. Toubin (1989) found that low solids fluxes can be both efficient and cost effective. However, these fluxes contain acids that ionise and therefore do not meet U.S. military specifications as currently written (Schneider 1987).

Synthetic resin, activated fluxes (more active than rosin fluxes, but less active than water soluble fluxes) are removed with solvents (Markenstein 1983). Compared to rosin fluxes, synthetic resin activated fluxes, because of



- i) Surface mounting variations: (a) SMCs single-sided, (b) SMCs double-sided, (c) mixed assembly, SMCs single-sided, (d) mixed assembly, SMCs both sides.

- ii) The steps involved in the assembly of Surface-Mounted Boards, by the different routes.

Figure II-3. SURFACE MOUNTING VARIATIONS AND ASSEMBLY STEPS. (Source: Lea 1988.)

Table II-1. FLUX TYPES

Flux	Cleaning Ability				Terpene With Water
	Military Approved**	Organic Solvent	Water	Water with Saponifier	
R (non-activated rosin)	• ^a	•		•	•
RMA (rosin, mildly-activated)	• ^a	•		•	•
RA (rosin, activated)	• ^{a, b}	•		•	•
RSA (rosin, super-activated)		•		•	•
WS (water soluble)	• ^c		•	•	
SA (synthetic resin, activated)	• ^d	•			•
Low Solids*					

* 1 to 10 percent solids.

** U.S. Military.

^a Per the requirements of MIL-F-14256.

^b Military approved for certain applications MIL-F-14256 Qualified Products List; also approved by U.K. Defence Standards.

^c Approved for use by U.K. Defence Standards.

^d Conditionally approved for use by U.K. Defence Standards.

Source: Adapted from Markenstein, Howard. 1983. "Solder Flux Developments Expand Choices." Electronic Packaging and Production, April 1983, pp. 39-42.

their activity, increase wettability of solder and yet are not as corrosive as water soluble fluxes.

There are a variety of formulations for water soluble fluxes. These fluxes contain large percentages of activators such as organic acids, hydrochlorides, hydrobromides, and amines dissolved in water or alcohol solvents. Water soluble fluxes, in general, allow faster soldering rates with fewer rejected boards and do not require a saponifier when cleaned using aqueous cleaning systems. Because water soluble fluxes as currently formulated are generally more corrosive than other fluxes, thorough cleaning is necessary to prevent subsequent board and component damage.

Although aqueous cleaning is used in numerous electronics industry applications, it is not approved for all applications. Water soluble fluxes do not currently meet U.S. military specifications and thus cannot be used for military applications in the United States; however, they can be used for British military applications (Baxter 1989).⁴ Some specialised boards contain materials such as polyimides and hybrid circuits that are incompatible with aqueous cleaning employing saponifiers. Also, some water soluble fluxes with glycol constituents attack the epoxy substrate of printed circuit boards leaving a porous surface with absorbed flux residues after cleaning. These residues, which are hygroscopic in many cases, can cause surface insulation resistance problems under conditions of elevated temperature and humidity. The majority of water-soluble fluxes do not cause this problem, but it is advisable to conduct tests before adopting these fluxes. Inorganic fluxes are

⁴ Provided that (1) the contractor meets Ministry requirements for equipment, personnel, procedures, etc., and (2) the product meets the ionic contamination specification of <1.5 $\mu\text{gm NaCl}$ equivalent per cm^2 of board area. British Interim Defence Standard, DTD 34/4-Issue 2 (issued in early 1989). All comments on this document have been received but the final Defence Standard has not yet been issued.

too corrosive for electronics soldering in most instances (Ellis 1989). Table II-2 lists common circuit board assembly contaminants.

2.2.3 Defluxing: Post Soldering Cleaning

Flux is removed from electronics assemblies to:

- remove corrosive flux ingredients;
- improve adhesion of conformal coatings;
- enable visual inspection;
- allow automatic testing;
- minimise leakage currents; and
- enhance product appearance.

The degree of post solder-flux cleaning varies widely depending on the final electronics application. For example, printed circuit boards that are used in toys and home appliances are cleaned perfunctorily, if at all (Soble 1979). In contrast, boards that are manufactured for military, space, medical, and other critical applications require high levels of cleanliness. Frequently, boards require cleaning for automatic testing rather than for reliability (IPC 1986). However, in applications where assemblies are exposed to elevated temperature and humidity, flux residues from other than Type R fluxes (see Table II-1) can corrode metallurgical traces on electronics assemblies and component leads. Table II-3 compares the necessary level of cleaning for a variety of electronics applications.

Flux type and product end use determine the appropriate flux cleaning technique. Solder fluxes usually are removed by solvent or aqueous cleaning. In a recent survey of U.S. companies manufacturing through-hole assemblies, approximately 46 percent used CFC-113, 36 percent used aqueous cleaning, 13 percent used other chlorinated solvents, and five percent did not clean (ICF 1987b).

Printed circuit board assemblies can be cleaned by scrubbing the surface clean with a brush in the presence of cleaning media (solvent or aqueous);

Table II-2. TYPICAL CIRCUIT BOARD ASSEMBLY CONTAMINANTS^a

Category 1*	Category 2	Category 3
Resin and Fibreglass Debris from Drilling and/or Punching Operations	Flux Activators Activator Residues Soldering Salts	Flux Resin Flux Rosin Oils
Metal and Plastic Chips from Machining and/or Trimming Operations	Handling Soils (Sodium and Potassium Chlorides)	Grease Waxes
Dust	Residual Plating Salts	Synthetic Polymers
Handling Soils	Neutralisers	Soldering Oils
Lint	Ethanolamines	Metal Oxides
Insulation	Surfactants (ionic)	Handling Soils
Hair/Skin		Polyglycol Degradation Byproduct
		Hand Creams
		Lubricants
		Silicones
		Surfactants (nonionic)

^a Contaminants may exhibit characteristics of more than one category.

*

Category 1 -- Particulate

Category 2 -- Polar, ionic, or inorganic

Category 3 -- Nonpolar, nonionic, or organic

Source: ANSI/IPC-SC-60 1987.

Table 11-3. SPECTRUM OF ELECTRONICS APPLICATIONS AND THE LEVEL OF CLEANING REQUIRED

Application	Classification	Current methods		Contamination control necessary	Possible future methods ^a		
		Cleaning necessary	Means		Cleaning necessary	Means	Contamination control necessary
Satellite Avionic instrumentation Submarine telecomms. Military applications Life-dependent medical	Top professional	Essential	Rosin/RA flux Combination cleaning or Solvent cleaning or Saponification	MIL or DEF ionic contamination	Essential	Rosin RA flux Saponification Water soluble OA Water clean	IEC ionic contam. plus overnight SIR
Automotive (brakes and motor) Land telecommunications	High professional	Essential	All flux types All cleaning methods	MIL or DEF ionic contamination usual, sometimes relaxed values.	Essential	As above	As above
Sophisticated industrial Computers Ordinary telecomms. Other automotive (not radio)	Professional	Yes	As above	As above	Yes	As above	IEC ionic contamination plus SIR for SMD
Industrial Non-life depend. medical Low-cost peripheral eqpt.	Medium professional	Generally	Rosin RSA Solvent cleaning	None	Yes (Probably)	Water soluble OA Water clean (Rosin + saponification)	Probably none, occasional spot checks
Low cost instrumentation Office equipment TV EHT circuits	Bottom professional	Frequently	Rosin RSA Solvent clean	None	No	"No-clean" rosin flux	IEC ionic control before soldering especially for SMD
Non-consumer audio-visual quality consumer goods Automotive entertainment Public address	Semi-professional	Rarely	Rosin RSA	None	No	As above	None
Radio-TV and other entertainment electronics, home electronics, especially mass-produced	Consumer goods	No	Any rosin	None	No	As above	None

^a This is an indicative but not exhaustive list of future methods.

Source: Adapted from Ellis 1988a.

dipping the entire circuit board into a series of baths containing cleaning fluid; using an automatic set of revolving brushes and cleaning fluid; using ultrasonic equipment and degreasing/defluxing fluid (provided the components are adequately resilient); or using some combination of solvent spray, immersion, and vapour cleaning (Matisoff 1986). High pressure sprays with warm solvents also are effective cleaners. Solvent cleaning, aqueous cleaning, or combinations of the two are the most common techniques for removing solder flux.

2.3 ALTERNATIVES FOR REDUCING OR REPLACING CFC-113 USE

2.3.1 Conservation and Recovery Practices

Conservation and recovery practices can significantly reduce CFC-113 consumption in electronic applications (Hoffman 1988, Kerr 1988, Wallace 1988). Improved operator training and practices, installation of engineering controls, and preventive maintenance can conserve CFC-113. Solvent can be recycled as well. Conservation practices are outlined in the "Code of Practice for the Design, Construction and Operation of CFC-113 Degreasers" (Report EUR 9510 EN, 1984)⁵ and in a "Manual of CFC-113 Solvent Management Practices" (FitzGerald 1989a). These methods are summarised below.

2.3.1.1 Improved Operating Practices

Recommended work practices for batch cleaning include the following:

- Prevent drafts around degreaser;
- Ensure that the workload is not too large to displace vapour through the "piston effect";
- Use cleaning machine manufacturer's recommended procedures for start up and shut down;
- Optimize manufacturing schedules to minimize work being processed on an intermittent basis;
- Position work to minimize drag-out

⁵ This Code of Practice is published by the Commission of the European Communities, Directorate -- General Information Market and Innovation, Luxembourg.

- Complete solvent condensation on workpiece before raising work to the freeboard zone dry-off;
- Ensure that speed of work entry and exit does not disrupt vapour blanket.
- Attach spray nozzles below vapour level;
- Place degreaser on level flooring;
- Repair all leaks;
- Pump solvent in and out of machines with minimal air interfaces; and
- Use drain-free work piece carriers.

One company has prepared a solvent conservation guide for its manufacturing locations that use in-line cleaners (Brox 1989a). It includes the following for consideration:

- Operator awareness and training;
- Routine maintenance of equipment and seals and gaskets;
- Reduction of air currents;
- Equipment optimization with assistance by the manufacturer;
- Elimination of boards after soldering and before cleaning; and
- Board orientation to minimize drag-out

There are storage and handling procedures and equipment that also reduce solvent losses. Storing and handling of CFC-113 is an area for attention to minimize releases. Solvent should be sorted and transferred in closed vessels. Bulk quantities of CFC-113 usually are stored in low-pressure tanks fitted with vent dryers containing silica gel. This ensures that on cooling, only dry air fills the vacuum created by contraction; with warming, the solvent/air mixture expands and is expelled, by bypassing the dryer. Typically this occurs at a rate of two percent of the stock per year (Clementson 1988b). CFC-113 loss can be reduced by using completely sealed, high-pressure tanks which prevent solvent evaporative vapour losses, and by storing drums in well-ventilated, dry, cool areas.

Decanting solvent from drums (often via valves that close improperly) into open containers increases the likelihood of spillage and CFC-113 loss through evaporation. The use of barrel pumps and seal bungs to reduce losses when transferring the CFC-113 from storage containers to cleaning machines

should be encouraged. Careless practices of leaving barrel bungs not in place result in significant losses. Operators should be instructed to keep the open-top vapour degreaser covers closed when degreasers are not in use.

Upgraded filters in solvent distillation apparatus will result in fewer filter changes and lower losses of CFC-113. And still bottoms can often be sent for reclamation and recycling.

2.3.1.2 Engineering Controls

Engineering controls can increase CFC-113 conservation and recovery. The European code cited earlier specifies design requirements for CFC-113 batch degreasers including:

- Maximum temperature of 17.8°C for cooling water;
- Vapour level at mid-point of condenser;
- Freeboard height between 50 and 75 percent of degreaser width;⁶
- Low solvent level detector/heat cut-out; and
- Specific parts handling speeds (33-75 cm-min⁻¹ vertical plane; 66-151 cm-min⁻¹ horizontal plane).

To minimise solvent loss, batch degreasers can be retrofitted or redesigned with an increased freeboard height. (The freeboard height is the space between the top of the vapour and the rim of the tank). Other engineering controls include retrofitting automatic hoists and programming them for proper entry and exit speeds. The programming should provide dwell time for evaporation while the assembly is in the vapour zone. Dwell time allows the assembly to dry and the machine to retain more solvent. Vapour losses can be reduced further by adding degreaser lids or covers that automatically close when the assembly is removed. Inefficient hand-operated

⁶ The Committee disagreed with this recommendation and arrived at a consensus opinion that the height should be at least 75 to 100 percent of degreaser width.

vapour degreasers can be replaced with one new in-line conveyerised solvent defluxer.

As with batch cleaners, there are engineering controls that will reduce solvent losses with in-line cleaners. Equipment enhancement methods increased freeboard, increased compressor capacity, and extra cooling coils on inlets and outlets. The manufacturers of the equipment and experts in refrigeration can help in these area. Rationalization of cleaners can be considered in the search for solvent loss reduction. Here one cleaner may be able to handle the output from two or more soldering machines. Large losses occur in cleaners that are under used. CFC-113 evaporates when cleaners sit in an idle mode, and frequent start ups and shut downs compound the problem.

2.3.1.3. Solvent Recovery

Solvent losses can be reduced by solvent recovery systems that conserve solvent and minimise fresh solvent use. Estimates of CFC-113 solvent losses due to work place emissions in a typical plant can be as high as 90 percent.⁷ Figure II-4 shows where the solvent losses occur in a typical plant.

A two-stage carbon adsorption steam-regenerated solvent scrubber collects solvent exhaust fumes. However, the increased costs associated with operation and maintenance of this equipment versus the quantity of solvent recovered should be evaluated against the benefits of converting to other alternative cleaning media. A two-year payback on a sophisticated carbon adsorption system based on 1988 costs of CFC-113 has been determined for one system (FitzGerald 1989b). This system handles the vapours from four in-line cleaners. In this example, the manufacturing location starts with solvent losses in the vicinity of one kilogram per square metre of board produced.

⁷ One company has estimated 90 percent (Ahmadzai 1989a) and another major company has confirmed the 90 percent value (FitzGerald 1989b).

CFC-113 Losses in a " Typical " Plant

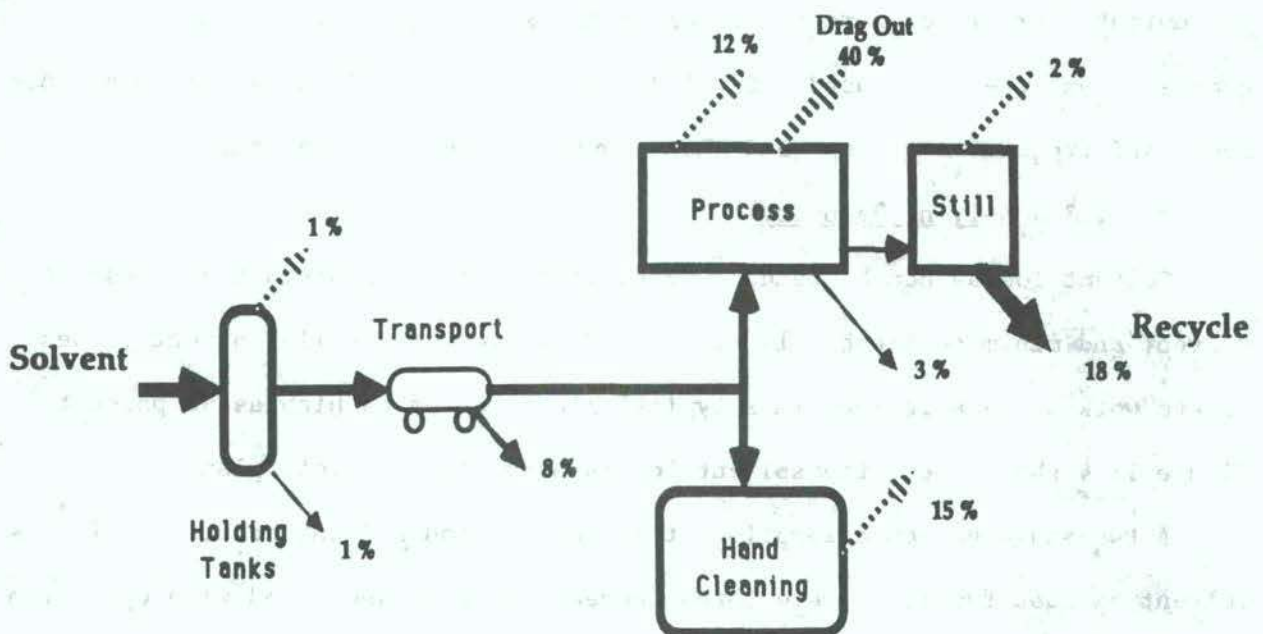


Figure II-4. 82 PERCENT OF SOLVENT IS LOST IN A "TYPICAL PLANT." (Source: Northern Telecom, 1989 CFC Program.)

For manufacturers which have higher losses, often in the area of two kilograms per square metre of board produced, the payback will be better.

Numerous solvent blends are used in the industry; not all are recoverable to the same extent. The choice of solvent blend can be a major factor in reducing consumption. Table II-4 compares CFC-113-based solvent grades for recoverability. The high yield grades in Table II-4 can be distilled either in a functional degreaser or in a small dedicated still. The recovered solvent may be recycled without additional treatment depending on the product being cleaned, the effect of soil removal, and the cleaning solvent used.⁸ Alcohols or other solvents present in azeotropes or blends may require monitoring and replenishment. Still bottoms with concentrated contamination typically contain about 40 percent CFC-113 solvent which can be recovered at a larger central still or by an independent solvent service.

Non-azeotropic blends typically contain 25 to 35 percent isopropanol or ethanol. These solvent blends are non-flammable and effectively remove fluxes. During operation, as CFC-113 is lost to the atmosphere by diffusion, the alcohols concentrate in the remaining solvent. In Europe, detectors are widely used to measure the increase in vapour temperature that results from alcohol enrichment. The heating system automatically shuts down the degreaser or still before cleaning efficiency is lost or before the concentrated alcohol vapour poses a flammability threat. CFC-113/ethanol/methyl acetate ternary azeotrope is the most commonly used flux-removal solvent in parts of Europe, while CFC-113/methanol binary azeotrope is the most commonly used solvent in the rest of Europe and the United States (Clementson 1988a).

⁸ Cleaning active metal surfaces such as aluminum requires periodic replenishment of the specific stabiliser system(s) used.

Table II-4. COMPARISON OF RECOVERABILITY BETWEEN
CFC-113 SOLVENT GRADES

Grade	Major Use	Recoverability In-House (Yield)
Straight CFC-113	Vapour cleaning of plastic/ metals/glass	High
Azeotropes		
CFC-113/alcohols	Flux removal	High
CFC-113/acetone	Vapour cleaning of plastics	High
CFC-113/methylene chloride	Vapour cleaning of metals	High
Non-Azeotropes		
CFC-113/high bp ¹ alcohols	Flux removal	High
CFC-113/low bp alcohols	Flux removal	Low
CFC-113/water emulsions	Precision cleaning and drying	Low
CFC-113/displacement surfactants	Drying	High
CFC-113/Lubricant	Metal working (e.g., riveting)	*

¹ bp = boiling point

* Recovery not practised.

Source: Adapted from Clementson 1988c.

One U.S. company has estimated savings of \$250,000 (U.S.) per year by recycling solvent wastes in house (Wallace 1988).

2.3.2 Alternative Solvents

This section discusses solvents that can replace CFC-113 use in electronics industry applications including 1,1,1-trichloroethane, hydrocarbon/surfactant blends (such as terpenes) other organic and alcohol derivative solvents, and solvent blends. Aqueous cleaning is discussed separately in Section 2.3.3.

2.3.2.1 1,1,1-Trichloroethane

1,1,1-Trichloroethane⁹ is one effective substitute for CFC-113 in electronics industry operations. Although a volatile organic compound, the U.S. EPA has exempted 1,1,1-trichloroethane from classification as a volatile organic compound (VOC) (HSIA 1987). Furthermore, it is nonflammable. It is possible, therefore, that some substitution of 1,1,1-trichloroethane will occur as CFC-113 becomes less available and users face rising prices. However, 1,1,1-trichloroethane has been identified as an ozone depleting substance and may be added to the Montreal Protocol in 1990.

2.3.2.2 Other Chlorinated Solvents

Trichloroethylene, perchloroethylene, and methylene chloride also are effective cleaners. They are also volatile organic compounds. However, each of these solvents is considered carcinogenic. The U.S. EPA has classified trichloroethylene in Category B2 as a "probable human carcinogen," while the International Agency for Research on Cancer (IARC) has classified this solvent in Group 3, a substance not classifiable as to its carcinogenicity in humans (HSIA 1989c). The IARC has classified perchloroethylene in Group 2B as a

⁹ 1,1,1-Trichloroethane is also referred to as methyl chloroform, TCA, and CH_3CCl_3 .

substance considered "possibly carcinogenic to humans" (HSIA 1989a).¹⁰ Finally, the U.S. EPA has classified methylene chloride in Category B2 as a "probable human carcinogen," while the IARC has classified methylene chloride in Group 2B as a substance considered "possibly carcinogenic to humans" (HSIA 1989b). Chlorinated solvents will be selected substitutes for CFC-113 in some cases. For example, in the United States trichloroethane continues to be used even with new regulations that reduce the allowable worker exposure to the chemical.

2.3.2.3 Hydrocarbon/Surfactant-Based Solvents

Hydrocarbon/surfactant blends, such as terpene-based blends, are a viable alternative for cleaning some electronics assemblies (Hayes 1988). Terpenes may also be VOCs. Terpenes generally are isoprene oligomers, but may include derivatives such as alcohols, aldehydes, and esters. According to one manufacturer (Hayes 1988), terpenes display the following characteristics:

- work effectively in close spacing (clean SMDs);
- work at low (room or slightly higher) temperatures;
- are noncorrosive (pass the copper mirror test);
- have low viscosity and are low foaming; and
- remove both polar and non-polar contaminants.

Depending on the use, the concentration of terpene will vary. Equipment specifically designed for terpene cleaning is necessary because of material compatibility, combustibility, and odour concerns associated with terpenes (Attalla 1988). Cleaning machines using terpene solvents must be designed for safe operation because of low closed-cup flash point (47°C) and potential room temperature flammability associated with spray mist (Dickinson, Guth, Wenger 1989). Conventional fire suppression technology is not sufficient if the

¹⁰ A final decision has not been made by the U.S. EPA as to the classification of perchloroethylene.

material is sprayed. In addition, adequate containment of terpene mist and vapours should be provided to control odour and minimise material losses. Figure II-5 shows cleaning equipment features for terpene-based solvents. Another manufacturer (Kenyon 1989) proposes a non-terpene hydrocarbon solvent blended with a surfactant which is used in a similar way. This material has the reported advantage of lower vapour pressure.

Hydrocarbon/surfactant blends clean rosin flux residue from both wave soldered and reflow soldered assemblies. These solvents dissolve and emulsify rosin residues, which are then removed by mechanical action and aqueous rinsing. Underbrush cleaning is used for wave soldered assemblies; spray cleaning is used for reflowed surface mount assemblies, as well as wave-soldered assemblies. Underbrush cleaning has been used successfully in commercial production (Wenger & Munie 1988). Other methods such as centrifugal and agitated immersion cleaning also have been proposed. Underbrush cleaning facilities usually are charged with 95 to 110 litres of a water and hydrocarbon/surfactant blend mixture and heated to 38°C (Wenger and Munie 1988). Hydrocarbon/surfactant blend cleaning of reflowed surface mounted assemblies requires a special cleaning machine.

All board and component materials that have been tested are compatible with hydrocarbon/surfactant blend-based solvents except some silicone polymers and synthetic rubber materials such as polychloroprenes. Table II-5 compares the cleaning performance of hydrocarbon/surfactant blend solvents versus CFC-113 for specific types of flux. Aqueous and terpene cleaner waste may be hazardous. Only limited testing of these chemicals has been completed to date. Waste solvent or waste water should be effectively treated, disposed of or destroyed to prevent creating new environmental problems in solving concerns about stratospheric ozone depletion. More information on health and

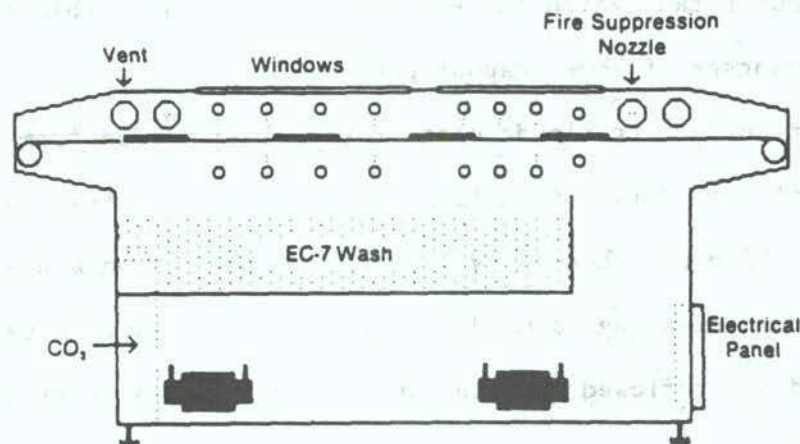


Figure II-5. DIAGRAM OF BOARD CLEANING EQUIPMENT USING TERPENE-BASED SOLVENTS. (Source: Attalla, Gary. 1988 (December). Vitronics/Gram Corporation, New Market, N.H. "Designing Cleaning Equipment for the Terpene Alternative." Surface Mount Technology. pp. 43-45.)

Table II-5. A COMPARISON IN CLEANING PERFORMANCE:
TERPENE-BASED SOLVENTS VERSUS CFC-113*

Board Number	Flux Type	Cleaner	Relative Contamination (%)*
1	RMA	CFC	73
1A	RMA	Terpene	57
2	RA	CFC	98
2A	RA	Terpene	66
3	RA	CFC	88
3A	RA	Terpene	66
4	RA	CFC	98
4A	RA	Terpene	66
5	RA	CFC	100
5A	RA	Terpene	48
6	RMA	CFC	24
6A	RMA	Terpene	9
7	RMA	CFC	98
7A	RMA	Terpene	90
Average CFC	83%		
Average Terpene	58%		
Terpene Improvement over CFC: 30%			

* The 100 percent level is the contamination measured for board 5 when cleaned in a commercial in-line solvent cleaner. All comparisons are for boards cleaned under typical commercial use conditions. Ionic flux residue was determined using an Omega Meter 600-SMD. Data courtesy of Electrovert USA Corp., Arlington, Texas.

Source: Hayes 1988.

safety issues associated with this alternative will become available as development continues. When choosing a product of this nature, care should be taken to ensure not only that the rinse waters meet the local biodegradability requirements but also that the surfactant used in the blend is environmentally acceptable.

2.3.2.4 Other Organic Solvents

Organic solvents such as ketones, aromatics, aliphatics (mineral spirits), and alcohols remove solder fluxes and many polar contaminants. They are in general volatile, flammable, and their emissions are considered VOCs. Generally, they are used only in small quantities in well ventilated areas or under inert atmospheric conditions (IPC 1986). Table II-6 summarises the physical properties of selected organic solvents and alcohols; Table II-7 compares their relative cleaning effectiveness; and Table II-8 compares common laminate types for rigid electronics. Tables II-9a, II-9b, and Table II-10 compares chlorinated solvents and alcohols' compatibility with polymers commonly used in industry.

Three other organic solvents have been proposed as possible CFC-113 substitutes: pentafluoropropanol (5 FP), HCFC-225ca, and HCFC-225cb. Their physical properties are summarised in Table II-11. The long-term toxicity of these possible alternatives still needs to be investigated.

An appropriately designed machine using alcohols¹¹ in accordance with the safety and excise regulations can remove rosin fluxes. Laboratory experiments indicate that isopropanol (IPA) is about twice as effective as CFC-113 azeotrope blends and distills for much longer periods before its effective

¹¹ This usually refers to isopropanol. Chronic toxicity rules out methanol, and ethanol would present legal problems in many countries because distillation may require special permits and additional duties might have to be levied.

Table II-6. PHYSICAL PROPERTIES OF OTHER ORGANIC SOLVENTS

PROPERTIES	Acetone	Methyl Ethyl Ketone	Mineral Spirit	Methyl Isobutyl Ketone	Xylene Mixed Isomers	Toluene	Methanol	Ethanol	Iso-propanol	N-propanol	Iso-butanol	N-butanol	Sec-butanol	Tert-butanol
Boiling Point, °C	56	80	158	115	127-159	110	64	78	82	97	107	117	99	83
Flash Point, °C	-9.4	-5.0	40.6	17.8	26.7	4.4	11	14	12	22	29	36	23	11
Relative Evaporation Rate, $\text{CCl}_4 = 100$	139	97	2.6	47	45	58	58	31.7	28.3	21.7	11.7	8.3	15	-
Liquid Density, 20°C, g/cm^3	0.7899	0.8049	-	0.8008	0.868	0.867	0.792	0.795	0.787	0.815	0.803	0.811	0.808	0.726 ^a
Solubility Parameter (J/cm^3) ^{1/2}	41.84	38.91	31.38	35.14	36.82	27.24	60.66	53.14	48.11	49.79	46.86	48.53	46.44	42.67
Kauri-Butanol Value	-	-	36	-	94	94-105	-	-	-	-	-	-	-	-
Specific Heat, 20°C, $\text{J/gm}^\circ\text{C}$	2.13	2.22	-	2.09	1.67	1.71	2.47	2.55	2.51	2.47 ^b	2.42	2.34	2.26	3.05 ^a
Latent Heat of Vaporisation at Boiling Point $\text{J/g}^\circ\text{C}$	520.5	443.9	-	3,674	341.8	362.7	1,226	879.0	201.1	225.8	147.6	148.1	144.6	140.6
Surface Tension, 20°C, $\text{X}10^{-3} \text{ N/m}$	22.7	24.6	-	22.7	28.9	28.4	22.6	22.8	22.6	22.9	22.0	24.6	22.0	20.7
Viscosity, 20°C, $\text{X}10^{-3} \text{ N.s/m}^2$	0.304 (25°C)	0.404	-	0.542 (25°C)	0.69	0.5866	0.625	1.22	2.40	2.26	2.90	2.95	2.65	2.31 ^c
Solubility, wt. % water in solvent, 20°C (68°F)	-	11.8	-	1.8	0.02	0.04	∞	∞	∞	∞	15.0	20.1	65.1	∞
wt. % solvent in water, 20°C (68°F)	-	26.8	-	2.0	-	0.05	∞	∞	∞	∞	9.0	7.7	15.4	∞

^a 26°C (79°F)^b 25°C (77°F)^c 30°C (86°F)

Source: IPC 1987. Post Solder Solvent Cleaning Handbook.

Table II-7. RELATIVE CLEANING EFFECTIVENESS OF ORGANIC SOLVENTS

Contaminants/Residues	Hydrocarbons and Derivatives			Blends
	Alcohols	Ketones	Aromatics/ Aliphatics	Blend/ Azeotrope
<u>PARTICULATES</u>				
Resin and Fibreglass Debris	M	M	M	M
Metal and Plastic Machining Debris	M	M	M	M
Dust	M	M	M	M
Handling Soils	M	M	M	M
Lint	M	M	M	M
<u>POLAR, IONIC, INORGANICS</u>				
Fingerprint Salts	E	E	I	G
Rosin Activators	E	I	I	G
Activator Residues	E	I	I	G
Cutting Oils	G	G	I	G
Temporary Solder Masks/Solder Stops	G	I	I	G
Soldering Salts	I	I	I	I
Residual Plating Salts	I	I	I	I
Residual Etching Salts	I	I	I	I
<u>NONPOLAR, NONIONIC, ORGANICS</u>				
Resin Fixative Waxes	E	E	G	E
Waxes	I	G	G	G
Soldering Oils	E	E	E	E
Cutting Oils	E	E	E	E
Fingerprint Oils	E	E	E	E
Flux Rosin	E	E	G	E
Markings	I	E	E	G
Hand Cream	G	E	G	E
Silicones	I	I	I	I
Tape Residues	G	E	E	G
Temporary Solder Masks/Solder Stops	I	I	I	G
Organic Solvent Films	E	E	E	G

Legend: E = Effective in dissolving contaminant.
 I = Ineffective in dissolving contaminant.
 G = Grey area (moderately effective).
 M = Mechanical action required.

Source: IPC 1985.

Table II-8. COMMON TYPES OF LAMINATE FOR RIGID
PRINTED CIRCUIT BOARDS

Resin	Reinforcement		Classification
Phenolic	Paper	Sheet	FR-2, X, XP, XX, XXP, XXX, XPC, etc.
	Cotton	Fabric	C, CE, L, LE
	Asbestos	Sheet	A
		Fabric	AA
	Glass	Fibres	G-2
		Cloth	G-3
	Nylon	Fibres	N-1
Amino (Melamine)	-	-	ES-1, ES-3
	Glass	Cloth	G-5, G-9
Epoxy	Paper	Sheet	FR-3
	Glass	Cloth	G-10, G-11, FR-4,* FR-5
Alkyd (Polyester)	Glass	Mat	GPO-1, GPO-2
Silicone	Glass	Cloth	G-7
Polyimide	Glass Cloth	Polyaramide cloth	

* Most common. MIL-P-13949.

Source: Adapted from Lea 1988.

Table 11-9a. RESISTANCE OF THERMO-SETTING RESINS TO SOME CLEANING SOLVENTS

Thermo Setting Resins ^b	Resistance to cleaning solvents ^a											
	CFC-113			Methyl Chloroform*			Trichloroethylene			Alcohols		
	20°C	Boiling ca 48°C	Stress Corrosion	20°C	Boiling ca 80°C	Stress Corrosion	20°C	Boiling ca 90°C	Stress Corrosion	20°C	60°C	Corros
Diallylphthalate (PDAP)	0	0		0	0		0	0		0	0	
Melamine formaldehyde (MF)	0	0		0	0		0	0		0	0	
Urea formaldehyde (UF)	0	0		0	0		0	0		0	0	
Unsaturated polyester (UP)	0	0		0	0		0	0		0	0	
Epoxy Plastics (EP)	0	0		0	0		0	0		0	0	
Phenolic resins, phenol formaldehyde (PF)	0	0		0	0		0	0		0	0	

^a Key: 0 = No effect
 1 = Little or no effect
 2 = Some effect
 3 = Extensive effect, not recommended
 x = Stress corrosion

^b Including material with and without composites with glass fibres, asbestos, paper, minerals and artificial fibres.

Source: Ahmadzai 1989d.

Table II-9b. RESISTANCE OF ELASTOMERS TO SOME CLEANING SOLVENTS

Elastomers	Resistance to cleaning solvents ^a							
	CFC-113		Methyl Chloroform		Trichloro-ethylene		Alcohols	
	20°C	60°C	20°C	60°C	20°C	60°C	20°C	60°C
Natural Rubber (NR)	1-2	1-2	3	3	3	3	0	0-1
Styrene rubbers, butadiene/styrene (SDR)	0-1	1	3	3	3	3	0	0-1
Isobutylene/isoprene	0	0-1	1-2	2	2	3	0	0-1
Ethylene-propene rubbers (EPR)	1	1	2	2-3	2-3	3	0	0-1
Chlorinated, sulphonated polyethylene (OSM)	0	0	1-2	2	2	3		
Urethane rubbers (UR)	0	0-1	2	2-3	2	3	0	0-1
Polysulphide rubbers (T)	0	0	0-1	0-1	1	2	0	0
Neoprene rubbers, chloroprene (CR)	0	0	1-2	2-3	2-3	2-3	0-1	1
Silicon rubbers, polysiloxane (SiR)	1-2	1-2	1-2	1-2	2	1-2	0-1	1
Hexafluoropropene/vinylidene-fluoride (FPM)	0	0	0	0	0	0	0	0
Nitrile rubbers, butadiene/acrylonitrile (NBR)	0	0	1	1-2	1	1-2	0-1	1

^a For gradation of compatibility, see Key:

Key:

- 0 = No effect
- 1 = Little or no effect
- 2 = Some effect
- 3 = Extensive effect, not recommended
- x = Stress corrosion

Source: Ahmadzai 1989d.

Table II-10. THE RESISTANCE OF THERMO-PLASTICS TO SOME CLEANING SOLVENTS

Thermoplastics	Resistance to cleaning solvents ^a													
	Perchloro-ethylene with 15% pentanol		CFC-113			Methyl Chloroform ^a			Trichloroethylene			Alcohols		
	Stress Fluid 25°C	Corrosion Vapour in Air 40°C	20°C	Boiling ca 48°C	Stress Corrosion	20°C	Boiling ca 80°C	Stress Corrosion	20°C	Boiling ca 90°C	Stress Corrosion	20°C	60°C	Corrosion
Acrylonitrile butadiene styrene (ABS)			0	0		2-3	3	x	3	3	x	0	0-1	(x) higher temp.
Cellulose acetate (CA)			0	0		0	1	(x) higher temp.	1	2	x	0-1	1	(x) higher temp.
Cellulose acetate butyrate (CAB)			0	0		0-1	1-2	x	1-2	2-3	x	0-1	1-2	x
Cellulose acetate propionate (CAP)			0	0		0-1	1-2	x	1-2	2	x	0-2	1-2	x
Polyethylene (PE)			0	0	x ^b	0	1-2	x ^b	1	1-2	x ^b	0	0	x ^b
Ionomeric plastics			0	0		0	2-3	x	0-1	1-3	x	0	0-1	(x) higher temp.
Chlorinated polyether			0	0-1		0	0		0	0		0	0	
Polyamide(PA) ^c 6-6 6-6 w/33% glassfibre 6-10 11 o 12 Trogamide T	x		0 0 0 0 0	0 0 0 0 0	d (x) with ethanol	0 0 0 0-1 0	0 0 0 1-2 0	d x	0 0 0 0-1 0	0 0 0 1-2 0	d x	0 0 0 0 1	0 0 0 0 2	d x higher temp.
Polycarbonate (PC) PC + 30% glassfibre	x	x No cracks	0	0	(x) boiling	2	3	x	2	3	x	0	0	
Linear Polyesters (PETP) ^e			0	0		0	0-1		0	0-1		0	0	
Polymethyl methacrylate (PMMA)			0	0	(x)	1	2	x	3	3	x	1-3 ^g	3	x
Polyimide			0	0		0	0		0	0		0	0	
Polysulphone			0	0	f	0-1	2	x	3	3	x	0	0-1	f
Polypropene (PP) ^h			0	0		0	1-2	(x) higher temp.	1	1-2	(x) higher temp.	0	0	
Polyphenylene oxide modified with styrene butadiene (PPO/SB)			0-1	1	x	3	3	x	3	3	x	0-1	1	x
Polystyrene (PS)			0	0-1	x	3	3	x	3	3	x	0	0	x
Polystyrene butadiene (SB)			0	0-1	(x) higher temp.	3	3	x	0	0	(x) higher temp.			
Polystyrene acrylonitrile (SAN)			0	0		3	3	x	3	3	x	0	0-1	(x) higher temp.
Polybutylene Terephthalate PBTP + 30% glassfibre		No cracks	0											
ASA, SAN med with acrylate rubber			0	0		3	3	x	3	3	x	0	0-1	(x) higher temp.
Fluoroplastics (PTFE, FEP, CTFE, PVDF, PVF)			0	0		0	0		0	0		0	0	
Polyvinyl chloride (hard, soft, modified) (PVC)			0	0		0	2	x higher temp.	1	2	x	0	0-1	

Table II-10 (Continued)

^a Key: 0 - No effect
 1 - Little or no effect
 2 - Some effect
 3 - Extensive effect, not recommended
 x - Stress corrosion

^b Danger for stress corrosion where smelting index >0.6, especially at temp 750°C.

^c High crystalline polyamides swell less in solvents than low crystalline polyamides.

^d Polyamides conditioned in ordinary room atmosphere (20°C, 50-60% relative humidity) do not have stress corrosion. Dried amides with low water absorption (<0.3 wt.%) can stress corrode in solvent.

^e Components of linear polyesters with glass fibre contents that have been worked (e.g., lathed) subsequent to form injection have a reduced chemical resistance, in general (capillary effects due to glass fibres).

^f Higher mechanical loading at room temperature can induce stress corrosion.

^g Resistant to alcohols <30 vol. % and even more resistant towards 150 propanol then ethanol >30 vol. %.

^h Even modified with ethane - polypropene rubber.

ⁱ PTFE - polytetrafluoroethylene
 FEP - fluorinated polyethylene-propylene
 CTFE - polymonochloro-trifluoroethylene
 PVF - polyvinyl fluoride
 PVDF - polyvinylidene fluoride

^j Cleansing solutions effect on softened PVC varies according to the type and quantity of softener used. In general, increased use of softeners reduces resistance to solvents.

Source: Ahmadzai 1989d.

Table II-11. PHYSICAL PROPERTIES OF PENTAFLUOROPROPANOL (5FP),
HCFC-225ca, AND HCFC-225cb

Physical Properties	Potential CFC-113 Substitutes			
	5FP ^a	HCFC-225ca ^b	HCFC-225cb ^b	CFC-113 ^b
Chemical Formula	CF ₃ CF ₂ CH ₂ OH	CF ₃ CF ₂ CHCl ₂	CClF ₂ CF ₂ CHClF	CCl ₂ FCClF ₂
Molecular Weight	150	202.94	202.94	187.38
Boiling Point (°C)	80.7	51.1	56.1	47.6
Density (g/cm ³) @ 25°C	1.51	1.55	1.56	1.56
Surface Tension (X10 ⁻³ N/M)	19	16.3	17.7	17.3
Kauri-Butanol Value	36	34	30	31
Flash Point (°C)	None	None	None	None

Sources: ^a Daikin 1989.

^b Asahi Glass 1989.

quality drops. Ellis (1989) reported that isopropanol effectively cleaned military RA fluxes to present MIL-P-28809 cleanliness requirements. Machines designed for the use of flammable solvents are commercially available. The equipment range covers:

- Cold solvent cleaners with brush option;
- Hot solvent cleaners with ultrasonic option;
- Vapour phase batch cleaners with ultrasonic option; and
- In-line continuous cleaners, with spray and ultrasonic option.

Ancillary equipment for solvent recycling also is available.

A large European electronics manufacturer currently is operating a modified conveyerised in-line alcohol cleaner. The machine, depicted in Figure II-6, cleans both through-hole and surface-mounted assemblies. The equipment has an on-line still for recycling, and the system is explosion-proof. Sensors monitor the solvent vapour level and activate a warning alarm at 20 percent of the lower explosion level (LEL). A machine shut-down procedure is automatically activated at 40 percent of the LEL. Additional precautions include water-based fire protection equipment and nitrogen gas purging of the ultrasonic transducer (40 kHz) chambers. The current spray system is designed to operate at a pressure of 0.8 bar. However, work is underway to increase the spray pressure to 35 bar (Hoffman 1989a). The temperature of the cleaning media is approximately 70-80°C and no problems have been experienced with acidity since start-up in January 1988. The installation is authorised for a maximum emission of three kg isopropanol per 24 hours. Isopropanol consumption is approximately 16 kg/10 days (20 l/10 days). For a production rate of 100,000 PCBs per year, consumption of isopropanol reduced to one-half that of CFC-113, and costs of solvents reduced by ten percent. The cost of disposal, however, has not been accounted for.

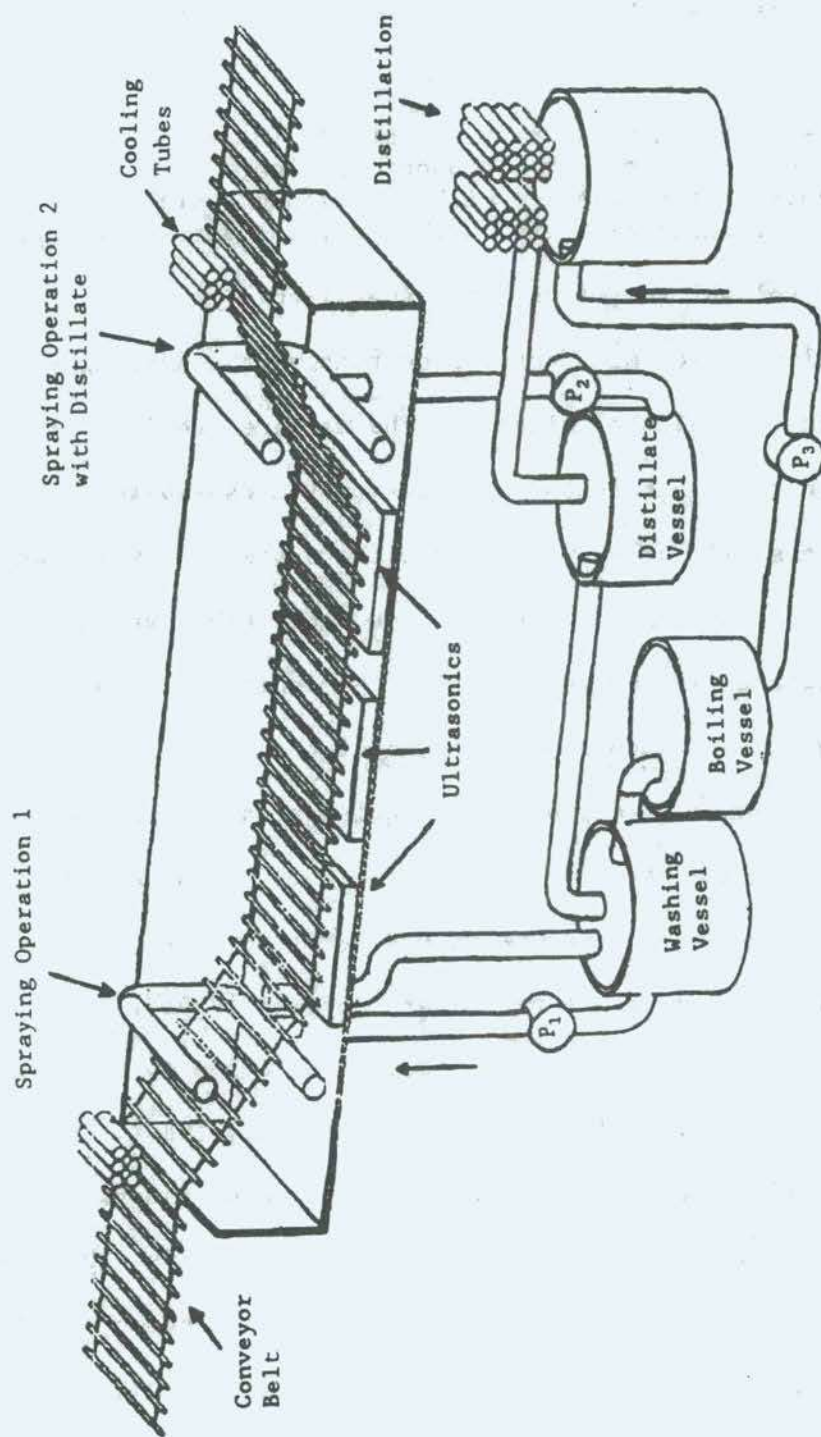


Figure II-6. DIAGRAM OF A MODIFIED CONVEYORIZED IN-LINE CLEANING MACHINE USING ALCOHOL SOLVENT. (Source: Hoffmann, M. 1989b).

A conveyorised in-line alcohol machine is currently available. The four module system operates at room temperature and consists of:

- a brush module, with an oscillating brushing option;
- a spray module (6 bar);
- a drying module (50-60°C); and
- an azeotrope regeneration module (50 l/h).

The machine uses an n-propanol:28.2 percent water azeotrope and is approved by the Federal Republic of Germany's TUV Authority. Underbrush cleaning and spray modules operate at 25°C. Drying is achieved via forced hot air blowing at a rate of 600 m³/h. The machine uses a frame conveyor system operating at a speed of 1-1.4 m/min. During full production, an azeotrope consumption of 0.6 l/h (approximately 0.85 kg n-propanol/24 h) is claimed.

2.3.2.5 Solvent Blends

Pure CFC-113 and chlorocarbon solvents, due to their nonpolarity, do not effectively remove ionic contaminants from boards. However, these solvents blended with alcohols such as ethanol and methanol effectively remove fluxes if used correctly. The low alcohol level in CFC-113/alcohol blends (less than 7 percent) in azeotropic mixtures prevents excessive toxic fumes from escaping the vapour degreaser. A number of companies have developed and are using a variety of solvent blends with significantly reduced amounts of CFC-113. These alternative blends can be used in the short-run. The consensus opinion of the Committee, however, was that these blends may not be viable long-term substitutes for CFC-113 because of the ozone depletion potential of the primary solvents in these blends.

One promising blend that does not depend on either CFC-113 or 1,1,1-trichloroethane has been introduced recently. This blend is an azeotrope-like mixture of HCFC-141b, HCFC-123, and methanol, and it is suitable for use in vapour degreasing operations to clean printed circuit board assemblies. The

blend has a low ODP (0.08), polar solvency for removing ionic soils, as well as low surface tension and viscosity for effective cleaning of surface-mounted components (Allied Signal and DuPont Electronics 1989).

2.3.3 Solvent Cleaning Processes and Equipment

Vapour degreasing is the most common solvent defluxing method. Vapour degreasers are either batch machines (see Figure II-7) or conveyorised in-line machines. Although vapour degreasing operations vary, most vapour degreasers are operated in several process steps. The board first is immersed in a boiling solvent sump (if the degreaser contains a secondary, external still for continually removing contaminants from the boiling sump; if there is not an external still, the assembly to be cleaned should not be placed in the boiling sump) where high temperatures and mechanical solvent mixing expedite cleaning. Once the board warms to the sump temperature, it is moved to just above the boiling sump, the liquid solvent is vaporised, and then rinsed with or immersed in a cooler solvent from the distillation sump. The board is allowed to cool, and then is placed into a pure solvent vapour zone above the distillation solvent sump. The vapours condense on the board and rinse off any remaining contaminants. Finally, the board is placed just below the freeboard zone, where the condensed solvent drips back into the distillation sump. The entire cycle typically takes 4 minutes and 30 seconds: 2 minutes in the boiling sump to dissolve the flux; 1 minute in the cool solvent distillate; 1 minute in the vapour phase; and 30 seconds in the freeboard zone (Ellis 1986). Ultrasonic agitators also can be used in the cleaning process. Ultrasonic cleaning is usually done judiciously because some ultrasonic frequencies may damage board components.

Solvents can be applied manually with a brush for small jobs; for larger jobs the circuit board typically is immersed in consecutively cleaner solvent

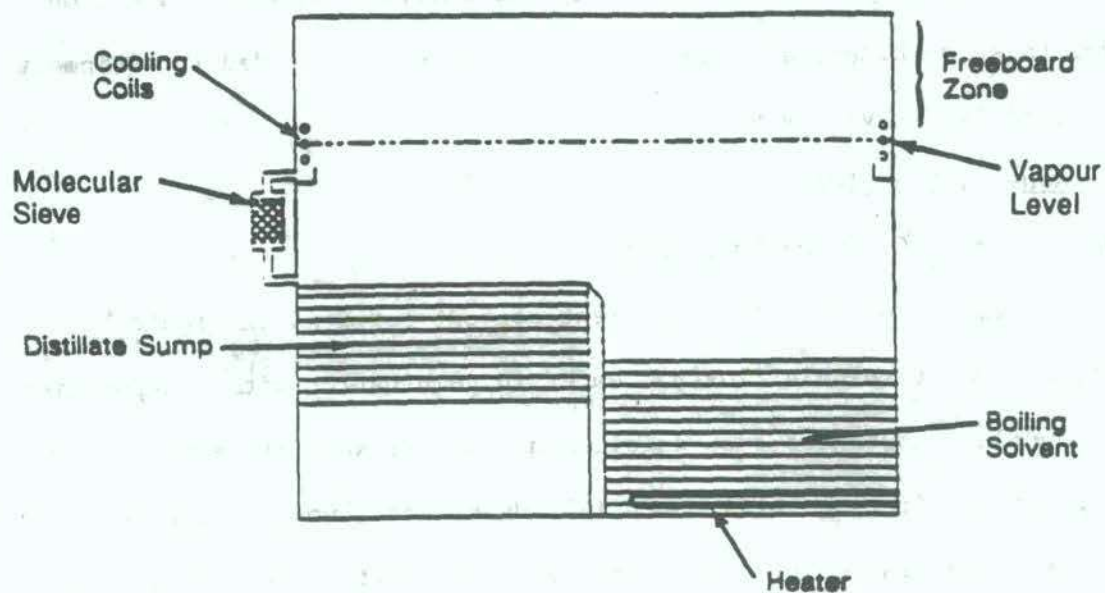


Figure II-7. DIAGRAM OF A VAPOUR DEGREASER. (Source: Ellis B.N. 1986. Cleaning and Contamination of Electronics Components and Assemblies. Electrochemical Publications. Ayr, Scotland.)

baths. Because solvent vapour rises in the open baths, expensive volatile solvents such as CFC-113 are not recommended. Alcohols can be used, but they present a fire hazard and careful design is necessary to minimise this risk. A closed system with a rotating solvent-coated brush reduces solvent loss but only cleans one side of the board. Alcohols and chlorinated solvents are most suitable for these machines, and cooling coils should be included in equipment openings to minimise solvent vapour emissions.

2.3.4 Aqueous Cleaning

2.3.4.1 Aqueous Cleaning Processes

As noted earlier, water is an excellent solvent for removing ionic contaminants and water soluble fluxes. Water in combination with a saponifier can remove nonpolar substances such as oil and rosin fluxes. Aqueous saponifier cleaning offers several potential advantages: no distillation equipment is required and cost savings can be realised if extensive pretreatment of the water (e.g., distillation, reverse osmosis, heating, etc.) is not required. However, the potential need for waste treatment and disposal may impact these advantages.

Because surface mounted components are placed closer to the board than traditional through-hole components, there has been concern that aqueous cleaning cannot adequately clean in the small gap underneath surface mounted components. It has been demonstrated however, that while difficult, it is possible to clean surface mount assemblies with aqueous cleaning (Danford and Gallagher 1987, Dickinson, Guth, Wenger 1989, Ellis 1987, and Wargotz, Guth, Stroud 1987).

Aqueous saponifier cleaning generally consists of a wash, rinse, and dry stage. In the wash stage, contaminants such as oils, grease, and rosin react with alkaline saponifiers (most commonly alkanolamines) to form a water

soluble soap via a saponification process. The wash solution pH should be between 10.5 and 11.8. A higher pH can damage plastic board materials such as laminates and coatings, or remove the marking inks on electronic components. The saponifier is less effective if the pH is lower than 10.5 (IPC 1986). Following exposure to the saponifier, the boards are rinsed. Because up to 10 percent of rosin flux may be nonsaponifiable, aqueous cleaning is most effective when combined with the high pressure and/or high volume sprays normally used in batch cleaners and in-line conveyors. Other important parameters include angle of impingency of the sprays and temperature of the cleaning solution. Finally, the cleaned boards are dried.

Water, water and alcohol mixtures, neutralisers, saponifiers, and detergents are used in aqueous cleaning. Pure water (deionised and filtered or reverse-osmosis water) removes water-soluble flux residues, and is frequently used as a final rinse. Tap water is effective for pre-washes, but is rarely satisfactory for final rinses of surface mounted assemblies, especially if the water contains high concentrations of dissolved salts and minerals. Pure water plus alcohol (five to eight percent isopropanol at 50°C) is an effective rinse. The alcohol reduces the surface tension, allowing the rinse water to penetrate underneath the components. The alcohol also speeds drying, dissolves organic residues (oils and fluxes), and suppresses wash-water foam in some machines. Chelating neutralisers, used with water-soluble fluxes, help dissolve organic and inorganic metal compounds and neutralise any residue acidity. In batch cleaners, neutralisers are frequently used in a hold bath. (The hold bath receives the circuits from the soldering operation.) Note that some of the chelating neutralisers may contain salts of ethylenediaminetetra-acetic acid (EDTA). Others are based on weak alkaline solutions of ammonium salts. In both cases, by definition, a chelating bath

may develop high heavy metal concentrations and the bath itself must not be disposed of into a public sewer.

If the level of ions, organics, or metal contamination is too high for electronics cleaning, water can be treated using deionisation, reverse osmosis, or both. One alternative is to filter to remove organics, use carbon to adsorb organic residues, and deionise to remove cations and anions. This option has a low capital cost and can produce satisfactory results (conductivity lower than two S- μ cm)¹² but may have a high operating cost, depending on the volume (Ellis 1986). In reverse osmosis, water is purified through high pressure filtration by passing it through a semipermeable membrane. Although the costs for large installations of reverse osmosis and deionisation are comparable (IPC 1986), reverse osmosis removes both ionic and nonionic contaminants. For small installations, only deionisation is viable.

There are no set standards for the maximum conductivity of the final rinse water; the allowable level is dependent upon a variety of factors, including the air drying process used, the tap water quality, and the final board application. For example, if the air knife effectively removes liquid water from the board, it is possible to use tap water with low concentrations of dissolved salts and minerals because the air knife will blow the residual water and dissolved contaminants from the board (IPC 1986). Generally water with a conductivity less than one μ S-cm is used for high reliability products;

¹² This measurement represents microsiemens per cube of one centimetre edge. The siemens is the unit of measure used to describe conductance (the reciprocal of resistance).

water with conductivity from one to ten $\mu\text{S-cm}$ is used for most other applications.¹³

2.3.4.2 Aqueous Cleaning Equipment

Mechanised brush cleaning machines, "dishwasher" batch machines, high throughput batch machines, and conveyorised in-line machines can be used to remove water soluble and rosin fluxes.

Mechanised brush cleaning equipment commonly is used in the communications and consumer product industries to remove mildly activated rosin fluxes from the underside of boards. It is used on boards that are incompatible with aqueous immersion techniques due to unsealed components. Frequently, boards require cleaning for automatic testing rather than for reliability (IPC 1986).

"Dishwasher" batch machines are similar in appearance to household dishwashers (see Figure II-8). These machines have several cleaning stages. The boards first are loaded into the machine in racks, and the machine is filled with water to a designated level. The water then is heated and sprayed onto the boards, which are rinsed at least three times and dried using an air fan and heater. A typical dishwasher batch machine has a throughput of ten m^2 per eight hour shift. This throughput rate can be a disadvantage because most soldering machines have at least twice this throughput (Ellis 1986). These machines are fairly effective but tend to operate on long cycles. High throughput batch machines are two to three times more expensive than conventional batch machines and require more floor space. However, they offer several benefits. Compared to dishwasher batch machines, high throughput

¹³ Water with conductivity from 10 to 100 $\mu\text{S-cm}$ can be used for rinsing, although not for high reliability products. Water with conductivity from 100 to 1,000 $\mu\text{S-cm}$ can be used for industrial electronics applications if used with an air knife.

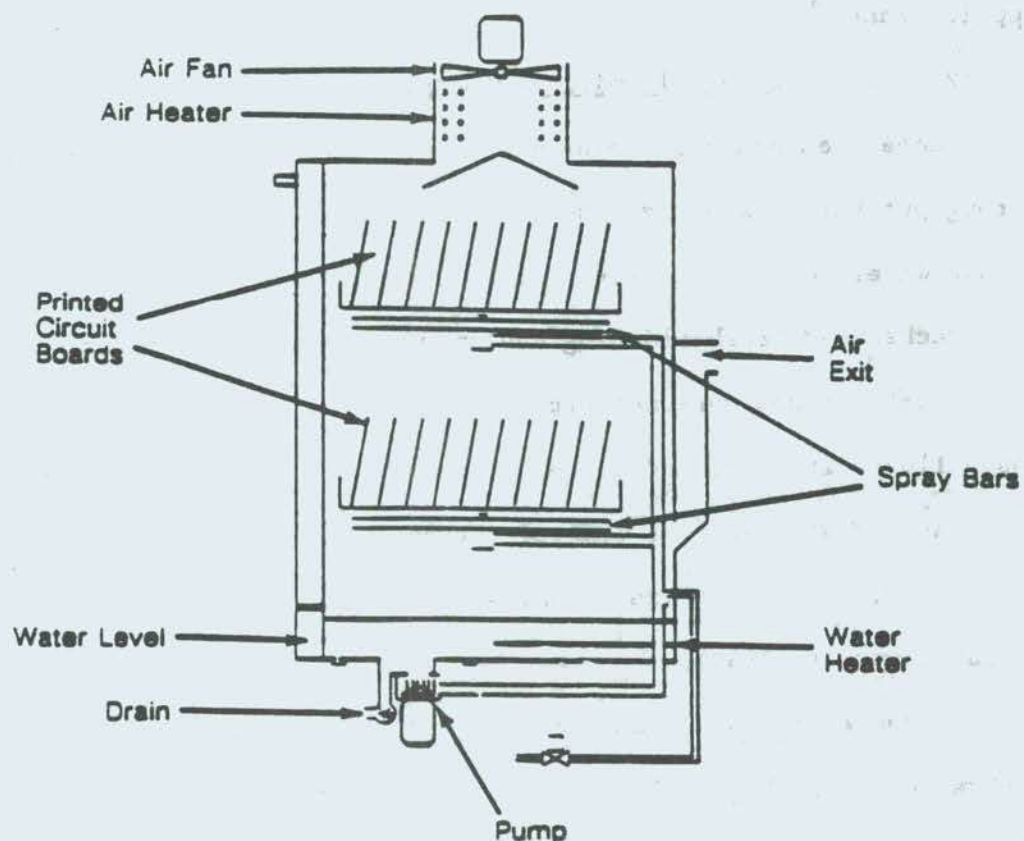


Figure II-8. DIAGRAM OF AN AQUEOUS CLEANING BATCH "DISHWASHER." (Source: Ellis B.N. 1986. Cleaning and Contamination of Electronics Components and Assemblies. Electrochemical Publications. Ayr, Scotland.)

batch machines clean three to eight times more thoroughly, consume only 25 percent as much water, and have electricity costs 20 percent lower than dishwasher batch machines (Ellis 1986).

High throughput batch machines differ from conventional dishwasher batch machines in that the wash water remains in the tank and is not drained each cycle. During the two to three minute wash cycle, 50°C water is pumped to high pressure jet sprays that wash the printed circuit board assemblies. The machine is stopped for a 15 to 30-second period to drain the water. The boards then are rinsed with water for 20 to 40 seconds using fan sprays. Excess tank water is drained, and the boards are dried with air knives and a heater.

In-line conveyorised machines, often tailored for specific applications, typically are more expensive than batch machines. In-line machine cleaning processes include pre-wash, recirculating detergent wash, recirculating rinse, final rinse, air knife, and a hot air dryer (IPC 1986). If a rosin flux is used, a hot detergent solution first saponifies the rosin flux in a recirculating detergent wash. New saponifier is added as needed (when the saponifier becomes ineffective or contaminated). One machine may have several recirculating stages. Typically, water is pumped from the sump to nozzles which spray the water onto the board. A final rinse cleans off any remaining contaminated water. Air knives help maintain a high level of board cleanliness, as they blow moisture and contaminants off the board. A schematic example is illustrated in Figure II-9.

2.3.4.3 Surface Mounted Assemblies

A major concern of the electronics industry has been the applicability of aqueous cleaning for cleaning surface mounted assemblies. Because surface mounted components are placed closer to the board than traditional through-

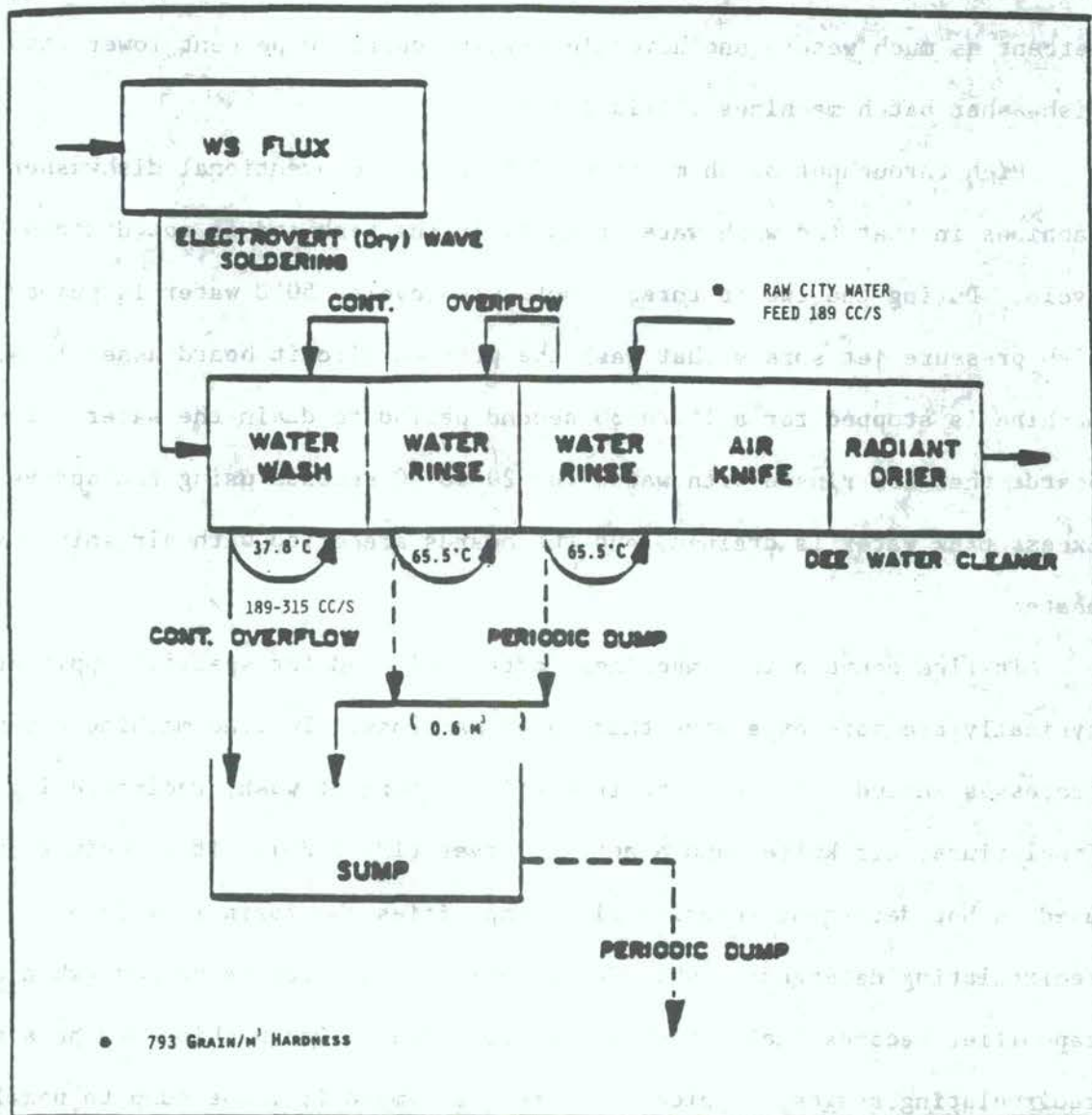


Figure II-9. SCHEMATIC OF A POSSIBLE AQUEOUS IN-LINE CONVEYORIZED MACHINE. (Source: Bernstein, Stan and Green, James. 1981. "Mass Soldering and Aqueous Cleaning Processes Operated in Compliance with Water Pollution Regulations." Electronic Packaging and Production.)

hole components, there has been concern that aqueous cleaning cannot adequately clean in the small gap underneath surface mounted components. It has been demonstrated however, that while difficult, it is possible to clean surface mount assemblies with aqueous cleaning (Danford and Gallagher 1987, Dickinson, Guth, Wenger 1989, Ellis 1987, and Wargotz, Guth, Stroud 1987). To clean surface mounted assemblies the cleaning solution not only must penetrate underneath the board components, it also must circulate energetically and then be removed. Thus, the cleaning process is dependent on a number of physical factors including (1) surface tension of the cleaning solution (high surface tension ensures capillary penetration, lower surface tension ensures circulation); (2) solution viscosity (low viscosity ensures circulation); (3) mechanical energy (high mechanical energy ensures circulation and scrubbing action); (4) temperature (high temperature ensures minimum viscosity and a molecular scrubbing action) which increases the chemical reactivity of the cleaning solution; and finally (5) chemical energy (high chemical energy aids cleaning).

Aqueous cleaning of surface mounted assemblies is feasible when the equipment is designed with these assemblies in mind. Machines that impart high mechanical energy to the solution can clean satisfactorily under surface mounted assemblies. The mechanical energy is provided by high pressure, medium, or high volume jets. Solid jets with an angle of incidence between 10° and 30° wash satisfactorily. Curtain sprays at a similar angle are better for rinsing. An oscillating system, either linear or an arc, gives complete coverage without shadowing (Ellis 1989).

2.3.5 Other Cleaning Alternatives

2.3.5.1 Combination Cleaning

A combination of cleaners can be used if no single solvent removes all contaminants from the electronics assembly. Many contaminants which are solvent-soluble are not water-soluble, and vice versa. Rather than considering solvent and aqueous cleaning as mutually exclusive processes, they can be used in tandem to achieve a higher level of cleanliness than is possible by using one method only. In a combination cleaning process, vapour defluxing solvents are used to penetrate underneath components and remove primarily organic contaminants resulting from the soldering process and handling operations. The solvent cleaning process is followed by aqueous in-line, conveyorised cleaning of the dried electronics assemblies using a water soluble saponifier system. After exposure to the heated (typically 60 to 70°C) water-saponifier solution, the assemblies are rinsed with water (distilled, deionised, or tap water) to remove saponified contaminants and residual saponifier. Finally the electronic assemblies are dried by heated, forced air drying. The aqueous cleaning process can remove rosin flux residues and many ionic contaminants which are not effectively removed by CFCs or other organic solvents.

Combination cleaning has been shown to be extremely effective and consistent in cleaning multiple configuration military electronic hardware designs to the requirements of MIL-P-28809 since 1975 (Felty 1986, 1988). Research has shown that combination cleaning can significantly increase the level of cleanliness (Bruensback 1987).

2.3.5.2 Ice Particle Cleaning

Recently two companies jointly announced the introduction of a new technology that can be used to clean printed circuit boards. The machine is

called an "ice cleaning apparatus" and it does not require CFC-113 or 1,1,1-trichloroethane for operation. The cleaning process uses a spray of ice particles that can range from 0.1 to 300 microns in diameter. The hardness and size of the particles as well as the pressure and angle of the spray can be controlled as needed (Nikkei Sangyo Shinbun 1989, Denpa Shinbun 1989).

2.3.6 No-Clean Alternatives

2.3.6.1 Low Solids Fluxes/"No Clean" Assembly

By carefully evaluating and selecting components and assembly processes, benign low solids fluxes can be used to eliminate cleaning in some instances. Traditionally, the electronics industry has used, and is still using, rosin fluxes containing between 15 and 35 percent solids content for wave soldering electronics assemblies (through-hole and single-sided printed circuit boards). In the early 1980s, a number of German manufacturers concerned about both economics and high production volumes, wanted to (1) carry out "bed of nails" testing on printed circuit board assemblies immediately after wave soldering, without the problems created by the presence of rosin residues; and (2) eliminate defluxing. Since then numerous low solids fluxes containing one to ten percent rosin (or resin, or both) have been formulated and tested. Table II-12 summarises test results of some commercial low solids fluxes.

Recently, low solids fluxes have been applied successfully at a number of assembly plants with wave or drag soldering technology (Svensson 1989a). The application of low solids fluxes has eliminated the need for cleaning. Even with reflow soldering based on low solid pastes, formation of solder balls can be avoided provided that all stages (from solder paste screening to reflowing) are closely monitored (Svensson 1989b).

Depending on the solder mask or resist and the low solids flux used, little or no visible residue remains on the boards after soldering. In many

Table II-12. TEST RESULTS OF COMMERCIAL LOW SOLIDS FLUXES

Test	Flux A	Flux B	Flux C	Flux D
Specific Gravity	0.832	0.795	0.801	0.810
Total Solids	2.3%	1.1%	5%	3%
Acid No.	18.0	17.5	20.0	21.2
Halide	None	None	None	None
Water Extract Resistivity (ohm-cm)	26,000	21,400	20,000	23,000
Silver Chromate Paper Test	Passed	Passed	Passed	Passed
Copper Mirror Test ^a	Marginal	Passed	Passed	Failed
Corrosion Test	Failed	Passed	Passed	Failed
Surface Insulation (B.S. 5626 Method) ^d	1.0E8 ^b	2.2E11 ^b	1.0E12 ^b	1.0E7 ^b
Resistance (Ohms)	1.0E7 ^c	1.0E14 ^d	1.0E12 ^d	2.0E6 ^d

^a Copper Mirror Test according to MIL-F-14256 D.

^b Initial conditions.

^c 24 hours.

^d B.S. -- British Standards.

Source: Adapted from Wang 1988.

cases, the remaining residues, if any, dry and rapidly harden. Automatic testing can be done without cleaning the boards. Because low solids fluxes are generally considered non-corrosive and have high insulation resistance, in many cases it is unnecessary to remove them, even for cosmetic reasons. The use of such fluxes should be tested for corrosivity.

A major U.S. company has performed additional tests on low solids fluxes (Guth 1989). The test results demonstrated an inverse relationship between surface insulation resistance (SIR) and the quantity of low solids flux applied and revealed the importance of process selection and process control in the application of a number of low solids fluxes (Guth 1989b). Aging studies have shown that large quantities of post-solder low solids flux residues can be detrimental. These concerns resulted in the design of a new fluxing system that uses an ultrasonically-controlled spray to disperse the flux (U.S. Patent #4,821,948, April 18, 1989). This system is commercially available. Other advantages of this system include minimal deposition of flux on the topside of circuit boards which can be detrimental, and a closed flux reservoir system that prevents alcohol evaporation (specific gravity changes) and water absorption.

Although the use of low solids fluxes is still a relatively new technology, the need to reduce CFC-113 consumption should lead to more widespread adoption of low solids fluxes.

The conversion of a soldering line from a conventional to a low solids flux should not be expected to pass without adaptation of the process parameters and possibly the soldering machine itself. Some users have experienced initial difficulties when starting up with these fluxes, but a little perseverance generally resolves problems such as maintaining an adequate foam head, measuring and adjusting the flux solids, preventing water

from entering the flux, regulating the quantity of applied flux, and adjusting the preheaters to a more critical degree. Conventional fluxes are more tolerant of minor variations in the process parameters. Optimisation of the process parameters using low solids flux can be assisted by using the Taguchi method (Taguchi and Wu 1985).

2.3.6.2 Controlled Atmosphere Wave Soldering

There are two new soldering processes using controlled atmospheres. One process operates under a vacuum (Soltec 1988). The other process is designed to work with less flux (SEHO 1988). The process operates under a nitrogen atmosphere and applies finely divided activators via ultrasonic injection. The carboxylic acid activators include formic acid, acetic acid, citric acid, and adipic acid (Stahl 1989). Figure II-10 illustrates a typical controlled atmosphere wave soldering machine. The particular features that make this process preferable to the well established and widely used method of soldering under atmospheric conditions (i.e., in the presence of oxygen) are: (1) soldering takes place with metallically pure solder (i.e., in an oxide-free soldering module, oxygen levels in and above the bath are monitored by solid electrolytes at less than two ppm); (2) oxide formation is greatly reduced on the printed circuit boards both before and after soldering (dross formation is reported to be only 10 percent of that generated in normal soldering machines, i.e., 0.5-1.0 kg/day); (3) the system operates without conventional rosin or resin fluxes; and finally, (4) post-cleaning required for assemblies wave soldered on equipment currently in use and utilising conventional fluxes (rosin, inorganic or synthetic fluxes) is eliminated for many applications. The residues remaining on the printed circuit boards after soldering are claimed to measure less than 2.5 micrograms/square centimetre NaCl equivalent.

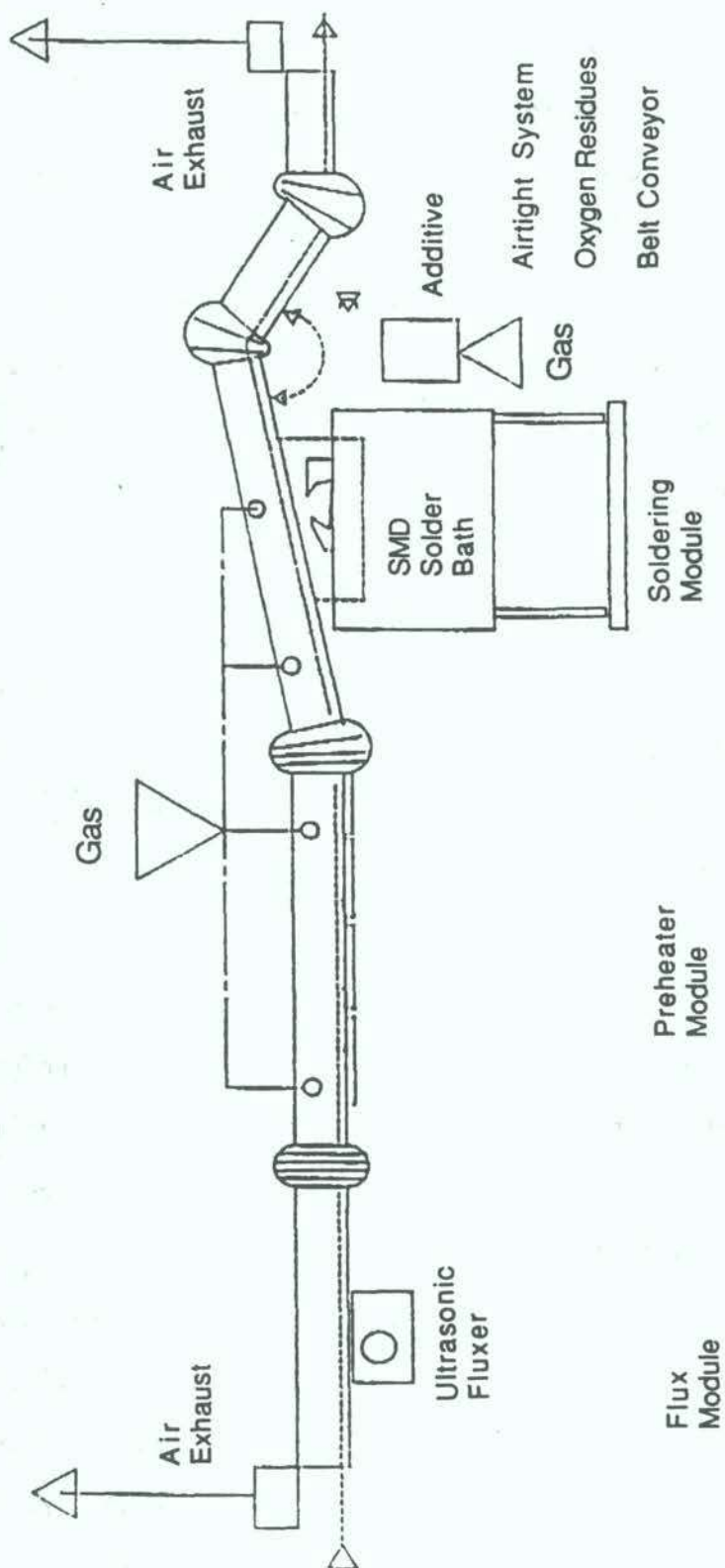


Figure II-10. DIAGRAM OF AN INERT GAS WAVE SOLDERING MACHINE. (Source: SEHO 1988.)

Controlled atmosphere wave soldering has been tested by a large German electronics manufacturer with numerous conventional wave soldering systems in operation. Preliminary test results show no significant differences in the quality of solder joints. Boards tested by another company after controlled atmosphere wave soldering found better solderability. These preliminary tests showed an order-of-magnitude decrease in solder defects (Brox, 1989b). In addition, several European and North American companies will be using the controlled atmosphere process soon to wave solder both through-hole and surface mounted assemblies. Results are preliminary and tests are underway to further quantify the process.

2.4 COST OF ALTERNATIVES

2.4.1 Cost of Conservation and Recovery Practices

The cost of increasing the freeboard (creating an extension on the existing tank and relocating the cover) on a solvent degreaser is relatively small and requires minimal additional utility cost. Required maintenance also is minimal and should result in lower operating costs (IPC 1985).

The costs of implementing conservation practices for in-line cleaners are minimal in most cases and result in savings ranging from five to twenty percent depending on the option. Cleaning systems enhancements and bulk chemical handling systems are more expensive to implement. The installation of activated carbon adsorption systems is a capital intensive alternative. Recurring operation and maintenance costs should also be considered. They are, however, effective in reducing solvent loss. While the investment required is substantially more than the addition of basic engineering controls, the addition of an activated carbon adsorption system may be an attractive option if solvent loss has to be reduced by 80 to 90 percent from uncontrolled levels. While costs can be saved by reducing solvent losses from

existing systems, and the system may pay for itself in a relatively short time, this concept should be considered an interim measure since the remaining losses may be unacceptable in the long-run.

2.4.2 Comparison of Solvent and Aqueous Cleaning Costs

Aqueous cleaning is an accepted method of cleaning electronics assemblies. Numerous studies have documented the success of individual companies switching from solvent to aqueous cleaning (Lambert 1987, Jancuk 1983, Caci 1987, Danford 1987). Some of the representative cost comparisons presented in these studies are examined below (Ellis 1986, Manko 1986, ICF 1987b).

Many variables influence cleaning costs, including water quality, energy consumption, the level of cleanliness required for a particular board application, the flux type used, and the number of boards processed. Ellis (1986) compared the total costs of cleaning printed circuit board assemblies using aqueous and solvent cleaning systems. The costs were originally developed in 1983 from Swiss data and expressed in Swiss Francs (Table II-13); Ellis (1987) concluded that the relative costs should be similar in the United States as well. Labour costs were calculated assuming that boards cleaned via an in-line conveyerised process were automatically moved from the soldering machine to the washer, and then manually stacked after washing. For batch cleaning, the analysis assumed that the boards were manually placed in racks, fed into the machine, and then manually unloaded and stacked.

Cost comparisons are summarised in Figure II-11 and assume the use of an activated rosin flux. The curves show that aqueous cleaning (batch or in-line) is less expensive than solvent cleaning under most circumstances.

Figure II-12 compares the cost of removing water soluble organic acid flux by aqueous batch and in-line cleaning techniques. These costs are

Table II-13. COST COMPARISON OF AQUEOUS AND SOLVENT CLEANING TECHNIQUES
(in 1988 dollars)^a

VARIABLE	COST
Electronic Specifications	220 x 160 mm packing density 12.5 eq DIL ₁₄ /dm ²
Cost of Fluorinated Solvent/Methanol Azeotrope	\$2.67/kg
Cost of Saponifier (used at a 5% dilution)	\$7.36/l
Water Treatment: Reverse osmosis and deionisation (0.7-1 megohm-cm) assumed to be used in conjunction with other plant processes	\$47.00/m ³
Cost of Electricity	\$0.037/kw/h
Labour Costs	\$18.20/hr
Capital Cost: Aqueous Batch Cleaner	\$6,200
Capital Cost: Solvent Batch Cleaner	\$12,800
Capital Cost: Aqueous In-Line Cleaner	\$62,100
Capital Cost: Solvent In-Line Cleaner	\$76,800
Depreciation	5 years
Interest Rate	5%
Rent and Heating	\$610/m ² /year

^a Originally in 1983 Swiss Francs, the costs were first converted to 1983 U.S. dollars using a conversion factor of 2.10 (the exchange rate from Statistical Abstract 1987, U.S. Department of Commerce, U.S. Government Printing Office, Washington, D.C., p. 839). The costs were then converted to 1988 U.S. dollars based on various indices for selected expenditure classes in the U.S. "Economic Report of the President" transmitted to Congress, January 1989.

^b The capital cost of the solvent in-line cleaner is composed of two principal components: the capital cost of the cleaning machine is \$44,100 (Ellis 1986), and the capital cost of the recirculating still is \$32,700 (Fitzgerald 1989).

* Biodegradation

Source: Ellis 1986.

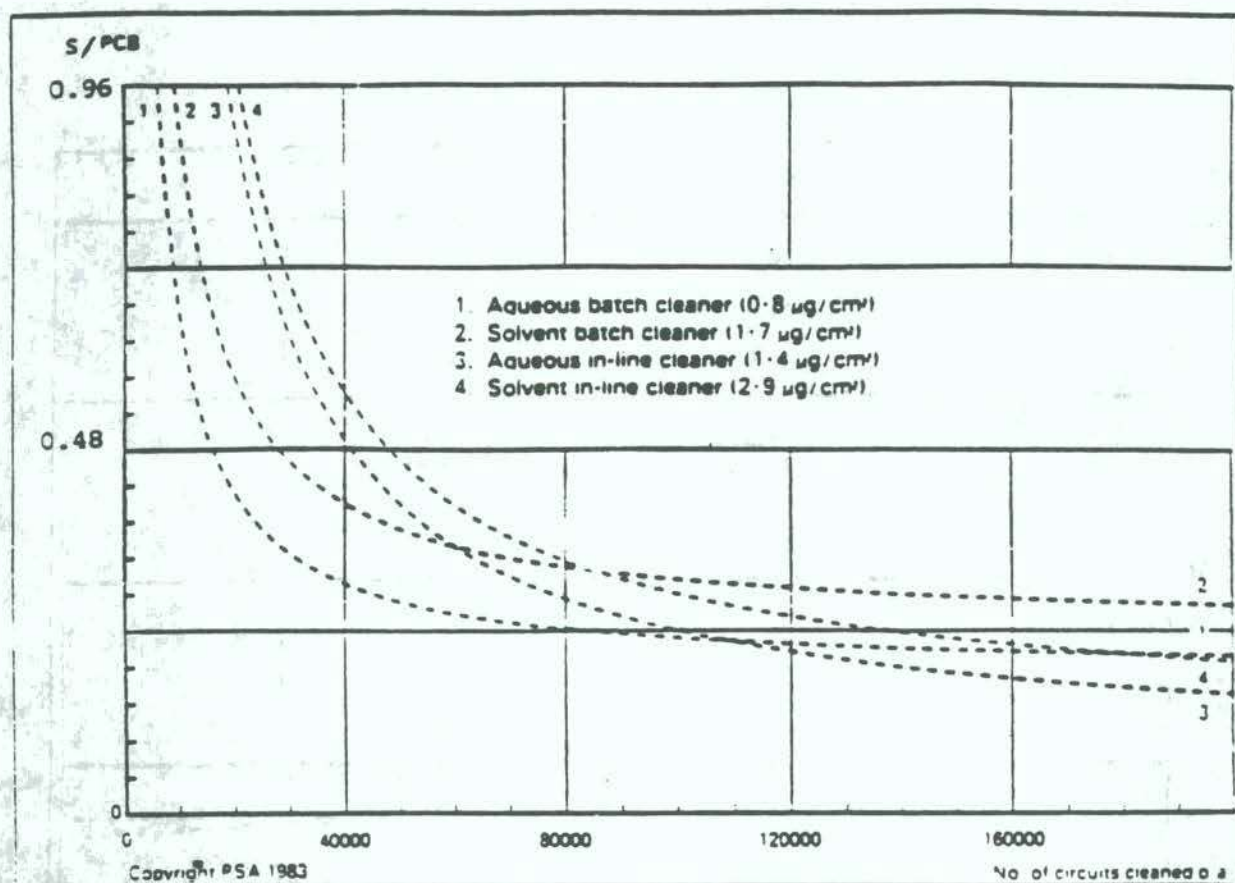


Figure II-11. COST OF ACTIVATED ROSIN FLUX REMOVAL USING AQUEOUS AND SOLVENT CLEANING METHODS. (Source: Ellis, B.N. 1986. Cleaning and Contamination of Electronics Components and Assemblies. Electrochemical Publications, Ayr, Scotland.)

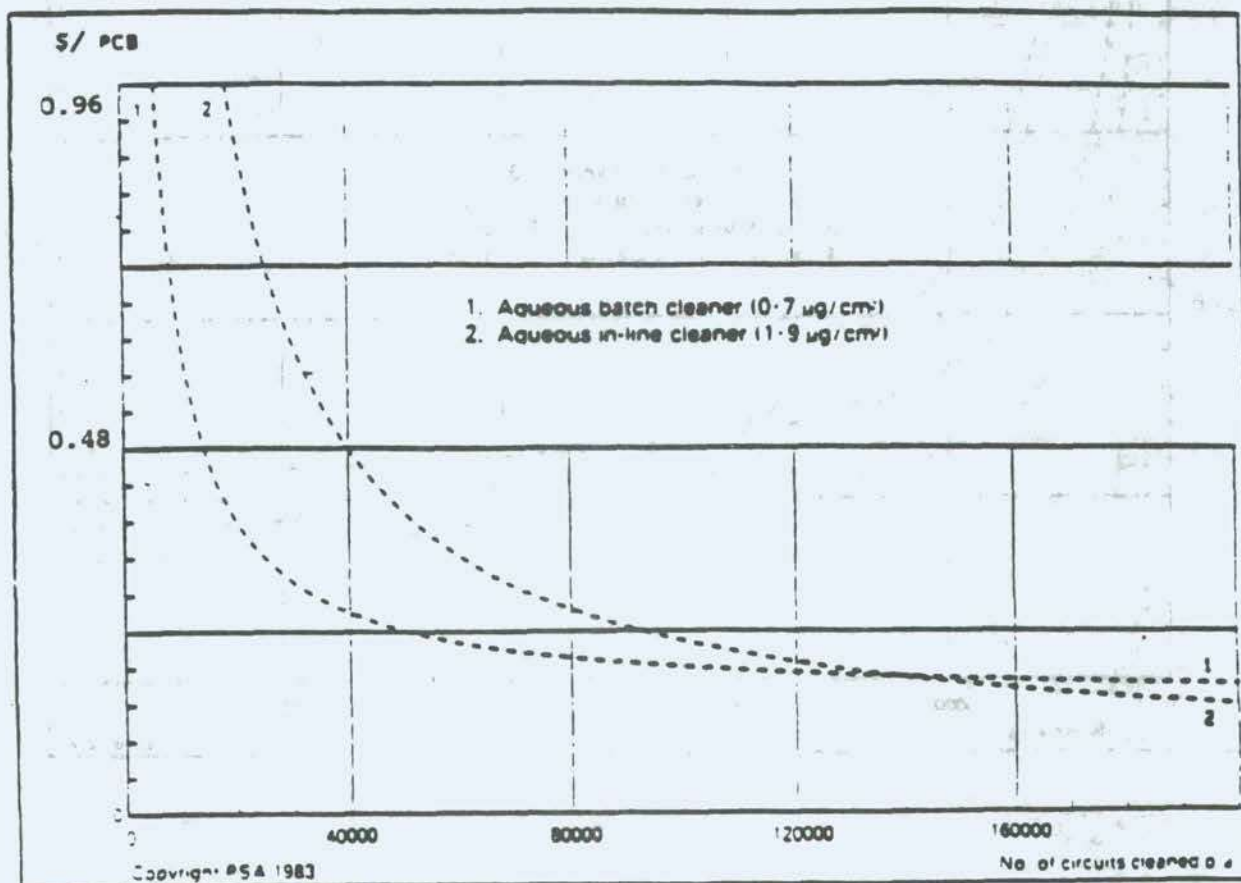


Figure II-12. COST OF WATER SOLUBLE ORGANIC ACID FLUX REMOVAL USING AQUEOUS CLEANING METHODS. (Source: Ellis, BN. 1986. Cleaning and Contamination of Electronics Components and Assemblies. Electrochemical Publications, Ayr, Scotland.)

slightly lower than the cost curves in Figure II-11 because a saponifier is not needed.

Manko (1986) compared the costs of aqueous and solvent in-line cleaners of similar size. The analysis assumed that equipment depreciated over five years, and used 1,1,1-trichloroethane material cost as a basis for evaluation, assigning it a cost of 100 units. Labour and maintenance costs were equal for both cleaning processes and are, therefore, not reported. Table II-14 compares the cleaning cost for aqueous and solvent in-line cleaners. Cleaning costs were lowest for systems using a rosin flux and 1,1,1-trichloroethane solvent. Cleaning costs for aqueous and CFC-113 based systems using a rosin flux were roughly equal. The low material cost of the aqueous system is offset by the high energy costs for operation. Adding a water treatment system to an aqueous system may reduce energy costs by allowing recirculation of heated water, but also may increase operating costs due to supply costs (FitzGerald 1989c).

A U.S. EPA-sponsored conference on CFC-113 use and alternatives compared the costs of aqueous and non-aqueous cleaning methods (ICF 1987b). Participants did not make detailed comparative cost estimates, but concluded that a substantial portion of the existing CFC-113 flux cleaning on non-surface mounted components could be accomplished by aqueous cleaning at equal or lower costs.

A high fraction of large manufacturers can switch to aqueous cleaning at costs equivalent to CFC-113 cleaning, but fewer small manufacturers may voluntarily make the change. The cost of cleaning equipment for small manufacturers can be higher than the savings in operating costs. The costs of switching from solvent to aqueous cleaning can vary by geographical location and by company. Major costs for large companies may include installation,

Table II-14. COMPARATIVE IN-LINE CLEANING COSTS FOR AQUEOUS-
AND SOLVENT-BASED CLEANERS
(thousand 1988 dollars)^a

Solvent	Solvent	Flux	Equipment ^b	Materials	Energy	Total
Degreaser	1,1,1-Trichloroethane	Rosin	210	110	100	420
Degreaser	Freon TE	Rosin	280	250	100	630
Degreaser	1,1,1-Trichloroethane	Rosin	210	120	100	430
Washer	D.I. Water only	Water Soluble	220	50	240	510
Washer	D.I. + Neutraliser	Water Soluble	220	100	240	560
Washer	D.I. Water + Additive	Rosin (or) W.S.	220	140	240	600

^a The 1986 costs reported in Manko 1986 were converted to 1988 U.S. dollars based on consumer price indices for selected expenditure classes. Source: "Economic Report of the President," transmitted to the U.S. Congress in January 1989.

^b 5 Years depreciation.

Source: Adapted from Manko, Howard 1986. Soldering Handbook for Printed Circuits and Surface Mounting. Van Nostrand Reinhold Company, Inc., New York, NY.

testing, and wastewater treatment costs (depending on the stringency of effluent regulations in the local or state jurisdiction).

2.4.3 Cost of Other Cleaning Alternatives

Using low solids fluxes can eliminate the need for post-solder cleaning in many situations. Without the need for cleaning, there are no costs for the acquisition of cleaning equipment and maintenance; therefore, material and operating costs are reduced. Along with cost reductions, space savings and process simplification can be realised. Additionally, the need for any post-solder assembly and cleaning steps are eliminated in cases where components that are incompatible with the cleaning process must be manually inserted and soldered.

Another alternative is a controlled atmosphere wave soldering system. This method can eliminate the need for post-soldering cleaning. The costs of controlled atmosphere wave soldering are competitive with conventional wave soldering. An important aspect in the above calculation, however, is the cost involved in the delivery and consumption of nitrogen. The system is cost efficient, compared to conventional soldering systems, as long as nitrogen consumption remains under the stipulated levels.

2.5 ENVIRONMENTAL CONSIDERATIONS

No-clean soldering techniques present fewer environmental concerns because they eliminate the need for cleaning altogether. For aqueous and hydrocarbon-surfactant cleaning alternatives, the toxicity and biodegradability of the cleaner needs to be verified and biochemical oxygen

demand (BOD₅), chemical oxygen demand (COD), volatile organic compound (VOC) emissions, and heavy metals¹⁴ monitored.

Aqueous cleaning processes using saponifiers/surfactants/tensides can generate high pH (10-11) effluent. This pH level can be adjusted downward if required by using a mini-neutraliser plant. However, neutralisation is not normally required since rinse water effluent effectively dilutes the saponifier.

Another aspect of aqueous processes is the introduction of tensides/surfactants into the environment. The effect of a tenside is dependant upon its biodegradability, its toxicity to organisms, and its bioaccumulation properties. While not all tensides/surfactants are hazardous, however, the nonylphenoethoxylate group has generated concerns in Scandinavia. It is, therefore, important to evaluate the aqueous systems regarding their generation of tensides.

Bernstein and Green (1981) found that aqueous cleaning processes for removing rosin flux (saponification processes), water soluble flux (water cleaning only), or water soluble/neutralised flux, required treatment for heavy metals and pH prior to disposal. Ion exchange is one common method of treating heavy metals. Heavy metal content also may be reduced by an order of magnitude when oil intermix is used in the solder wave. Water-soluble oils are highly effective but may cause effluent foaming. The BOD₅ of the rinse water is typically 20 to 50 mg/l and 95 percent typically degrades within 15 days (Ellis 1989).

¹⁴ The amount of BOD₅, COD, VOCs, and heavy metals found in wastewater effluent depends on the number of boards processed and the cleaning process used.

"Zero-discharge" aqueous cleaners are available (Russo and Fischer 1989). These closed-loop water recycling systems minimise the discharge of process water and the need to treat discharge water. Such systems also reduce water consumption and energy costs and also produce low ionic content rinse water.

2.6 POTENTIAL GLOBAL REDUCTION OF CFC-113 USE IN ELECTRONICS INDUSTRY APPLICATIONS

2.6.1 Trends in CFC-113 Use in the Electronics Industry

The main advantage of using CFC-113 to clean electrical assemblies is that it is not detrimentally aggressive towards most polymers, elastomers, coatings, and polymer symbolisation used on electronic components. Over the past 25 years, there has been a slow but steady change from solvent-sensitive encapsulants and coatings (polystyrene, wax coatings, and alkyd paints) to more solvent-resistant materials, notably epoxies. Consequently, although still a major consideration, the solvent-sensitivity issue is less important than it once was, even for conventional, leaded components (Clementson 1988b). However, many polyurethane, acrylic, and silicone coatings used on electronic assemblies are sensitive to some solvents and hydrocarbon/surfactant blends including terpenes, especially chlorinated, aromatic, and ketone solvents.

More recently and dramatically, the development and rapid adoption of surface mount technology has reduced the size of the assemblies to be cleaned. This reduction in size results from components being densely packed on the board. Thus, the area to be cleaned is smaller and less cleaning solvent is used. The development and adoption of surface mount technology is projected to grow through the mid-1990s while the use of through-hole assemblies is projected to level off and then decrease as shown in Figure II-13. Currently the use of conventional components or mixed surface mounted technology/conventional components in many sectors of the electronics industry sustains

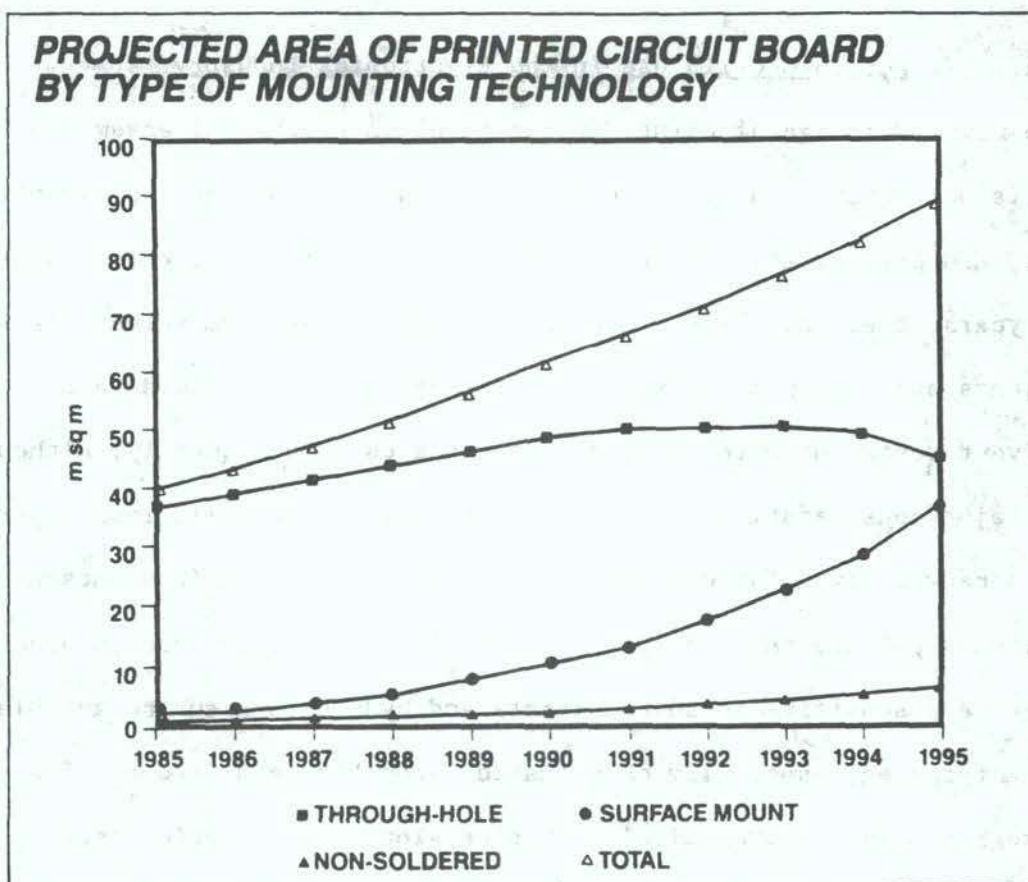


Figure II-13. PROJECTED AREA OF PRINTED CIRCUIT BOARD BY TYPE OF MOUNTING TECHNOLOGY: 1985-1995. The quantity of solvent required for cleaning printed circuit board assemblies depends on the surface area of printed circuit boards. (Source: Clementson, 1988a.)

the use of CFC-113 based formulations of mild strength. CFC-113 use in the future, therefore, can probably be effectively reduced in light of the developments in which materials used for components are likely to be solvent resistant and the increases in available alternative solvents which will offer equal if not better performance.

2.6.2 Potential Increase in Conservation and Recovery Efforts

As stated earlier, CFC-113 solvent losses in the electronics industry are estimated to be as high as 90 percent of total solvent consumption. Part of this loss occurs during cleaning; the rest is lost during recovery or other handling operations. The loss/consumption ratio is higher for small companies with a small installation compared to large companies with sophisticated cleaning equipment. One major communications company estimates that up to 75 percent of CFC-113 consumption can be eliminated through conservation and recovery (Kerr 1988).

It is estimated that electronics companies with less than 25 employees emit 40 percent of the total CFC-113 solvent losses and consume up to six times as much CFC per m² of printed circuit boards cleaned than do larger companies. If this estimate is accurate, countries with large numbers of small companies could reduce their emissions significantly (Brazing and Soldering 1988).

2.6.3 Potential Increase in the Use of Alternatives

Most of the technical limitations for using aqueous cleaning for non-surface mount assemblies could be addressed through the redesign of components, assemblies, and manufacturing processes. Board design and component designs have a large effect on the type of cleaning process ultimately used. If the board is designed with aqueous cleaning in mind, then aqueous cleaning can be accomplished with a minimum of difficulty (ICF 1987b).

An estimated 50 percent of current CFC-113 use results from U.S. military specifications. Industry experts agree that there would be an enormous interest in aqueous cleaning if U.S. military specifications allowed manufacturers to meet performance criteria using a choice of flux and cleaning methods. The military's requirement for RMA flux has become a de facto standard in the electronics industry. Most company internal cleaning specifications are guided by military specifications, even for boards not produced for the military. With a performance based, military specification, companies would evaluate and implement aqueous cleaning (ICF 1987a). The U.S. military has agreed to change military specifications based on a joint DoD/EPA/Industry benchmark test program now underway. An alternative solvent which is demonstrated to clean as well or better than the benchmark cleaning level set by this program will be accepted by the military for use in manufacturing military electronics equipment. Equipment manufacturers will be able to choose an alternative solvent from the significantly wider range of cleaners to provide acceptable cleaning of products manufactured for the U.S. military.

There have been instances where the use of water soluble, non-rosin fluxes in the production of military electronic hardware have met with documented success (Stach 1979, Stach 1980, McBryde 1985, Felty 1988). The driving forces behind the use of these fluxes and aqueous cleaning (as far back as 1979) were:

- Scarcity and escalating cost of petroleum products and derivatives;
- New U.S. EPA regulations on cleaning solvents;
- Reducing costs through yield improvement; and
- Faster processing with improved solderability.

In such cases, waivers granted by specific branches of the military resulted in improved yields, increased product through-put and reliability, reduced cost, and decreased emissions of organic solvents to the atmosphere. To successfully implement such production systems, however, the electronics hardware should be carefully designed with adequate controls and monitors to ensure all assemblies are properly cleaned and to maximise cleaning efficiency.

Recent coordinated efforts by the U.S. military and industry have resulted in a new U.S. military standard, MIL-STD-2000, which addresses the standard requirements for soldered electronic assemblies. This standard allows the contractor (with adequate documented testing and evaluation) to use non-CFC solvents and aqueous cleaning. The contractor's documentation and evaluation results must prove that the selected cleaning media is compatible with materials used in the electronics assembly. Also, evidence must show that the cleaning process is controlled and that it cleans assemblies to the requirement of the military standard.

Design changes can facilitate the use of CFC-113 alternatives in the electronics assembly industry. For example, a higher component standoff and sturdier packages to withstand high-pressure sprays could be designed. Aqueous cleaners can blow cleaning fluid at boards at pressures as high as 1.38×10^6 Pascals (Pa) to effectively clean tight spaces (Eden News 1989). Elliott and Gileta (undated) tested solvent spray cleaning in a new in-line cleaner at pressures up to 1.72×10^6 Pa. This technique proved to be a viable alternative for removing rosin flux residues. If the manufacturing process was considered at the design stage, more products might be developed which do not require cleaning. Where cleaning is required, users should consider fluxes whose residues do not need to be removed.

CHAPTER 3

PRECISION CLEANING APPLICATIONS

3.1. OVERVIEW

Precision cleaning applications are characterised by the extremely fine level of cleanliness required to keep delicate instruments and surfaces operating effectively. Precision cleaning processes remove contaminants from metal, plastic, and glass substrates to a degree of micrometer fineness. Computer disk drives, gyroscopes, miniature bearings, medical equipment and supplies, and optical components are examples of instruments which require precision cleaning. In this chapter, precision cleaning applications are organised according to their engineering applications. These include precision instruments that must be cleaned to a micrometer level of cleanliness during manufacturing, testing, or assembly, during specialised manufacturing processes, and during maintenance cleaning.

CFC-113 has traditionally been the cleaning solvent of choice for precision cleaning applications because of its chemical inertness, low toxicity, nonflammability, low surface tension, and low water solubility. However, a number of companies have successfully tested and are using CFC-113 alternatives to clean precision instruments. Companies also are implementing conservation and recovery practices to reduce CFC-113 use in the short-term. Possible alternatives include alcohols and HCFC/alcohol blends, 1,1,1-trichloroethane¹ and other chlorinated solvents, hydrocarbons, aqueous cleaning processes, and biodegradable solvents. Although much testing still

¹ 1,1,1-Trichloroethane is also referred to as methyl chloroform, TCA, and CH_3CCl_3 .

needs to be done for specific applications,² the Committee consensus is that alternatives will be able to substitute for CFC-113 use in virtually all precision cleaning applications by, or before, the year 2000.

3.2 CFC-113 USE IN PRECISION CLEANING APPLICATIONS

3.2.1 Precision Cleaning Processes and Equipment

Precision cleaning is used to remove contaminants from metal, plastic, and glass substrates to a degree of micrometer fineness. This involves processes carried out in: clean room or white room conditions;³ specialty maintenance operations; and plastic parts manufacturing. Most of the systems and components assembled (or disassembled) in clean rooms are mechanical assemblies in which fits and tolerances are extremely small (e.g., one micrometer clearance on a self-acting gas bearing gyroscope). Consequently, these assemblies are extremely sensitive to the presence of solid particulate contamination and very low levels of foreign fluid or polymeric contaminants. Precision cleaning is widely used in the space and communications industries, defense industries, medical industries, and optics and photo industries.

The standard equipment used in precision cleaning is a vapour degreaser comprised of a boiling sump, a hot clean rinse stage with ultrasonic generators, and a vapour blanket. These units are often fitted with mechanical handling equipment and installed at the incoming location adjacent to clean areas, so that parts, sub-assemblies, and proprietary components can be cleaned and sealed in bags being transferred to the clean room assembly

² Testing needs to be done not only to determine cleaning effectiveness but cost and environmental effects as well.

³ Clean rooms are supplied with air free from both inert and biologically active particles. Airlocked entry areas control access to clean rooms and dedicated protective clothing are required. Most components are preliminarily cleaned outside of the clean room. The cleaned parts are then placed in sealed containers and then transferred to the clean room.

area. Within clean room assembly areas, smaller CFC-113 vapour degreasers with ultrasonic generators are often installed close to inspection and assembly areas, so that local batch cleaning can be performed.

Bench-top ultrasonic cleaners are used in clean rooms and are often installed within laminar flow boxes. These ultrasonic units are cold cleaners in which water is used as the energy coupling medium. Clean glassware containing a small volume of CFC-113, often no more than 100 mls, is placed in the water such that ultrasonic energy can agitate and clean the individual components when they are placed in the solvent. This type of cleaning has a high loss to evaporation; 100 percent of the evaporated solvent is lost to the atmosphere because there are no cooling coils or other forms of vapour containment or collection. Often this technique is combined with particle counting in which the whole CFC-113 cleaning charge is filtered through an ultra-filter after cleaning so that the contaminant particles may be counted under a microscope.

Gyroscope flushing rigs are dedicated systems designed specifically for a particular gyroscope. Coupling fixtures attach these rigs to the gyroscope instrument casing. Clean CFC-113 is forced through the gyroscope via ultra-filters at high pressure in an open-ended process to remove flotation fluid during rework, or to clean an assembly before filling it with oil.

Hydraulic system flush and spray booths are similar to gyroscope flushing rigs but are larger. The flush mechanism pumps CFC-113 through the hydraulic systems to remove hydraulic fluid. These cleaning machines often have hand-held spray cleaners for manual cleaning of valve seats. Many are "dead loss" systems in which the solvent evaporates and is removed from the work areas by extraction fans.

3.2.2 Precision Cleaning Applications

Precision cleaning is discussed in this report in terms of the following engineering applications: cleaning precision instruments during manufacturing, testing or assembly; cleaning during specialised manufacturing techniques; and maintenance cleaning.

3.2.2.1 Cleaning Precision Instruments During Manufacture, Assembly, and Testing

Precision cleaning is used to remove contaminants from delicate and complex instruments such as computer disk drives, inertial guidance systems (gyroscopes), hydraulic control systems, optical components, and micro-switches. Traditionally, CFC-113 has been effective in precision cleaning the following delicate instruments.

Disk Drives. Disk drives are magnetic storage devices that store information in computer systems. Disk drives have a very small tolerance for contamination during assembly. Contaminants must be controlled at the submicrometer level for the drives to work effectively.

Gyroscopes. Precision cleaning is used to clean the mechanical components of inertial guidance systems (gyroscopes).⁴ Parts are repeatedly cleaned at all stages of gyroscope assembly to remove handling contamination and particulate material. Repeated cleaning is important in gyroscope gimbal assemblies because suspension bearings lubricated with solid film are sensitive to solid particulate contamination. Cleanliness maintains torque values of a few microgram (μg) centimetres. To reduce precessional drift, cleaning often is performed in small ultrasonic cleaners using CFC-113.

⁴ Inertial guidance systems or gyroscopes include rate gyroscopes, displacement gyroscopes, and rate integrating gyroscopes. Displacement gyroscopes typically are used in auto-pilots. Rate integrating gyroscopes are used in precise inertial navigation systems in missiles, satellite controls, commercial aircraft, and underwater systems.

In rate-integrating gyroscopes, the flotation fluid surrounding the inner gimbal is a per (trifluorochloro) ethene. When the viscosity of the fluid must be engineered, secondary fluoropolymers are added. Typically these fluids are poly (1,1-difluoro)ethene. Other fluorinated, high density materials, such as perfluorotrialkylamines, also are used in the assembly and testing stages.

Although the floated gyroscope technology is being superseded by solid state, optical systems, commercial and military gyroscope equipment will remain in service for many years. Because these gyroscopes need to be serviced and maintained, there is a long term requirement for compatible solvents for manufacturing spare sensors and gyroscopes and for cleaning existing units.

Hydraulic Control Systems. Hydraulic military vehicle control systems have control valves with extremely small diameter bores as well as parts such as polymeric-O-ring seals and gaskets. These systems are flushed to remove the working fluid and to remove all particulate contamination during assembly, after functional testing, and during field maintenance. CFC-113 has traditionally been the solvent of choice because of its chemical stability and noncorrosive properties. Smaller tactical weapon systems often use a gas control system in which a source of high pressure gas, either chemically-generated (e.g., extruded double-based propellant) or a "cold" compressed gas such as nitrogen at $3.56 \times 10^7 \text{ N/M}^2$, controls valves to actuator systems. Gas controls require extreme cleanliness as they are sensitive to particulate contamination. Gas control systems are pressure tested, and water often is used as the test fluid. Many hot gas control units have long blind galleries from which it is difficult to remove water by oven evaporation. Water-displacing mixtures based on CFC-113 effectively dry these systems.

Optical Components. CFC-113 solvent and alcohol azeotrope or surfactant solvents are widely used in cleaning processes during grinding and polishing operations and prior to applying vapour deposition coatings in optics fabrication. The surface cleanliness of glass and metal optical elements are critical to ensure adequate adhesion of optical coatings and freedom of movement in low torque pivots with small clearances. Recently, manufacturers of glass-based optical elements have shifted away from CFC-113 cleaning solvents. However, for metal-based optical elements such as highly polished or diamond turned (machined) aluminum reflective elements, the use of chemically inert CFC-113 solvents is critical. The highly sensitive metal surfaces are extremely reactive in a fresh, non-oxidised state, and cleaning with substitute chlorinated solvents would detrimentally affect the metal.

Pressurised CFC-113 is also used for cleaning dust and particles from high definition cathode ray tube shadow works and electron guns. CFC-113 solvent is very efficient as the high specific gravity allows non-metallic particles to be floated off precision parts (Nemoto 1989).

In the past, CFC-113 was used in many drying operations to prevent streaking and water spot deposition on pre- and post-coated optical element surfaces. Many of these applications, however, have been replaced with high vapour pressure organic solvents.

Electrical Contacts. Micro-switches used for critical switching functions require extremely clean contacting surfaces. CFC-113 often is used to clean these surfaces. The switches also can be cleaned using CFC-113 after assembly to remove particles or oily material deposited during assembly.

Most electrical contacts in connectors, slip-rings, potentiometers, microswitches, and relays have precious metal contacts such as gold, gold alloys, and platinum metals. Precious metal contacts are used in the defense

industry where "single shot" devices require a long storage life (up to 15 years) and must operate with 99 percent reliability. High surface contact resistance is a problem as many of these devices are closed "cold" (i.e., without an applied voltage) because of safety requirements. These specifications are met by CFC-113 cleaning. CFC-113 also is used to clean sliding contacts, such as slip rings and potentiometers.

Medical Equipment Applications. The small blind holes increasingly found on complex surgical equipment have made it difficult to remove the water from this equipment.⁵ A majority of surgical instruments now are first dried using CFC-113 water-displacing materials and then are sterilised. Orthopaedic prostheses such as hip joints and knee joints are dried using a similar process. CFC-113 also is used to clean pipe-runs, bedside control systems, and main control panel equipment after installation and during maintenance cleaning of hospital piped-oxygen systems. The high volatility and nonflammability of CFC-113 allows the flushing solvent to be blown through the oxygen system without risk of explosion. Remaining trace amounts of solvent do not present a toxicity risk. The chemical stability of CFC-113 and the absence of stabiliser chemicals helps ensure that organic contaminants can be removed from the metal parts of the oxygen systems without risk of corrosion.

Plasma cleaning in carbon tetrafluoride/oxygen atmospheres has been experimentally used to clean ceramic and some metallic parts free of all organic contaminants. The process is probably not suitable for some base metals.

Plastic Assemblies. CFC-113 is used to remove mould release agents from a variety of plastic mouldings such as ABS electronic cabinet mouldings,

⁵ In the past, surgical instruments were dried after washing and then sterilised in hot air ovens.

domestic white goods accessories, medical parts, syringes, spoons, bottles, and sample vials. The advantage of using CFC-113 in this industry is that there is no risk of surface attack or "crazing," which often occurs with other solvents.

3.2.2.2 Specialised Manufacturing Techniques

Precision cleaning also is a component of specialised manufacturing techniques such as auto-rivetting of commercial aircraft wings and precision application of special lubricants.

Auto-Rivetting. Commercial aircraft wings often are used as fuel tanks. These wings, therefore, must be of minimum weight and maximum strength, have a long corrosion-free life, and be fuel tight. Auto-rivetting is used to meet these requirements.⁶ Traditionally, major aircraft companies have used CFC-113 for auto-rivetting because the stock being drilled for commercial aircraft wings is much thicker than that on the wings of fighter aircraft. A proprietary CFC-113 solvent blend is sprayed on the drill tool during cutting and on the rivet slug as it is placed into the bore. Although the rivet slug is anodised, the freshly-drilled bore surface is not protected. The solvent spray protects the assembly as it is formed and frees the joint of entrapped moisture or acidic components that might encourage corrosion. The solvent rapidly evaporates and helps cool the form.

Because of the large size of the wing assemblies and auto-rivetting machines, the auto-rivetting must be done in large open assembly shops. A non-toxic, nonflammable solvent such as CFC-113 works well in this equipment.

⁶ In this process, the wing skins are clamped to the stringers, a double counter sunk hole is drilled through both components, and an appropriate rivet slug is placed into the bore and the head machined flush with the outer wing surface.

Application of Special Lubricants. The surface of miniature precision bearings is coated with a thin oil film to prevent the oil film from breaking and forming menisci between contacting surfaces. To ensure that the film remains stable over many years of storage life, a lubricant such as a CFC-113 solvent solution is applied to the bearings. The penetrating power of CFC-113 solvent allows the solution to "wet" the bearing almost instantly. The solvent evaporates immediately, leaving a stable oil film on the bearing surfaces. Perfluoroether lubricants, which are used in space applications due to their extremely low vapour pressure ($<1.33 \times 10^{-14}$ Newtons/m² at 20°C) and low temperature viscosity curve, use CFC-113 as a carrier for thin film application and to clean bearings as these lubricants are insoluble in the usual engineering solvents.

3.2.2.3 Maintenance Cleaning

Maintenance cleaning applications include precision cleaning of avionics equipment, decontamination of glove boxes in the nuclear industry, and precision cleaning of electronic sensors associated with offshore oil rigs such as remote cameras and well loggers. Large commercial airline workshops use large amounts of CFC-113 solvents to clean avionics equipment.⁷ In the nuclear power industry, pieces of ancillary equipment that become contaminated with radioactive dusts are removed in glove boxes using remote handling systems. With continued use, the boxes themselves become contaminated. Glove boxes can be decontaminated by spraying with CFC-113 to remove radioactive dusts. The low surface tension and high volatility of CFC-113 provides good wetting and penetration for particle removal. The low flammability and low

⁷ Larger aircraft components are cleaned using other chlorinated solvents, such as trichloroethylene and perchloroethylene in vapour degreasers, and 1,1,1-trichloroethane as a cold cleaner.

toxicity of CFC-113 are the main reasons for using CFC-113 on offshore oil rigs where CFC-113 is used to clean sensors such as remote cameras, drill head attitude indicators, and well loggers.

Pressurised CFC-113 is used for cleaning dust and particles from reticles used during the manufacture of semiconductors. The reticle is a patterned glass plate through which light is directed on wafers to create circuitry. CFC-113 solvent is very efficient as the high specific gravity allows non-metallic particles to be floated off reticles (Nemoto 1989).

3.3 ALTERNATIVES FOR REDUCING OR REPLACING CFC-113 IN PRECISION CLEANING

CFC-113 has evolved as the preferred solvent cleaning method in precision cleaning because of its chemical inertness, low toxicity, nonflammability, low surface tension, and low water solubility. However, a number of companies are testing and successfully implementing alternative cleaning methods, as well as conservation and recovery techniques to reduce CFC-113 use in the short-run. Possible alternatives include alcohols and HCFC/alcohol blends, perfluoro carbocyclic compounds, hydrocarbons, aqueous cleaning, and biodegradable solvents.

3.3.1 Conservation and Recovery Practices

Conservation and recovery can be applied effectively where precision cleaning is confined to clean room instrument assembly. Solvent segregation and recovery can be used where centralised, large scale processors make recovery practical. Recycling solvent via distillation at the point of use (vapour degreasing plant) conserves solvent.

Equipment manufacturers are developing a new generation of degreasers that will reduce vapour losses of CFC-113 solvents. These losses also can be reduced with carbon adsorption techniques. Using recycled solvent is an

option not practised by most users. Military specifications and a perception that recycled solvent lacks purity have discouraged its widespread use.

3.3.2 Alcohols and HCFC/Alcohol Blends

Based on material compatibility, alcohols may be the best alternative for component cleaning. Explosion-proof boiling alcohol cleaners using isopropanol could be a practical alternative to CFC-113 in many applications. For bulk cleaning of parts at the incoming stage, this alternative could be considered; isopropanol may be unacceptable within clean room areas, however, because of flammability risks and operator discomfort resulting from alcohol odours.

HCFC/alcohol blends are other possible substitutes for CFC-113 in precision cleaning applications. They are chemically inert, but the presence of alcohols could present a risk to certain metals, notably beryllium. The most promising substitutes, HCFC 141b and HCFC 123, have chemical compositions that may allow these solutions to be used with the chloro-fluoro polymer flotation fluids found in gyroscopes.

Isopropanol and acetone operating in conjunction with ultrasonics have been evaluated as alternatives to using CFC-113 in precision cleaning (Mobjork 1989). The following components and instruments were subjected to overall evaluation in this testing:

- Servo component system;
- Hydraulic series ram screw;
- Accelerometer cut-out;
- Horizon indicator;
- Horizon gyroscope;
- Gyroscope motor components;
- Flight position indicator;
- Turn and bank indicator;
- Reduction vent valve for oxygen;
- Oxygen pressure regulator; and
- Parachute swivel connector.

All components and instruments were retrieved from production except for the oxygen vent and pressure regulator which were manually contaminated. Due to the flammability of isopropanol and acetone, special explosion-proof batch vapour phase cleaners were used in this evaluation.⁸ A number of precision components were cleaned in isopropanol or acetone.

Cleaned with isopropanol:

- Swivel connector parts contaminated with low temperature grease;
- Gyroscope instruments;
- Reduction vent valve connections in an oxygen system contaminated with oils and greases; and
- Oxygen system gas regulators contaminated with soot and char.

Cleaned with acetone:

- Servo-gear piston contaminated with anti-corrosion oil;
- Serie servo contaminated with hydraulic oils, grease, and particulates; and
- Accelerometer cut-out contaminated with silicone oil.

Isopropanol proved to be a viable substitute for CFC-113 and generally is compatible with non-metallics. However, the use of acetone as a viable

⁸ These ultrasonic vapour phase cleaners are designed for flammable liquids. The machines are fire- and explosion-proofed according to the DIN-standards and approved by the Federal Republic of Germany's TUV authority. The safety features include a monitoring sensor that activates an alarm system at 20 percent and 40 percent of the Lower Explosion Limit (LEL) of the solvent in use. At 20 percent of the LEL level, a warning light is activated and the exposed bath is isolated by a lid that closes automatically. The 40 percent LEL level sets off a siren alarm and activates a machine shut-down procedure. The exhaust fans, however, remain functional and a facility is provided for connection to a general room isolation system. The ultrasonic oscillators (typically 40 kHz) positioned in the primary sump are continuously purged with nitrogen/inert gas and a system is available for recycling the purged gas. Temperature in the cleaning sump is maintained by a thermostat at 50°C (+ or - 3 to 4°C). The vapour zone chamber is at the temperature of the boiling solvent. General heating is achieved indirectly by heated water. The cooling coils are fed by tap water. The other functions are similar to the conventional CFC-113 degreaser (e.g., a desiccator adsorbs condensed atmospheric moisture and water introduced during the process). A special explosion-proofed pump is also available for refilling operations.

alternative needs to be studied carefully, since it is highly aggressive towards many polymers.

3.3.3 Perfluoro-Carbocyclic Compounds

A group of fluorinated carbocyclic compounds (e.g., perfluoromethyl cyclopentane) could be considered as CFC-113 alternatives for some precision cleaning applications. Many of these compounds are inert, nonflammable, and non-toxic. Their major disadvantage is their high cost. If considered part of the capital cost of cleaning equipment, however, and used as an entirely closed, minimal loss system, these compounds could be viable alternatives in small scale component cleaning operations.

Other fluorochloro compounds include HCFCs 141b, 123, 225ca, 225cb, and pentafluoropropanol. The first two may have low boiling points for precision cleaning applications, but the two 200 series compounds, with boiling points of 51.1°C and 56.1°C respectively, offer possibilities for the small essential applications of CFC-113. If long-term toxicity tests prove satisfactory then these compounds could present a viable alternative to CFC-113 despite their cost.

3.3.4 Chlorinated Solvents and Other Organic Solvents

1,1,1-Trichloroethane is an effective substitute for CFC-113 in precision cleaning operations. The U.S. EPA has not classified 1,1,1-trichloroethane as a volatile organic compound (VOC) (HSIA 1987). In addition, it is nonflammable. It is possible, therefore, that some substitution of 1,1,1-trichloroethane will occur as users confront rising prices and decreased CFC-113 availability. However, 1,1,1-trichloroethane has been identified as an ozone depleting substance and may be added to the Montreal Protocol in 1990.

Trichloroethylene, perchloroethylene and methylene chloride are also effective solvents for precision cleaning. However, each of these solvents is

considered carcinogenic to some extent. The U.S. EPA has classified trichloroethylene in Category B2 as a "probable human carcinogen," while the International Agency for Research on Cancer (IARC) has classified this solvent in Group 3, a substance not classifiable as to its carcinogenicity in humans (HSIA 1989c). The IARC has classified perchloroethylene in Group 2B as a substance considered "possibly carcinogenic to humans" (HSIA 1989a).⁹ Finally, the U.S. EPA has classified methylene chloride in Category B2 as a "probable human carcinogen," while the IARC has classified methylene chloride in Group 2B as a substance considered "possibly carcinogenic to humans" (HSIA 1989b). The Committee believes it is unlikely that users would switch to these three chlorinated solvents.

Other organic solvents such as ketones and esters were used prior to the widespread availability of CFC-113 and chlorocarbons and still are used on a limited basis for instrument precision cleaning. Flammability and toxic hazards are the disadvantages of using these solvents. Some of these organic solvents may be aggressive towards polymers.

3.3.5 Aqueous Cleaning

Successful cleaning of both disk-drive parts and gyroscope components using aqueous detergent processes has been reported. One major company has switched from a CFC-113 disk drying process to a hot water/air drying system in some applications (Wolf 1988). Aqueous cleaning may be the most likely substitute for CFC-113 cleaning of precision components in the instrument assembly industries, but such cleaning may require a rapid and spot-free dewatering system. The development of a zero ozone-depleting

⁹ A final decision has not been made by the U.S. EPA as to the classification of perchloroethylene.

dewatering/drying system is important to the introduction of aqueous cleaning in the precision instrument industry.

A recent study undertaken by a major U.S. company to investigate alternatives to CFC-113 in cleaning processes for disk-drives emphasised aqueous cleaning processes combined with ultrasonics, spray, and hot-air drying to clean parts at high throughput (Ming 1989).¹⁰ The following cleaning systems were used:

- CFC-113/Methanol Blend/Ultrasonic Cleaning System. A 4-stage CFC-113 cleaner was used. Each degreaser had a boiling sump and an ultrasonic tank containing CFC-113 solvent blend. The degreasers were equipped with 0.5-micron filtration and solvent distillation accessories. Total cleaning time was 8 min. exclusive of 0.5 min. of drip-dry period.
- Water/Ultrasonic Cleaner. An ultrasonic cleaner was used at 40 kHz ultrasonics with a 0.02 percent by aqueous surfactant at 50°C. The 4 minute washing cycle was followed by a 2 minute rinse with deionised water. The cleaned parts were blown dry with ambient air at a pressure of approximately 3.5×10^5 Newton/m².
- Water Spray Cleaner. The part to be cleaned was first sprayed with an aqueous solution (0.02 percent aqueous surfactant by volume) and then sprayed with DI water at a pressure of approximately $1-1.5 \times 10^5$ N/m². The part was then passed through a clean air curtain at 3.5×10^5 N/m² and subsequently dried under low-pressure ($0.7-1.5 \times 10^5$ N/m²) clean, dry-air heated to about 66°C.

Cleanliness levels resulting from these systems were evaluated using:

- Particulate Counting Tests;
- Turbidity and Enhanced Turbidity Tests;
- Multiple Extraction Tests;
- Organic Contaminant Tests (gas chromatography/mass spectrometry);
- Ionic Contaminants; and

¹⁰ The disc-drive parts cleaned included: E-coated aluminum die casting; stainless steel; zinc-plated chromated, conversion coated steel; E-coated, magnesium die casting; stainless steel; and polycarbonate.

Dryness Evaluation (visual and gravimetric methods).

Among the three cleaning processes, the water cleaning processes were, overall, as effective as the CFC-113 process in removing particulate contaminants from disc-drive parts. The water cleaning processes worked better than the CFC-113 process in removing ionic contaminants, but were less effective than CFC-113 cleaning in removing hydrophobic organic contaminants. The drying rate of CFC-113 cleaned parts was approximately 2-3 times faster than parts cleaned by an off-the-shelf aqueous cleaner. However, residual moisture was removed effectively by both processes. The data support the conclusion that an aqueous cleaning system with ultrasonics and spray is an effective alternative to using CFC-113 to clean disk drives.

Aqueous ultrasonic cleaning also has been successfully used to clean inertial guidance and navigation systems and components that are used by most missiles and aircraft in the U.S. Department of Defense inventory (Patterson 1989).

Alternatives to CFC-113 cleaning of inertial systems, gyroscopes, accelerometers, and related gaskets, bearings, and housings include biodegradable aqueous-based systems, and non-chlorinated/halogenated hydrocarbons such as alcohols, ketones (acetone), hydrocarbon/surfactant blends, and petroleum distillates. The alternatives may be a combination of systems using ultrasonics, high pressure sprays, surfactants, and ancillary equipment. The following contaminants have been successfully removed using aqueous detergents and ultrasonics:

- A highly fluorinated, long chain polymer lubricant;
- Polychlorotrifluoroethylene, a viscous heat transfer fluid with a low coefficient of expansion;
- Long chain hydrocarbon oils/grease;
- Finger prints;

- Inorganic particulate matter;
- Rust and other oxides; and
- Some carbonaceous char.

The cleaning equipment was a self-contained system that cleans by using detergents and water in a cylindrical cleaning tank agitated by ultrasonics. This aqueous system not only has offset use of CFC-113 and 1,1,1-trichloroethane, but has reduced process time as well (Peterson 1989). For example, whereas manual cleaning of gimbal rings takes approximately 15 minutes per ring, an aqueous ultrasonic system can clean 24 rings in 25 minutes.

The cleaner provided better cleaning results than those achieved with a solvent-based system. The self-contained system is a promising spray booth media for cleaning parts which cannot be subjected to ultrasonics and also for bench use where spot cleaning is done as part of the repair process.

Nuclear decontamination may be effectively achieved by an aqueous-based system and high pressure sand blasting. Also, Al_2O_3 and/or glass beads of 0.1 mm have been used successfully. In this process, the water evaporates and the residue is cast for disposal (Arvensen 1989).

3.3.6 Plasma Cleaning

Plasma cleaning is widely used in the gyroscope manufacturing industry. Components are exposed to ionised argon gas at low pressure which results in ultra-clean surfaces. Bearing surfaces commonly are cleaned in this way prior to lubrication. However, plasma cleaning is not a true alternative for solvent cleaning as it is always used after solvent cleaning, and does not remove particulate contamination.

3.3.7 Pressurised Air Cleaning

Filtered, contaminant-free pressurised air is increasingly being used as a substitute for CFC-113 to clean reticles, high definition cathode ray tube

shadow masks, and electron guns. While care must be taken to prevent static build-up, this method can substitute for the use of pressurised CFC-113 for removal of non-metallic dust and particles.

3.4 COST OF ALTERNATIVES

Table III-1 includes estimated costs of an explosion-proof, ultrasonic vapour phase cleaner. A replacement of about 125 cleaning systems using one to three tonne per year unit 1,1,1-trichloroethane with alcohol based systems annual operating cost for the alcohol based system is estimated to be \$6 million (in U.S. dollars) (Gals, Ostman, and Ostman 1989). The aqueous cleaning system is based on ultrasonic cleaning. For a facility cleaning 100 gimbal rings per month, 25 hours of technician time are required to clean 100 rings using CFC-113; this aqueous cleaning system can complete the job in two hours. The unrecoverable CFC-113 and 1,1,1-trichloroethane in the gyro bell covering operation cost more than \$175 per day (in U.S dollars). On the other hand, the cost of DI Water and detergent is minimal. Therefore, considerable cost savings can be realised both in labour costs and solvent costs.

3.5 POTENTIAL GLOBAL REDUCTION OF CFC-113 IN PRECISION CLEANING APPLICATIONS

Some firms are far along in the investigation of alternatives for CFC-113 use in precision cleaning applications. As noted above, one computer manufacturer has switched from a CFC-113 disk drying process to a hot water/air drying system in its computer disk drive cleaning applications. Other computer manufacturers have instituted comprehensive plans for emission control in the short-term coupled with continued evaluation of alternative solvents to be used over the long-term. In addition, testing already conducted with alcohols and HCFC/alcohol blends indicate that when used in conjunction with ultrasonic processes, these could be successful replacements

Table III-1. ULTRASONIC EXPLOSION-PROOF VAPOUR PHASE CLEANER^a ESTIMATED COSTS

Component	Cost (U.S. Dollars)
1-Chamber Cleaner, non-standard equipment 40-40-40	\$47,800
2-Chamber Cleaners	
55-35-40	\$55,400
35-25-30	\$71,700
80-45-40	\$71,900
3-Chamber Cleaners	
55-35-35	\$61,300
35-25-30	\$56,250
80-45-40	\$80,000
EX-classified filter system and pump	\$ 2,600
EX-classified drum pump	\$ 1,950

^a Cleaner for acetone or alcohol; sump zones may be designed according to customer specifications, e.g., in accordance with the available immersion baskets.

^b Wholesale prices vary widely from country to country.

Source: Ahmadzai 1989b.

for CFC-113 in a number of precision cleaning applications. An alcohol/acetone blend is being investigated by some companies as a viable alternative.

In most precision cleaning environments, therefore, conservation methods can be implemented immediately to reduce current CFC-113 use and emissions. The long-term prospects for development of alternative cleaners and cleaning equipment that does not depend on CFC-113 are excellent. By, or before, the year 2000, the use of alternatives should replace CFC-113 in precision cleaning applications.

In clean room instrument assembly precision cleaning, conservation and recovery can be applied effectively. For example, in large, well organised companies, vapour degreasers can be modernised with freeboards and mechanical parts handling. In addition, redistillation can be introduced and solvent charges collected for commercial recovery.

With proper materials management, segregated solvent collection can be established and "clean" solvent sent for recovery or redistilled in-house. Large companies, could immediately reduce CFC-113 usage by as much as 85 percent annually using this method. Such a material management program requires employee education and participation, and some capital outlay. In small and medium enterprises, however, informal methods of cleaning are commonly employed. The logistics of collecting solvent for recovery may be too complex to be economical in these settings.

Market penetration of alternative solvents currently is small. The changes in existing and pending legislation affecting various alternatives make it very difficult for companies to make firm plans for future plant and process changes. This difficulty is particularly relevant in the case of 1,1,1-trichloroethane and its mixtures, to which many users were beginning to turn in response to the initial terms of the Montreal Protocol. Now, with the

possibility that 1,1,1-trichloroethane may be added to the Montreal Protocol in 1990, many users are waiting for further guidance before deciding on which alternative solvent to use.

As supplies of CFC-113 are reduced and are likely to become more costly, there will be pressure to move from current contaminant sensitive technologies towards less sensitive solid state systems. The service life of some current defense or commercial equipment could be reduced by requiring replacement with new technologies earlier than originally planned.

CHAPTER 4

METAL CLEANING APPLICATIONS

4.1 OVERVIEW

Metal cleaning applications include all applications in which metal parts are cleaned during manufacturing or maintenance except for those metal parts that are included in precision cleaning applications.¹ CFC-113 is one of a number of cleaning solvents used to clean metal parts. This chapter describes a number of alternatives that clean metals effectively, including 1,1,1-trichloroethane² and other chlorinated solvents, aqueous cleaners, solvent blends, no-clean alternatives, and plasma cleaning. The Committee consensus is that CFC-113 used in metal cleaning applications can be replaced by these alternatives by the year 2000 or sooner, and that a 90 percent reduction in CFC-113 use could be achieved within five years using the alternatives discussed in this chapter. Seventy-five percent of the short-term reduction in the use of CFC-113 is expected to be achieved through alkaline and emulsion cleaner substitution.

4.2 CFC-113 USE IN METAL CLEANING APPLICATIONS

4.2.1 Metal Cleaning Applications

Metal cleaning is a surface preparation process that removes organic compounds such as greases and oils, particulate matter, and inorganic soils from metal surfaces. Metal cleaning is usually an essential part of the

¹ See Chapter 3. Delicate and intricate metal parts that must be cleaned to a degree of micrometer fineness are considered precision cleaning applications in this report.

² 1,1,1-Trichloroethane is also referred to as methyl chloroform, TCA, and CH₃CCl₃.

production process as it prepares parts for subsequent operations such as assembly, painting, coating, electroplating, inspection, further machining and fabrication, or packaging. Metal cleaning also involves the cleaning and preparation of moulds used to cast metal parts.³ Metal cleaning usually is done on flat or formed sheet metal or on milled and machined metal stock. Tubing, engine parts, motors, nuts, bolts, screws, and rivets are common configurations.

Machined parts tend to have complex and curved surfaces with holes and pockets that can trap particulate matter. Parts may be cleaned multiple times during the manufacturing process. In large facilities, a wide spectrum of metals and alloys may require cleaning using the same cleaning system. For example, at one location the U.S. Air Force cleans 15 metal alloys during aircraft maintenance operations (Bellar 1988).

4.2.2 Metal Cleaning Solvents

Traditionally, chlorinated solvents such as trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), perchloroethylene (PCE), and methylene chloride (MC) were used for metal degreasing (ICF 1988). CFC-113 use as a metal cleaner began in the 1970s, as concerns increased about the toxicity and the effects of long-term, low-concentration exposure to some chlorinated solvents. In the U.S., the use of CFC-113 as a metal cleaner almost doubled from 1974 to 1983, from an estimated 26,000 metric tons to 4.80×10^7 kilograms.

4.2.3 Metal Cleaning Processes

4.2.3.1 Cold Immersion Cleaning

Immersion cleaning is the most common method of cleaning with ambient temperature solvents. Most immersion cleaning operations are fairly simple

³ CFC-113 is also used in degreasing operations as a drying medium after cleaning.

and use halogenated solvents, organic solvents, or blends near room temperature. The basic technique involves immersing or dipping a part by manually, mechanically, or hydraulically lowering the part into a tank containing solvent. The simplest immersion cleaners achieve cleaning simply by soaking the article in solvent. Most soils, however, even if solvent-soluble, require agitation for adequate cleaning (ASTM 1981). Therefore, immersion/dip cleaning usually is used in conjunction with other operations such as mechanical agitation or ultrasonic cleaning. Immersion cleaning also may be used to remove heavy soils prior to manual cleaning or vapour degreasing. Solvent usage in immersion cleaning is relatively high due to solvent drag-out with parts. In addition, there usually is not a vapour level control (condenser, cooling coils) on the equipment.

Mechanical agitation allows non-soluble particles to be stripped away from the parts, thus producing cleaner parts than a simple dip tank (ASTM 1981). Mechanical agitation is produced by agitating the solvent bath or the metal part. The solvent can be stirred with a motor-driven propeller or a circulating pump, or can be ultrasonically agitated using transducers and an ultrasonic generator. Parts can be agitated by placing them on an agitation platform. Air-agitated dip tanks also increase cleaning efficiency by helping to remove non-soluble soils, but because this process greatly increases solvent loss by raising the evaporation rate, it is not a viable option for cleaning enhancement.

Small containers may be used for maintenance cleaning of electronic parts; large containers may be used for cleaning large machined parts or large volumes of smaller parts in baskets (ICF 1989). Even if the immersion tanks are small, there are often many cleaning stations and the solvent may be changed frequently (Eureka 1978). Thus, this method commonly uses a

relatively large volume of solvent since there is no controlled vapour level. While many container sizes exist, a typical container (tank) size is about 30 centimetres by 60 centimetres, containing solvent to a depth of 75 centimetres; the working volume of solvent ranges from about 50 to 400 litres (ICF 1989). Tanks are often fitted with recirculation pumps to flush parts. Particulate filters and stills are integrated in some units to maintain solvent quality.

4.2.3.2 Vapour/Hot Liquid Cleaning

Vapour degreasing is a process that uses the hot vapour of a chlorinated or fluorinated solvent to remove soils, oils, greases, and waxes. A basic vapour degreaser unit is an open-top steel tank with a heat source at the bottom to boil the solvent and a cooling zone near the top to condense the solvent vapours. The vapours displace the lighter air and form a vapour zone above the boiling solvent. The hot vapour is condensed when it reaches the cooling zone by condensing coils or a water jacket, thus maintaining a fixed vapour level.

Parts are cleaned by lowering them into the vapour zone. The temperature differential between the hot vapour and the cool part causes the vapour to condense on the part and dissolve the contaminants. The condensed solvent and contaminants then drip into the boiling solvent. Because they are heated by condensation of the solvent vapours, parts dry instantly upon withdrawal from the vapour zone.

Vapour degreasing is more effective than cold cleaning, where the solvent bath becomes increasingly contaminated. In vapour degreasing, the parts are washed with pure solvent because contaminants removed from the part usually boil at higher temperatures than the solvent and therefore remain in the liquid solvent. Despite the soils contained in the solvent from

previously cleaned parts, the boiling solvent produces essentially pure solvent vapours provided that the contaminant level in the boiling sump is kept low. Heavy contamination will contaminate the vapour by upward splashing of bursting bubbles or by forming an azeotrope with the solvent.

Metals can be cleaned using one of several batch degreasing methods. These methods are: vapour phase only, vapour-spray-vapour, warm liquid-vapour, or boiling liquid-warm liquid-vapour. Modifications to the basic vapour degreaser process are designed to accommodate various cleaning cycles, requirements, or parts configurations. These modifications include spraying or immersing the parts in boiling or cool solvent. Immersion vapour degreasing cycles include a warm liquid-vapour cycle and a boiling liquid-warm liquid-vapour cycle. Immersion vapour degreasing is used to clean small parts packed in baskets, to clean the inside of tubing, or to clean intricately patterned parts contaminated with particularly heavy or adherent soil. The four vapour methods are discussed further below.

Vapour-Phase Only: The simplest degreasing system is the straight vapour method. With this method, solvent vapour condenses directly on the part, dissolves the organic contaminant, and removes it and any particulate residue from the part surface by dripping back into the boiling solvent. When the part reaches the vapour temperature, vapour condensation ceases and cleaning is complete. Parts are dry when removed from the tank. Few manufacturers currently make vapour-phase-only units because with the simple addition of a vapour spray device the effectiveness and applications of the machine are greatly increased.

Vapour-Spray-Vapour: This cleaning method is similar to the vapour-phase- only cycle with the addition of a pure distillate rinse step. In this process, the metal part is lowered into the vapour zone where the

condensing solvent cleans the metal. After condensation, the part is sprayed with warm solvent. The spray pressure forces the solvent liquid into holes and helps remove insoluble soils that cannot be removed by vapour alone.⁴ The warm spray also lowers the temperature of the metal part. After spraying, the cooled metal part causes further condensation of vapour for the final rinse. This technique also can remove solvent-insoluble soils, such as buffing compounds, if the part is sprayed immediately upon entering the vapour before the vapour heat can affect the compounds and make them difficult to remove. Vapour-solvent spray-vapour is the most frequently used cleaning cycle (ASM 1982).

Warm Liquid-Vapour Cycle: During the warm liquid-vapour cycle, the part is held in the vapour zone until condensation stops, and then lowered into the warm liquid. Alternatively, parts may be directly lowered into the warm liquid. Mechanical agitation of the warm liquid removes additional soil. The part is transferred from the warm liquid to the vapour zone for a final rinse.

Boiling Liquid-Warm Liquid-Vapour Cycle: This cycle cleans small, intricate parts that are packed closely together in baskets; tubing interiors, or parts with heavy or adherent soil. A part first is held in the vapour zone and then is lowered into the boiling liquid. In some processes, the part is lowered directly into the boiling liquid. Once immersed in the boiling solvent, the violent boiling action scrubs off heavy soil deposits, metal chips, and insolubles. Prior to the final vapour phase cleaning, the metal surface temperature of the part is lowered by transferring the part to warm liquid. This method requires large quantities of solvent and is impractical

⁴ Spray pressures for standard degreasers should range from 6 psi to 8 psi (40 KPa to 55 KPa) (ASM 1982). Excessive pressure disturbs the vapour zone and causes a high solvent emission rate.

for large parts because of the large volumes of liquid solvent required for immersion.

4.2.3.3 Conveyor Cleaning

Conveyorised cleaning equipment using CFC-113 is generally configured with a spray cleaning stage, immersion in up to three boiling liquid sumps with ultrasonics to enhance cleaning, and in some cases a superheated drying zone. Small batch degreasing machines using CFC-113 may also use ultrasonics to enhance cleaning of small parts and equipment. Also, vibratory conveyorised machines which move small parts in a screw pattern upward through chlorinated solvent liquid and vapour are still used.

4.2.3.4 Manual Cleaning

Metal surfaces can be hand-wiped with a cloth, brush, or sponge that is moistened with solvent. The solvent container or tank can be moved within the shop as cleaning is needed (ICF 1989). Prior to final assembly, aircraft surfaces are often hand-wiped clean. Although widely used, manual cleaning is an inefficient method of cleaning parts and does not lend itself to routine continuous operations (Eureka 1978). It is most appropriate for infrequent maintenance cleaning.

4.2.3.5 Spraying and Flushing Techniques

The efficacy of spraying and flushing cleaning techniques depends on the solubility of the soil (Eureka 1978). Spraying and flushing equipment usually consists of a solvent tank, feeder hose, spray gun, overspray containment, and baskets to hold the parts during cleaning. Solvent is usually supplied by a mechanical pump or a compressed air mechanism. These methods can only be used to clean outer metal surfaces. Soils trapped in complex or intricate part structures are not easily cleaned using this operation (Eureka 1978). Because there is relatively little physical enhancement afforded by either spraying or

flushing, it is difficult to remove insoluble soils. Flushing can clean external and internal part surfaces such as metal castings, tubing, and heat exchangers.

4.3 ALTERNATIVES FOR REDUCING OR REPLACING CFC-113 USE IN METAL CLEANING APPLICATIONS

Given the varying processes used in metal cleaning, process-specific alternatives for CFC-113 and methods for reducing CFC-113 must be developed. The alternatives that are appropriate for reducing CFC-113 use in vapour cleaning processes, for example, may not translate to cold immersion processes. Table IV-1 summarises the alternatives that can be used for each type of cleaning process. The control approaches discussed here include solvent conservation and recovery practices, and the use of alternative cleaning media such as aqueous cleaners, plasma cleaning, solvent blends, and emulsion cleaners.

4.3.1 Conservation and Recovery Practices

Methods of conserving and recovering CFC-113 solvents range from simple procedures for manually removing large contaminants prior to degreasing to adding various filtration apparatuses. The range of control options is presented below.

4.3.1.1 Improved Operating Practices

The amount of soil initially entering the wash tank can be minimised by hand wiping to remove large contaminants prior to degreasing. Also, a single, centrally-located system for removing the heavy contaminants decreases the amount of cleaner used. Process innovations include modifying the cleaning and assembly sequence to reduce the amount of cleaner required or eliminating the need for manual cleaning by preventive measures such as packaging or wrapping parts between assembly steps or wearing gloves while handling parts.

Table IV-1. VIABLE ALTERNATIVES TO EXISTING METAL CLEANING
PROCESS SOLVENTS

Substitute	Cold Immersion	Hot Immersion	High Pressure Spray	Manual
Alkaline Cleaners		X	X	
Emulsion Cleaners		X	X	X
Low Vapour Pressure Solvent Blends ^a				X
Hydrocarbon/Surfactant Blends	X			X
Naphtha	X			X
Naphtha-Terpene Blends	X			X
Steam			X	

^a Non-halogenated mixtures.

Source: Evanoff 1989.

4.3.1.2 Gravity Separation

Simple liquid-phase separators can be integrated into the vapour-condensate line where water contamination is present. Introduction of water into the system can be minimised by reducing the disturbance of the vapour blanket in the degreaser and by ensuring that parts are not coated with water or water-based contaminants.

Commercially-available gravity separators can be sized to retrofit existing degreasers. Gravity separators operate on the principal that water and solvent will separate into two distinct phases with sufficient residence time. A standpipe drains the lighter water phase, while the heavier solvent phase flows to either a bed of molecular sieves for further purification or back to the solvent-boiling sump or still.

4.3.1.3 Water Adsorption

Trace amounts of water dissolved in the solvent phase, generally ranging in concentration from 100 to 1000 mg/l, can be removed by passing the solvent through a packed column of molecular sieves or similar desiccants. Moisture control minimises hydrolysis, maintains cleaning performance, and avoids possible rust problems with mild steel parts. This process keeps the water content under 100 mg/l. Molecular sieves 8 to 12 mesh in size and controlled pore sizes of three to five angstroms remove most traces of water. Columns can be designed using simple mass transfer principals. Once they are saturated with water, the beds are regenerated by passing hot air (400-500°C) through the bed for 30 to 60 minutes or by removing the sieves from the column and placing them in a 200°C oven for up to 24 hours. It is particularly important to use water adsorbers if the solvent is blended with alcohols and/or if amphoteric metals (e.g., aluminium, magnesium, zinc, or their alloys) are being cleaned.

4.3.1.4 Single Plate Distillation

An additional still can be used to further concentrate still bottoms and recover additional solvent for reuse, particularly at facilities with numerous stills subject to high soil loadings. The combined still bottoms, generally containing 60 to 80 percent solvent, can be further concentrated to recover an additional 50 to 75 percent of remaining solvent. Due to the low boiling point of CFC-113, single-plate distillation combined with product filtration and desiccation produce a virgin quality solvent product, assuming that no other solvents (e.g., ketones, alcohols) have been introduced as contaminants. The oil can be concentrated for reuse in cases where a single oil or other heavy hydrocarbon soil is used.⁵

On-site recycling using single-plate distillation is economical when approximately 30 litres/day of solvent waste are generated (Schwartz 1986). This estimate is dependent on solvent price and should prove economical for lower generation rates of CFC-113 in the future.

4.3.1.5 Reuse in Alternative Applications

Solvent from an in-process still may be sufficiently clean for application in other less demanding plant degreasing operations. For example, waste solvent from the final product cleaning operation may be acceptable for degreasing in maintenance operations.

4.3.1.6 Off-Site Solvent Recovery

If on-site recycling is impractical or uneconomical, professional companies can be hired to recover the solvent. One study (DuPont Bulletin 1978) estimates the cost for this service at 50 to 90 percent of solvent cost.

⁵ For systems using trichloroethylene, 1,1,1-trichloroethane, or perchloroethylene, a thin film evaporator or other means of fractional distillation is necessary to achieve virgin solvent quality.

Recyclers will conduct a site inspection and a chemical and physical property characterisation of a representative sample of the waste solvent before accepting material. To optimise recovery, a waste solvent segregation programme is recommended. Waste-solvent containers should be clearly labelled and should meet transportation and safety requirements. Many solvent manufacturers and distributors are now offering services whereby the waste solvent can be recovered and returned. A discount is given proportional to the amount of solvent recovered.⁶ If the recovery plant does not reconstitute stabilisers in the distilled solvent, the user may need to conduct acid acceptance tests and add stabilisers accordingly, especially if amphoteric metals are being cleaned.

4.3.1.7 Waste Treatment and Disposal

Waste materials from recycling facilities are generally disposed of by some form of thermal destruction. Wastes from degreasing processes are primarily hydrocarbon and solids residues but can contain anywhere from 20 to 70 percent solvent and water condensate depending on the source. Waste waters can be treated using activated carbon to remove trace solvent prior to discharge or can be packaged and sent to a commercial waste disposal firm for treatment. Still bottoms and unrecoverable solvent wastes are disposed of by thermal destruction in commercial hazardous waste incinerators or industrial furnaces, which are primarily cement kilns. These hazardous waste incinerators must include an acid gas scrubbing system. If a waste or still bottom has sufficiently high heating value ($>2.33 \times 10^7$ J/kg) and low chlorine content (less than three percent chlorine by weight), it can be used directly as a supplemental industrial furnace fuel feedstock. Costs of disposal at an

⁶ These services are also available from solvent cleaning equipment manufacturers and through waste exchanges and brokers.

industrial furnace generally are 30 to 50 percent less than the costs of disposal at a commercial hazardous waste incinerator.

4.3.2 Alternative Solvents Including Chlorinated Hydrocarbons

Several chlorinated hydrocarbons are effective metal degreasers, including trichloroethylene, perchloroethylene or tetrachloroethylene, methylene chloride, and 1,1,1-trichloroethane. Table IV-2 lists common metal cleaning solvents and indicates the cleaning process in which each solvent is commonly used. Solvent blends used for metal cleaning in cold immersion or manual wiping operations include non-halogenated solvent blends (e.g., Stoddard Solvent) or blends of halogenated solvents with hydrocarbons and/or oxygenated solvents (frequently referred to as safety solvents).

1,1,1-Trichloroethane is an effective substitute for CFC-113 in metal cleaning operations. The U.S. EPA does not classify 1,1,1-trichloroethane as a volatile organic compound (VOC) (HSIA 1987). In addition, it is nonflammable. It is possible, therefore, that some substitution of 1,1,1-trichloroethane will occur as users confront rising prices and less availability of CFC-113. However, 1,1,1-trichloroethane has been identified as an ozone depleting substance and may be added to the Montreal Protocol in 1990.

Trichloroethylene, perchloroethylene and methylene chloride are also effective solvents for metal cleaning. However, each of these solvents is considered carcinogenic to some extent. The U.S. EPA has classified trichloroethylene in Category B2 as a "probable human carcinogen," while the International Agency for Research on Cancer (IARC) has classified this solvent in Group 3, a substance not classifiable as to its carcinogenicity in humans (HSIA 1989c). The IARC has classified perchloroethylene in Group 2B as a

TABLE IV-2. METAL CLEANING SOLVENTS AND PROCESSES

Solvent	Processes			
	Cold Immersion	Vapour/Hot Liquid	Conveyor	Manual
CFC-113		X	X	X
Trichloro-ethylene	X	X		
1,1,1-Tri-chloroethane	X	X		X
Methylene Chloride	X			
Perchloro-ethylene		X		
Blends ¹	X			X

¹ Includes halogenated and non-halogenated mixtures.

Source: Evanoff 1989.

substance considered "possibly carcinogenic to humans" (HSIA 1989a).⁷

Finally, the U.S. EPA has classified methylene chloride in Category B2 as a "probable human carcinogen," while the IARC has classified methylene chloride in Group 2B as a substance considered "possibly carcinogenic to humans" (HSIA 1989b). Chlorinated solvents will be selected substitutes for CFC-113 in many cases, particularly for metal cleaning. For example, in the United States trichloroethylene continues to be used in metal cleaning even with new regulations that reduce the allowable worker exposure to the chemical.

There are specific metal cleaning operations in which trichloroethylene, 1,1,1-trichloroethane, perchloroethylene, and methylene chloride are perceived to be the only alternatives to CFC-113 in the short-run. Lack of alternatives can result from concerns about corrosion of the substrate metal (e.g. mild steel), time restrictions between processes (e.g. degreasing as part of a metal heat treating operation), and requirements for removing extremely tough soils (e.g. waxes), or cleaning intricate parts configurations (e.g. tubes, metal honeycomb). In these special cases, use of trichloroethylene, perchloroethylene, 1,1,1-trichloroethane, or methylene chloride with the incorporation of the conservation and recovery practices discussed in this report may be a temporary (short-term) substitutes for CFC-113.

The U.S. Air Force has identified and tested biodegradable solvents that can replace chlorinated solvents and CFCs. Through this effort at least six alternative cleaning agents have been identified which meet a minimum criteria of biodegradability and corrosivity (Carpenter 1989). Samples were tested over a period of 168 hours and examined for general corrosion, crevice corrosion, and pitting corrosion. A wide variety of alloys were used in

⁷ A final decision has not been made by the U.S. EPA as to the classification of perchloroethylene.

testing.⁸ Six commercial cleaning agents were selected and these were based on blends of:

- petroleum distillate;
- ethyl ester;
- potassium hydroxide primed alcohol;
- 4-isopropenyl-1-methyl cyclohexene;
- alkyl acetate ester; and
- dipropylene glycol and monomethyl ether.

These six cleaning solvents effectively removed contaminants such as molybdenum sulphide greases and concentrated (30 percent) baked oils.⁹

The petroleum distillate (citrate) was applied in its concentrated form at ambient temperatures to remove oil, grease, and wax contaminations on all metals.

The ethyl ester performed satisfactorily on all metals when applied in its concentrated state at ambient temperatures.

The potassium hydroxide primed alcohol (butoxyethanol), removed grease, oil, and carbon contaminants from all metals at approximately 40°C at a dilution ratio of 1:1, and at approximately 60°C at a 1:3 concentration ratio.

The hydrocarbon, 4-isopropenyl-1-methyl cyclohexene, performed satisfactorily at ambient temperatures. It removed oil, grease, wax contaminations on all metals. The solvent has a flash point of 46°C.

The alkyl acetate ester, successful degreased on all metal surfaces in a concentrated form. It was applied at ambient air temperatures.

The dipropylene glycol and monomethyl ether, removed grease, oil, carbon, and wax contaminants on chromium, cadmium, bronze, iron, steel,

⁸ Copper, CDA110 ETP, Nickel 200, Aluminum 2024, Steel, C4340, Aluminum 7075, Aluminum 1100, Stainless steel, 410, Admiralty brass, Carbon steel C1020, Stainless steel, 310S, Inconel 750, Monel K-500, RMI titanium, Waspaloy alloy, and Magnesium AZ31B.

⁹ Some baked oil gives rise to adsorbed char-like dirt and is considered to be a difficult contaminant to remove from metal surfaces (Wikoff 1989).

stainless steel, nickel, copper, lead, brass and aluminum. The suggested concentration for application is 1:3 ratio at temperatures between 60°C to 80°C.

Other compounds that recently have emerged as potential metal degreasing solvents include hydrocarbon/surfactant blends, glycol ethers, dibasic acid esters, developmental hydrochlorofluorocarbons (HCFCs), and n-methyl pyrrolidone. These products are being tested for performance, toxicity, exposure limits, flammability, carcinogenicity, odour, recyclability, and cost. These alternatives will increasingly become available for commercial use over the next five years.

4.3.3 Solvent Blends

4.3.3.1 Vapour Degreasing

Solvent blends used for vapour degreasing include CFC-113/alcohol azeotropes and new azeotropic blends of hydrochlorofluorocarbons (HCFCs) and chlorinated solvents. These blends have ozone depletion factors associated with them, although these factors are lower than that of CFC-113. Few data are available at the time of release of this report on the use of these products in large, industrial vapour degreasers.

4.3.3.2 Manual Cleaning

For manual cleaning, a number of commercial solvent blends are available. These products are mixtures of aliphatic and aromatic hydrocarbons (naphtha, toluene, xylene), and oxygenated solvents (ketones, esters, and alcohols). Solvent blends commonly used for manual cleaning which do not contain CFC-113 or chlorinated solvents include Stoddard Solvent and the U.S. MIL-C-36876. Many of the hydrocarbon and oxygenated solvent blends are flammable; some have relatively low threshold limit values. In the U.S. where

tropospheric ozone formation is a concern, industrial use of these volatile organic compounds is discouraged and is closely regulated.

The newer blends being developed are optimised for maximum soil removal, minimum flammability and toxicity, and low composite vapour pressure/evaporation rate.

4.3.3.3 Cold Immersion Cleaning

Solvent blends of aliphatic naphtha with perchloroethylene, and/or methylene chloride are used in manual or immersion cleaning of heavy soils and greases in industrial maintenance operations. These blends are viable substitutes for CFC-113 where hydrocarbon residue from naphtha is not a problem and volatile organic compounds can be controlled. The newer blends being marketed have equal cleaning capacity and include high flash aliphatic naphthas and blends of aliphatic naphthas and hydrocarbon/surfactant blends.

4.3.4 Aqueous Cleaners

4.3.4.1 Alkaline or Acidic Cleaners

Alkaline cleaners are the most viable, broad substitute for halogenated solvents used in degreasing metals. An estimated 75 to 90 percent of the halogenated solvent degreasing operations for metals could be replaced with alkaline cleaners. Alkyl benzene sulphonates and other anionic surfactants are common active ingredients in alkaline cleaners. More recently, non-ionic surfactants have been included in some cleaning packages.¹⁰ Corrosion

¹⁰ Alkaline cleaners contain builders to help suspend soils and to prevent redeposition. Builders include sodium salts of phosphates, carbonates, silicates, hydroxides, and zeolites.

inhibitors are added to minimise the effect of the alkaline cleaners on the metal surface.¹¹

Alkaline cleaners have been used successfully in blends and pilot scale testing for numerous metal cleaning applications (Weltman 1988, Golden, et.al. 1988, Evanoff 1988, Suciu 1989). Hundreds of alkaline cleaning formulations are commercially available and more are currently under development. These products need to be tested to ensure that they are effective for specific applications, and that they minimise potential corrosion or residues harmful to the surface or downstream surface coating processes.

Acidic cleaners¹² are used to remove rust and scale and to clean aluminum, a metal susceptible to etching when cleaned with strong alkaline cleaners. Because organic solvents do not remove rust and scale, acidic cleaners generally cannot be used as substitutes.

4.3.4.2 Aqueous Cleaning Processes

Aqueous cleaning processes include ultrasonic cleaning, immersion cleaning, and spray cleaning. The equipment differs in design features and in the optional equipment included. Options include solution heaters, dryers, parts handling automation equipment, solution filtration, and solution recycle and treatment equipment. Ultrasonic cleaning, immersion cleaning and spray cleaning processes are described below.

¹¹ Silicate salts are typical corrosion inhibitors. Other additives include anti-oxidants, such as borates, stabilisers, and small amounts of water-miscible solvents, such as some glycol ethers.

¹² Acidic cleaners contain mineral acids (nitric, sulphuric, phosphoric, and hydrofluoric), chromic acid, or organic acids (acetic and oxalic), plus detergents, chelating agents, and small amounts of water-miscible solvents.

4.3.4.2.1 Ultrasonic Cleaning

Ultrasonic cleaning is a type of aqueous cleaning that effectively cleans intricate parts and contaminants that are difficult to remove, such as carbon and buffing compounds (Randall 1988a, Oakite 1988). Ultrasonic machines are used to clean numerous types and sizes of parts, from small metal components to large fabricated metal parts. However, for large tanks of several thousand gallons or more, the electrical power required for ultrasonics becomes prohibitively expensive. A design rule of thumb for ultrasonic systems is 10-15 watts/litre.¹³

Ultrasonic cleaning equipment creates submicron-sized vapour bubbles through cavitation by vibrating the cleaning solution at extremely high frequencies. These vibrations create countless microscopic bubbles in the cleaning solution. As the bubbles form and collapse, they create a scrubbing action that cleans the entire surface of the parts, including blind holes and very small cracks and recesses (Unique Industries 1988). This cavitation process creates extremely high temperatures and turbulence on a microscopic scale. Transducers vibrate the tank (and hence the cleaning solution) at frequencies from 25kHz to 40kHz (Branson 1988).¹⁴

One disadvantage of ultrasonic energy is its tendency to be absorbed by thick oil or grease contaminants. These contaminants are most effectively removed in a heated immersion tank with agitated cleaning solution or in a spray washer (Randall 1988b). Ultrasonic cleaning equipment tends to be expensive because of the sophisticated machinery used. It also uses relatively large amounts of electricity compared to agitation immersion

¹³ The noise generated by such a large system could create an employee health concern.

¹⁴ 1 kHz equals 1,000 vibrations per second.

cleaners of similar size (Racquet 1988). Aqueous ultrasonic cleaning equipment can be configured with other cleaning stages featuring parts and/or fluid agitation, or may be used as a step in a spray machine. The ultrasonic/spray combination is more common for solvent-based equipment than for aqueous equipment.

4.3.4.2.2 Immersion Cleaning

Aqueous immersion cleaning generally combines the cleaning action of a water-based solution with mechanical cleaning action. Immersion cleaning consists of four major steps: cleaning, rinsing, drying, and waste water treatment (recycling or disposal). The cleaned parts are rinsed with deionised or relatively pure water. The water contains additives to enhance wash solution displacement and decrease the amount of water drag-out prior to drying. Rinsing removes any remaining contaminants, cleaning solution drag-out, and may serve as a final finishing step. Drying helps prevent surface oxide formation, eliminates potential corrosion caused by solution penetration between close tolerance surfaces, and dries parts.¹⁵ Conventional convective ovens can be used for drying. For certain lower temperature drying requirements, vacuum dryers can be custom designed and fabricated.

The simplest aqueous immersion cleaning machine configuration consists of a single wash tank. The demands of most cleaning jobs, however, will likely require more complex equipment configurations. If a part must be cleaned to a high degree of cleanliness, or if the quality of downstream process solutions is a great concern, several wash and rinse stages would be required.

¹⁵ Some manufacturing processes require dried parts; others, such as many metal finishing process lines (anodising or electroplating), do not.

4.3.4.2.3 Spray Cleaning

Spray cleaning equipment washes the parts by spraying them with an aqueous cleaner. Depending upon the resilience of the surface to be cleaned, high velocity spray can be used to physically displace soils. The major differences among spray machines relate to the manner in which the parts are handled. Spray washers are of three general types: batch, conveyor, and rotary.

Another basic difference in spray cleaning equipment is the way in which each generates mechanical energy to clean parts. While the mechanical action of spray cleaning equipment is spray action, the mechanical action of an immersion machine may be created by ultrasonic waves, vertical agitation of parts, or bath turbulence. A custom spray machine can combine spray action with the mechanical action used in immersion equipment.

Batch Spray Equipment: Batch spray cleaning equipment consists of a tank to hold the cleaning solution and a spray chamber with a door. Although batch spray machines have a single spray chamber, it is possible to rinse parts in the same chamber by using a separate set of "plumbing" equipment to spray water on the parts. The rinse water is then channelled away from the tank holding the cleaning solution (Kelly 1988). These chambers can be manual or automated.

Batch spray machines can be used for maintenance or manufacturing applications, but generally do not clean as thoroughly as multiple stage machines. Because maintenance applications tend to have lower throughput requirements than manufacturing applications, batch spray machines usually are used for maintenance cleaning. For precleaning of heavy soils, large cabinet wash and rinse chambers with spray nozzles located around the perimeter are available and have been designed to accommodate objects as large as train

electric motors and engines. For removal of heavy greases and tars, high pressure steam is an excellent medium for precleaning and, for some equipment maintenance activities, will provide acceptable cleanliness. This approach has the advantage that the soil and condensate will rapidly separate into water and oil phases, and in most countries neither phase is considered a hazardous waste.

Conveyorised Spray Equipment: Conveyorised spray cleaning equipment consists of a tank to hold the cleaning solution, a spray chamber, and a conveyor to feed parts through the machine. A more complex conveyorised system includes multiple wash and/or rinse stages along the conveyor, each stage with its own tank. The rinse water may be recirculated, especially if it contains a treatment chemical such as a rust inhibitor. The rinse water may be discharged if throughput is high or if parts drag significant quantities of cleaning solution out of the wash stages.

Conveyorised equipment is usually used in manufacturing applications with high throughput requirements where parts have flat, even, controlled surfaces. The advantages of conveyorised equipment are high throughput and automated parts handling. If parts are processed before cleaning so that they may be handled automatically from a process conveyor, it may be unnecessary to manually handle the parts during cleaning. Conveyorised spray washers can clean all sizes of parts from a variety of industries. The amount of wash and rinse water required can be as low as 10 percent of that used in batch cleaning per unit surface area of the part. This approach reduces the amount of waste water generated as compared to immersion cleaning and rinsing. For small parts with uneven and curved surfaces that may not be readily cleaned with immersion and agitation, dishwasher-type units with rotating parts holders and multi-directional spray nozzles are available.

Rotary Spray Equipment: Rotary spray equipment is very similar to conveyorised spray equipment except for the manner in which parts are handled. A rotary machine employs a steel drum with a partition that spirals along the inner surface of the drum such that when the drum is rotating, parts will be transported along the length of the drum. The drum is perforated so the spray can impinge on the parts to be cleaned.

Rotary spray washers are designed to clean small parts, such as screw machine parts (e.g., nuts and bolts) and small metal stampings. Rotary equipment can clean large volumes of parts, but the parts must be able to withstand the tumbling action of the rotating drum. Parts with delicate outer diameter threads and polished parts that should not be scratched should be cleaned in a different type of machine using a basket with a locking lid that can hold the parts in place during cleaning (Taylor 1988). Because high throughput can be achieved with the rotary machine, the machine tends to consume more energy than other types of spray machines. The throughput ability of rotary equipment also makes it a good candidate for high volume manufacturing operations.

4.3.5 Emulsion Cleaners

Emulsion cleaners effectively clean metal parts using techniques such as ultrasonics or fluid circulation. In emulsion cleaning, a water-immiscible solvent is dispersed in the form of tiny droplets in the water phase using surfactants and emulsifiers. Emulsified solvents have a low vapour pressure, low evaporative loss, low flammability and flashpoint, and potentially lower solvent purchase cost than CFC-113. Disadvantages include low soil saturation capacity and difficulties in recycling and disposal. One promising group of emulsion cleaners is based on hydrocarbon/surfactant blends, including terpenes. Terpenes can be used in both manual and cold immersion cleaning

operations. Some of these terpene cleaners are commercially available (Suciu 1989).

4.3.6 Plasma Cleaning

Plasma cleaning is similar to thermal heating or cleaning,¹⁶ but the plasma energy can be much higher than that achieved thermally without the risk of damaging the part surface. During plasma cleaning, ion bombardment impinges plasma molecules (e.g., dry nitrogen or argon gas) and charges them to a higher energy state than the bond energy that exists between the contaminant and the substrate, thereby releasing the contaminant from the substrate. Plasma cleaning has been used to establish standard surfaces for testing the adhesion of various coatings and to clean laboratory vacuum systems (Balwanz 1979).

4.3.7 No-Clean Alternatives

A number of companies are beginning to market water-soluble and emulsifiable machining and metal forming lubricants, some of which are non-chlorinated. These products tend to be much easier to remove with aqueous cleaners, and are less of a concern for worker exposure. The use of hot water spray or hot water with ultrasonics is sufficient to remove most lubricants that contain emulsifier packages. In this case, the waste stream could be separated into oil and water phases. Each phase could be treated and possibly reused, or disposed in an environmentally acceptable manner. Other alternative lubricants under development include "dry" lubricants and thin polymer sheeting which can be peeled from the surface after the metal forming

¹⁶ Balwanz (1979) states that "thermal [cleaning] raises the temperature of a surface to drive off the more volatile, less tightly bound contaminants from surfaces, such as the use of heat to drive water vapour from stainless steel surfaces prior to welding."

operation. These products are in their infancy; they do, however, offer the potential for eliminating the need for degreasing.

Lubricant spray applicators which discharge a fine well-controlled mist can decrease lubricant usage without affecting product quality. Also, material flow through production should be reassessed to minimise the number of times that a part is degreased and to consolidate the cleaning operations into a centralised unit or location. In many plants, parts are degreased two and possibly three times before finishing and assembly. Consolidation of cleaning operations will decrease the amount of solution treated and waste generated (Evanoff and Weltman 1988).

Segregation and pre-cleaning of heavily soiled parts can extend bath life. Heavily soiled parts can also be routed separately through a single pre-cleaning system, which has the effect of decreasing the amount of contaminated cleaner being generated in the main production area cleaning systems, because the amount of soil entering these systems is minimised (Evanoff and Weltman 1988).

4.4 COST OF ALTERNATIVES

Because very few large-scale degreasing systems have been replaced with water-based cleaners at this time, a valid cost comparison between CFC-113 systems and aqueous cleaning systems is not possible. In general, the capital cost of replacing vapour degreasers with aqueous wash-rinse-dry cycles and cleaner regeneration and rinsewater recycle technologies will be greater than purchasing a high efficiency CFC-113 system complete with state-of-the-art air emissions controls. Contributing to this increase is the cost of rearranging plant operations to accommodate a doubling or tripling of required floor space, installation of tanks (which can include breaking of concrete or reinforcement of floors and structures) and sophisticated gantries and

conveyors. Small, simple systems which require wash-rinse only will tend to have lower capital costs than a comparable, new CFC-113 system.

In both cases, the operating costs for aqueous systems should be lower than CFC-113 systems since the cleaning material will be less expensive, less cleaning material will be used, disposal costs will be lower, and, depending on operating temperature and tank volume, energy costs may be reduced.

4.5 ENVIRONMENTAL CONSIDERATIONS

This document is not a risk assessment and therefore only contains a general description of some of the environmental health and safety issues. The health and environmental effects of these technical options need further investigation. Many of the soils removed by cleaners are themselves toxic. Certain commercial solvents are generally recognised as toxic while others are suspected but not confirmed as toxic. Other cleaners including aqueous and terpene cleaners may also be hazardous, however, only limited testing of these chemicals has been completed. Nonetheless, the use of some toxic chemicals is permitted in certain cases by governmental authorities with strict workplace controls and effective waste treatment and/or disposal. However, regulatory measures are not available in all locations. In these circumstances it may be prudent to select cleaning options that do not depend on workplace controls and waste treatment.

The carcinogenicity, mutagenicity (genotoxicity), acute, chronic, and developmental toxicity, neurotoxicity, and ecotoxicity of the alternative compounds that could be used in cleaning applications must be evaluated prior to their use. Waste solvent or waste water should be properly treated, disposed of or destroyed to prevent creating new environmental problems in solving concerns about stratospheric ozone depletion. Committee members do not endorse the worker safety, or environmental acceptability of any of the

technical options discussed. More information on health and safety issues of the alternatives will become available as development of technical options continues. This information will be useful in selecting alternatives to CFCs, 1,1,1-trichloroethane, and carbon tetrachloride solvents.

Aqueous cleaning processes may discharge glycol ethers, phosphates, high concentrations of silicates, and surfactants that are not readily biodegradable. Maximum use of in-house recycling reduces batch discharges, but authorities should be consulted to ensure that the local waste-water treatment facilities can effectively treat these chemicals. Discharges of dissolved metals and potentially harmful organics are of concern, and require effective application of industrial pretreatment technologies.

Solution treatment equipment can be integrated into the wash and rinse tanks used in immersion cleaning processes, depending on whether the goal is to maximise recycling of solutions or to pretreat all solutions prior to disposal. A number of treatment devices are available to fit the particular cleaners, soils, and tank designs.

Spent cleaning solutions often are alkaline and can contain pollutants such as oil, grease, and dissolved and suspended metals. The waste water will require treatment depending on the pollutant types and concentrations present. Disposal may include pretreatment prior to discharge or hauling by an authorised contractor. The frequency and amount of waste water discharge can be reduced by using any of a number of in-process solution maintenance techniques.

To maintain the quality of aqueous cleaning solutions, filtration devices and coalescing oil-water separators can be used to remove particulate matter, heavy oils, and grease. Belt, rope, disk, and floating skimmers can remove free floating oils from the surface of operating wash tanks. Rinse

tanks can be treated in a similar manner using fine mechanical filters in the 50 to 100 micrometer size range. If deionised water quality is required, activated carbon followed by a mixed bed of anion and cation exchange resins or a reverse osmosis membrane system can be used.

Microfiltration and ultrafiltration technologies can be used to treat batches of wash solution to break the cleaner-soil emulsion. If proper filter membrane pore sizes are selected, the treated cleaning solution can be adjusted to operating concentration and the concentrated waste (50 to 70 percent oil) can be packaged for disposal. For systems operating under light soil loading, a simple mechanical filtration process may be sufficient to extend wash solution life. Pressurised basket filters in the 50 to 100 micrometer range remove metal fines and other inorganic solids. A properly designed system can concentrate oil waste and recycle the bulk of the cleaner and rinsewaters. Manufacturers can provide simple titration procedures that determine the concentration and amount of alkalinity in the recovered cleaner for process quality assurance and adjustment.

Air emissions of chemicals associated with aqueous immersion cleaners will occur. The losses will result from entrainment of cleaning chemicals on parts removed from the cleaner and evaporation of chemicals from solutions heated to 49-72°C. Evaporation can be reduced through the incorporation of automated covers and modification of the gantry system that transfers parts between tanks.

The principal liquid waste stream from emulsion cleaners results from cleaning solution that is no longer recyclable, due to unacceptable pH or loss of cleaning power. If there are no organic materials with threshold limit values, and the metal content is quite low, the solution must be treated prior to discharge using pH adjustment and either organic treatment with an

activated sludge system or an industrial waste pretreatment process, such as metal ion removal. In many cases a cleaning solution can be pre-treated with pH adjustment, ultrafiltration, and if necessary, biological treatment prior to discharge.

Rinsewaters must be pre-treated with activated carbon to remove trace organics and with ion exchange resins to remove cations and anions prior to discharge. Discharge of the wash solution and rinsewater could be reduced if recycling equipment is used.

Oil removal systems remove sludge consisting of oils, greases, water, and inorganic solids. This material should be handled as a hazardous waste, unless analytical data and regulatory officials indicate otherwise.

4.6 POTENTIAL GLOBAL REDUCTION OF CFC-113 IN METAL CLEANING APPLICATIONS

For general degreasing of metal surfaces and parts, aqueous immersion cleaners and solvent emulsions can be substituted for all metal cleaning applications except those involving tubing, complex shapes, materials sensitive to water or oxidation, or time-critical processes. The Committee consensus is that the alternatives discussed in this chapter can reduce the CFC-113 used in metal cleaning by 90 percent or more with aqueous and emulsion cleaners being viable substitutes for over 75 percent of the current CFC-113 use. These alternatives could be substituted for CFC-113 within five years. The remaining complex cleaning applications can be substituted with sophisticated aqueous systems. However, these systems would require a major research and design effort and would have high capital costs. The alternatives will be able to substitute for CFC-113 use in virtually all metal cleaning applications by, or before, the year 2000.

CHAPTER 5

DRY CLEANING INDUSTRY

5.1 OVERVIEW

The dry cleaning industry is a relatively minor user of CFC-113, representing less than five percent of worldwide CFC-113 consumption in 1985. This use may be further reduced in the future by instituting specific operation and maintenance procedures, using HCFC substitutes currently under development and establishing centralised cleaning facilities. These substitutes are likely to be commercially available in the next three to five years. The Committee consensus is that the alternatives discussed in this chapter could replace all CFC-113 used in the dry cleaning industry by, or before, the year 2000.

5.2 CFC-113 USE IN THE DRY CLEANING INDUSTRY

Organic solvents are used to clean fabrics because, unlike water, they do not distort fibres. Water cleaning of many materials, combinations of linings, and interfacing in garments can shrink or stretch fabrics. CFC-113 is used as a dry cleaning solvent because of its low toxicity, stability, excellent solvency, nonflammability, and relatively low boiling point.¹

5.2.1 Dry Cleaning Equipment

Dry cleaning machines are designed to operate with only one solvent and currently are not easily converted to another solvent use. Some new machines

¹ The relatively low boiling point of CFC-113 minimises energy requirements and reduces the risk of damage when cleaning heat sensitive fibres. Perchloroethylene, the most widespread dry cleaning solvent, requires more energy than CFC-113 for solvent recovery from clothes and solvent distillation.

may be able to operate with a choice of solvents, given relatively minor modifications. Unlike some solvents that are used in machines where the clothes are transferred from a washer to a dryer (known as the transfer process), CFC-113 is used in totally enclosed dry-to-dry machines.² CFC-113 machines usually incorporate sophisticated solvent recovery systems (filtration and distillation) to ensure that the solvent is continually purified for reuse. The dry-to-dry design and solvent recovery process minimise solvent emissions. A typical CFC-113 dry cleaning machine cleans more than 50 kilograms of clothing for every litre of solvent consumed. This ratio implies an average commercial shop use rate of five to seven litres of CFC-113 per week, assuming that the dry cleaning machine is correctly used and maintained.

5.3 ALTERNATIVES FOR REDUCING OR REPLACING CFC-113 USE

5.3.1 Conservation and Recovery Practices

Solvent losses in dry cleaning machines result from poor recovery (drying), leakage, distillation losses, and incorrect handling during refilling and servicing. Table V-1 lists the reasons for losses from these machines. Improved operator practices and better engineering and controls could conserve much of the CFC-113 solvent currently lost. Recycling and recovery technology is already at an advanced stage where totally enclosed machines feature refrigerated condensation of solvent vapour and activated carbon adsorption of any trace emissions of vapour. Operation and maintenance practices also can ensure that CFC-113 emissions are low. Such practices

² A CFC-113 dry cleaning machine is similar to a combined washing machine/tumbler dryer, but uses an organic solvent rather than water and detergent. Clothes are washed and dried in the same machine, preventing solvent emissions that occur when clothes must be transferred to a dryer.

Table V-1. GENERAL SOURCES OF SOLVENT LOSSES
FROM DRY CLEANING MACHINES

Leakage at the distillation hatch
Leakage at the needle trap hatch
Leakage at the fluff filter
Leakage at the charging door
Leakage at the lids for the heating and refrigeration coils
Leakage at the main axel seals
Leakage at the pipe connections
Spillage during refilling
Clogged air cooled condensers
Substandard maintenance of the fluff filter
Inadequate cooling water flow
Solvent in the condensed water
Cleaning of the needle trap, especially during operations
Excessive build-up of fluff between the outer and inner drums
Negligence during filter replacement or improper machine design
Inadequate final distillation
Overloading
Incorrect assembly and installation
Humidity in the cooling system
Incorrect choice of temperatures
Substandard maintenance

Source: Ahmadzai 1989c.

include activating the drying fan prior to opening maintenance manholes, and daily cleaning or replacement of the fluff filter.

When a machine has not been operated for a number of hours, solvent vapours will fill the machine space. By activating the drying fan prior to opening maintenance manholes, the vapours can be regenerated. Machines can be equipped with a special timing device that activates the drying fan one to two minutes prior to opening the machine door, thereby reducing solvent losses. In general, inspection manholes for the cleaning chamber, needle trap and fluff filter should always remain closed during operation and should be opened for the shortest possible interval during servicing. In machines equipped with a needle trap that is separate from the regeneration system, special precautions should be taken when cleaning the trap and all residue from the needle trap should be placed in the fluff filter for drying.

Efficient operation of the refrigeration unit in dry cleaning machines can reduce CFC-113 losses by up to 25 percent. The average loss of CFC-113 in dry cleaning machines is estimated to be one to two percent per cycle. The large variations in the size of the loads processed by machines result in varying quantities of uncondensed vapours being left in the distillation units of machines. Monitoring devices are available to measure the various loads on the refrigeration unit or heat pump and to better control temperatures. All CFC-machines also can be fitted with a low pressure sensor and regulator for the cooling coils. Such a device monitors the optimal condition for coil operation and switches off the machine when excessive humidity builds up in the expansion vent or when the level of refrigerant is inadequate. In conjunction with installation of a low pressure device, the evaporation and condensation temperatures for the refrigeration cell can be adjusted. The

suppliers for the respective machines can provide the relevant values for optimal drying efficiency.

Filter replacement also is a significant point of solvent losses. A small filter, for example, contains approximately four to five kilograms of solvent after drainage. With proper filter replacement techniques, this solvent can be recovered in the cleaning drum of machines. Some machines, however, are equipped with one large filter or many small filters that do not fit the machine drum. Machines with more than four filters can be reconstructed so that filtration takes place only through two filters. Those filters not operating should be put aside for drainage and subsequent regeneration. Machines with a single filter that is too large for the drum can be equipped with sealed drainage vessels that are attached to the machine's regeneration system or stored and transported to a special regeneration facility.

A number of daily operation and maintenance activities also can be conducted to reduce solvent losses from CFC-machines. Because lower air velocity enhances drying time, the fluff filter should be cleaned or replaced daily. Prior to system start-up, the cooling water circulation system should be checked as well as the refrigeration system, refrigerant and oil levels. In addition, all seals and gaskets should be checked and adjusted daily. When operating the equipment, the machine should not be overloaded, and one should check that a batch is dry prior to opening the machine.

Other preventive maintenance practices include cleaning the distillery only when it is cold, ensuring that the temperature of the refrigeration cell does not fall below the freezing point of the solvent and regularly cleaning the temperature sensors. In addition, the pressure equalisation device should be checked to ensure that solvent is not allowed to escape, and the activated

carbon filter should be inspected to determine the amount of solvent recovered. Finally, condensed water from the aqueous separator should be collected in a transparent container. Before emptying the container, the liquid should be checked for the presence of any solvent. If solvent is present, it should be separated prior to emptying the container.

5.3.2 Alternative Solvents

A number of solvents can be used as CFC-113 alternatives in dry cleaning operations. Table V-2 lists several chemical characteristics of the alternatives discussed below.

1,1,1-Trichloroethane³ is an effective substitute for CFC-113 in dry cleaning operations. The U.S. EPA does not classify 1,1,1-trichloroethane as a volatile organic compound (VOC) (HSIA 1987). In addition, it is nonflammable. It is possible, therefore, that some substitution of 1,1,1-trichloroethane will occur as users confront rising prices and less availability of CFC-113. However, 1,1,1-trichloroethane has been identified as an ozone depleting substance and may be added to the Montreal Protocol in 1990.

5.3.2.1 Perchloroethylene

Perchloroethylene is the most widely used dry cleaning solvent. Due to its relatively strong solvency power, however, it is not suitable for every cleaning task. Perchloroethylene has recently been implicated in ground water pollution problems in several countries. In addition, some concerns have been raised about the accumulation of perchloroethylene in foodstuffs stored in premises adjacent to dry cleaning operations that use perchloroethylene.

³ 1,1,1-Trichloroethane is also referred to as methyl chloroform, TCA, and CH_3CCl_3 .

Table V-2. CHEMICAL CHARACTERISTICS OF SELECTED
DRY CLEANING SOLVENTS

Solvents	Flammability	Boiling Point (°C)	Heat Required to Boil One Cubic Metre ^a (J)	Kauri Butanol Value
CFC-113	NF ^b	47.6	323 x 10 ⁶	31
Perchloroethylene	NF	121.1	583 x 10 ⁶	90
Petroleum-Based Solvents	F ^c	157-196	N/A	36
1,1,1-Trichloroethane	NF	70.0-75.0	454 x 10 ⁶	124
CFC-11	NF	23.8	329 x 10 ⁶	60
Trichloroethylene	NF	85.9	549 x 10 ⁶	130
HCFC-141b	NF	32.1	282 x 10 ⁶	Not Tested
HCFC-123	NF	27.9	251 x 10 ⁶	Not Tested

^a Heat required to boil one gallon of solvent from 20°C.

^b NF - Nonflammable.

^c F - Flammable.

Sources: ABLCRS 1986, Rodgers 1989, Kirk-Othmer 1983, Basu 1989.

Some studies have implicated perchloroethylene as a possible human carcinogen, although recent toxicological and epidemiological evidence indicates that this is not proven (EPA 1989b). In the United States the government has recently allowed the continued use of perchloroethylene but with more stringent workplace and environmental controls. An increase in perchloroethylene use is possible with reduced CFC-113 availability. It is more likely, however, that users would tighten up their control mechanisms on existing CFC-113 machines to reduce leakages until such time as an alternative solvent becomes available.

5.3.2.2 White Spirit (Stoddard Solvent)

Although the flammability of white spirit effectively precludes its use in commercial shops, with proper precautions it can be a substitute for CFC-113 on many fabrics. In Australia, for example, a fabric labelling convention has been introduced that designates white spirit as a substitute for CFC-113 in the dry cleaning of specific fabrics (Standards Association of Australia 1987). Despite epidemiological studies, there are unresolved issues concerning the toxicology of white spirit. Also, the emission of hydrocarbon solvents into the atmosphere is receiving increasing attention by environmental regulators.

5.3.2.3 HCFCs

A number of HCFCs currently are under development and are likely to be available commercially in the next three to five years. Possible substitutes include HCFC-141b and HCFC-123.

5.3.2.4 Other Alternative Solvents

Other classes of chemicals, such as iso-paraffins, solvents derived from sugar cane, and hydrocarbon/surfactant blends are possible alternative dry cleaning solvents.

More research is necessary to determine how extensively these alternatives could be used in dry cleaning operations.

5.3.2.5 Centralised Processing Facilities

The establishment of centralised cleaning facilities could augment the controls on solvent losses that can be achieved at small, individual dry cleaning establishments. At centralised facilities additional investments in control devices and standardised operation and maintenance practices could effectively reduce total solvent losses.

5.4 COST OF ALTERNATIVES

Dry cleaning machines represent the largest single capital investment in setting up a dry cleaning operation. Because the majority of dry cleaning businesses are small, the high capital cost of dry cleaning equipment is an important cost factor in the alternative selection process. Dry cleaning machines usually are designed for 12 to 15 years of operation. Furthermore, most machines are designed to operate with a specific solvent and cannot be modified to use a different solvent. The costs of reducing and eliminating CFC-113 use, therefore, will be incurred in purchasing new machines that do not use CFC-113 solvents.

5.5 POTENTIAL GLOBAL REDUCTION OF CFC-113 USE IN THE DRY CLEANING INDUSTRY

Significant reductions of CFC-113 solvent losses from dry cleaning uses are possible, and a 50 percent reduction of these emissions by 1991 is realistic. In the short-term, conservation and recovery methods can be used to reduce CFC-113 consumption in dry cleaning industry applications. Increased technical training and education of personnel operating dry cleaning shops aimed at making them aware of the reasons for solvent losses, the measures they could adopt for reducing solvent losses, and proper maintenance and servicing procedures would be the first step in reducing solvent losses.

Losses also could be reduced if centralised cleaning facilities were established at which sophisticated engineering controls and operating procedures could be instituted and closely monitored. Finally, fabric-cleaning specifications should be set that designate alternative solvents such as white spirits as viable substitutes for CFC-113. Currently, most dry cleaning machines cannot be retrofitted to accept different solvents. As a result, long-term reductions in CFC-113 use will occur as the capital stock of machines turns over to new machines that do not use CFC-113. Over the long-term, alternative solvents, such as white spirits and the newer HCFCs could be used more extensively.

The Committee consensus is that CFC-113 use in dry cleaning industry applications can be reduced in the short-run by implementing conservation and recovery practices. No CFC-113 should be necessary in this end use by the year 2000. CFC-113 use can be eliminated over the next decade through the use of currently available alternative solvents, such as white spirit, and other solvents that are under development, such as HCFCs. Furthermore, the Committee agrees that garment manufacturers should be informed that clothing or other textile products that can only be cleaned in CFC-113 may, at some future date, no longer be able to be cleaned. It is recommended that labelling be introduced warning consumers that such garments may no longer be able to be cleaned.

CHAPTER 6

OTHER SOLVENT USES OF CFC-113 AND 1,1,1-TRICHLOROETHANE

6.1 OVERVIEW

Relatively small amounts of CFC-113 are used in a number of industry applications not discussed elsewhere in this report, including:

- use as a bearer media for coating and impregnation;
- use in vapour soldering technology;
- use in component drying;
- use in forced air cleaning of parts; and
- use in miscellaneous testing.

The Committee consensus is that all the CFC-113 used for these applications could be replaced by the alternatives discussed in this chapter by the year 2000 or sooner. Chapter 6 discusses these other solvent uses of CFC-113 as well as 1,1,1-trichloroethane¹ use in adhesives and aerosols.

6.2 BEARER MEDIA FOR COATING AND IMPREGNATION

In some applications, CFC-113 is used as a carrier of lubricants to reduce frictional damage. In a typical process, gold-plated contacts are dipped into a bath of CFC-113, two percent of which is a lubricant such as perfluorinated polyether. CFC-113 acts both as a cleaner and a lubricant bearer. Four CFC-113 alternatives have been identified for this application (Nordin 1988), and a viable alternative should be commercially available by 1991 (Nilsson 1988). These alternatives include the following:

- Use mechanical methods, such as spraying or rolling, to dispense the lubricant. (The problem of excessive application of the lubricant must be solved as the lubricant must not exceed four micrograms

¹ 1,1,1-Trichloroethane is also referred to as methyl chloroform, TCA, and CH₃CCl₃.

per contact. Developing a new application technology could take six months to one year);

- Apply the lubricant via emulsions. (These should be water-based emulsions if possible);
- Use an alternative solvent compatible with fluorinated lubricants. (HCFC-123 or HCFC-131 might be considered, however, these alternatives also contribute to ozone depletion); and
- Use an alternative lubricant. (The lubricants would have to be compatible with the plastics in use. Compatibility testing would probably take two years).

6.3 VAPOUR SOLDERING TECHNOLOGY

Vapour phase soldering, also known as condensation soldering, is a reflow method that involves boiling a liquid and introducing the cool electronic assembly with the unmelted solder into the hot vapour. The vapour raises the temperature of the cool electronic assembly and the solder until the solder melts. Because of its all-around heat application, vapour phase soldering is the only soldering process which, in principle, enables both sides of a substrate to be soldered simultaneously. It cannot, however, be used as the only soldering process in mixed assemblies because of the potential damage of temperature sensitive bodies on some leaded components (Pawling 1987). The primary liquids used in vapour phase soldering that are non-ozone depleting are non-flammable perfluorinated organic compounds.

The primary liquid used to generate vapour in a top-loading batch vapour phase solder system is costly. To minimise primary vapour losses, a less expensive secondary vapour blanket with a lower boiling point, such as CFC-113 (bp 46.6°C), often is used. The use of a CFC-113 secondary vapour blanket is estimated to cut losses of the primary vapour from standard top loading batch

equipment by a factor of 10 (Seidinger 1989). The CFC-113 also serves as a conduit for the release of toxic hydrofluoric acid and perfluoroisobutylene (PFIB) that may be generated when the primary vapour over-heats. To minimise vapour losses and emissions of toxic compounds, the blanket should be operated at a low a temperature. The interface of the two vapours forms a zone where the secondary vapour will also break down, releasing hydrochloric and hydrofluoric acids, phosgene, and carbonyl fluoride, all dangerous products that can be mostly eliminated by treating the condensate. This treatment will also reduce corrosion of the machine itself.

Three possible alternatives to using CFC-113 as a secondary phase vapour in reflow soldering include:

- Eliminate the use of a secondary vapour blanket. Although joint quality would not suffer, eliminating the secondary blanket could increase production costs for the reflow operation by a factor of ten. A primary vapour recovery unit is now available that claims to recover up to 80 percent of any primary vapour entering the extraction system. With this unit, net fluid costs could be reduced from approximately U.S. \$10-14/hr to U.S. \$3-4/hr.
- Use batch equipment that works without a vapour blanket. This equipment is currently available, and new models are being introduced.
- Use a secondary vapour blanket that does not deplete the ozone layer. Recently a perfluorocarbon liquid has been introduced as a possible substitute for the secondary blanket. It has a half life of approximately 1,000 years and does not contain chlorine, bromine, or hydrogen atoms.

Table VI-1 summarises a recent evaluation comparing CFC-113 and the substitute secondary blanket using vapour phase soldering equipment. The results of this test show that:

- both CFC-113 and the perfluorocarbon yield similar consumption figures;
- the rate of corrosion, as measured by the copper wire methods in the secondary zone, is somewhat lower for the perfluorocarbon;
- an equivalent amount of PFIB is generated for both chemicals; and
- the amount of total hydrohalic acids generated is much lower for the perfluorocarbon.

6.4 COMPONENT DRYING

Many electrical and electronic parts, such as pieces of optical equipment and delicate instruments, come into contact with water during processing. These parts must be dried promptly after cleaning to prevent rust, water stains, and general quality deterioration that can result in lower product reliability. A dedicated drying process is often used to achieve rapid drying. Typical dewatering techniques include:

1. Centrifugal processing and hot air drying;
2. Absorbent drying using alcohols such as ethanol, isopropanol, and acetone;
3. Vapour drying with non-CFC solvents, such as chlorocarbon;
4. Vapour drying with CFC; and
5. Displacement drying using CFC-113.

The trade-offs among these drying techniques are compared in Table VI-2.

Process recovery and conservation methods for CFCs in Alternative 4 are similar to the typical cleaning process systems.

Table VI-1. COMPARISON OF CFC-113 AND A SUBSTITUTE
PERFLUOROCARBON AS A SECONDARY VAPOUR BLANKET

Characteristic	CFC-113	Perfluorocarbon
Rate of Consumption (m^3/hr)	$1.14-1.51 \times 10^{-4}$	$1.14-1.51 \times 10^{-4}$
Vapour Temperature ($^{\circ}\text{C}$)		
Secondary vapour	55-60	58-61
Primary vapour	216-218	217-218
Rate of Corrosion (mm/yr)	$5.59 \text{ E-}2$	$2.03 \text{ E-}2$
PFIB Generation ($\mu\text{gm}/\text{m}^3/\text{hr}$)	<0.227	<0.227
HF Generation ($\mu\text{gm}/\text{m}^3/\text{hr}$)		
150°C	682 (8 HCl)	1,140
215°C	9,090 (240 HCl)	4,420

Source: Seidinger 1989

6.4.1 Drying Semiconductors

CFC-113 is used for displacement drying of semiconductor² materials such as wafers and integrated circuits. Integrated circuits, the major product of the semiconductor industry (Van Zant 1985), are a combination of electronic devices such as transistors, diodes, resistors, and capacitors, placed in a single semiconductor crystal.

CFC-113 is used to dry wafers during the fabrication of integrated circuits. Wafer preparation, oxidation, doping, and layering are the major steps in fabrication of an integrated circuit. Depending on the integrated circuit desired (e.g., Metal Oxide Semiconductors (MOS), bipolar, etc.) different process steps are repeated.

6.4.2 Drying Printed Circuit Boards

Of the four processes commonly used for critical drying of printed circuit boards during manufacturing, two processes use CFC-113. These processes involve:

- Dipping the wet circuits in a circulating bath of pure CFC-113. The water is displaced, floats on the solvent surface, and is pumped off the surface into a separator so that the boards are not re-wetted when removed. This bath is usually followed by passage of the board through a vapour degreaser containing a CFC-113/ ethanol azeotrope to remove residual water traces; and
- Dipping the wet circuits into a surfactant/CFC-113 mixture to emulsify the water, then using a vapour degreaser to remove the surfactant.

No estimates are available of the amount of CFC-113 used for this application, but the quantity is believed to be small (Ellis 1989). The other

² Semiconductors are materials with an electrical conductivity between that of a conductor and an insulator. They are either discrete devices such as transistors or thyristors, or integrated circuits that contain two or more devices in a single semiconductor crystal.

Table VI-2. COMPARISON OF DRYING TECHNIQUES

Dewatering Technique	Advantages	Disadvantages
Centrifugal processing and hot air drying	Low equipment cost, handling.	Can be used for simple shape products. High energy costs, spots.
Absorbent drying using alcohols	Drying at room temperature.	Large solvent consumption. Needs fire protection measures.
Vapour drying with non-CFC solvents	Satisfactory drying at 50°C or below.	Ozone depleting.
Vapour drying with CFC	Satisfactory drying at 50 C or below	High ozone depleting.
Displacement drying using CFC-113	Energy efficient, low operating costs.	Higher equipment costs. May leave a residual film. Depletes stratospheric ozone layer.

two critical drying processes use alternative solvents. The circuits can be dried by:

- Dipping the wet circuits into two successive isopropanol tanks fitted with dryers; and
- Dipping the wet circuits into a water-displacement product based on toluol. The water drains through a grid in the bottom of the tank.

CFC-113 use could be eliminated by switching to these two alternative drying processes. Isopropanol and toluol are volatile organic compounds.

6.5 WAFER CLEANING DURING SEMICONDUCTOR MANUFACTURING

The degreasing of semiconductors is part of the silicon wafer fabrication process. CFC-113 and 1,1,1-trichloroethane are used in the electronics industry to degrease semiconductors. Recently two companies jointly announced the introduction of a new technology for cleaning semiconductor wafers. The machine is called an "ice cleaning apparatus" and it does not require CFC-113 or 1,1,1-trichloroethane for operation. The cleaning process uses a spray of ice particles 30 to 300 microns in diameter delivered at close to the speed of sound at -50°C and below, and a vaporising of ice particles from 0.1 to 3 microns in diameter. The hardness and size of the particles as well as the pressure and angle of the spray can be controlled as needed. This process is designed for use at the vapour degreasing stage of wafer processing (Nikkei Sangyo Shinbun 1989, Denpa Shinbun 1989).

6.6 MISCELLANEOUS TESTING

CFC-113 is used to detect leaks in aircraft fuel-tanks. Any halocarbon solvent compatible with the products employed may be used as a substitute, including low ODP types. Helium is being applied successfully for lead detection (Algodsson 1989).

CFC-113 is also used for the chemical analysis of general CFC compounds, such as in the analysis of general CFC emissions, work-space concentrations, and quality testing. CFC-113 also is used as a solvent in analyzing oils and greases in aqueous solutions. Based on infra-red spectrophotometry, a special Swedish environmental control standard (SIS-028145) requires a solvent that does not contain C-H bonding. Both CFC-113 and carbon tetrachloride meet this standard. CFC-113 is used because of the toxicity and carcinogenic effects associated with carbon tetrachloride. Another alternative to using CFC-113 in chemical analyses is the Gas Chromatographic (GC) methods as a replacement for the infra-red spectro-photometric (IS) methods. However, due to variable C-H bonding in each sample, a correlation should be established between the IS and GC methods. It is estimated that CFC-113 alternatives could be commercially available by the end of 1994, and that all CFC-113 use can be eliminated by, or before, the year 2000.

6.7 USE OF 1,1,1-TRICHLOROETHANE IN ADHESIVES

1,1,1-Trichloroethane has several physical characteristics that provide desirable performance properties for adhesive applications. Table VI-3 presents physical properties of 1,1,1-trichloroethane compared to those of selected conventional solvents used in adhesive applications. 1,1,1-trichloroethane and methylene chloride have no flash point.³ The other conventional solvents in the table have low flash points and low explosion limits and, therefore, are considered flammable solvents.

1,1,1-Trichloroethane also displays low water affinity. Only 0.05 grams of 1,1,1-trichloroethane can be dissolved in 100 grams of water at 25°C. Therefore, it is used as a coalescent in some water-based adhesive systems.

³ Flash point temperature is the lowest temperature at which vapours above a volatile combustible substance ignite in air when exposed to flame.

Table VI-3. PHYSICAL PROPERTIES OF COMMON ADHESIVE SOLVENTS

Solvent	Flash Point Open Cup (°C)	Flammable Limit in Air 25°C (Volume %)		Water Soluble in 100g Solvent (g)	Kilograms/ Litre 20°C
		Upper	Lower		
1,1,1-Trichloroethane	NF ^a	15.0	7.5	0.05	1.314
Methylene Chloride	NF	22.0	14.8	0.20	1.316
Toluene	7.22	7.0	1.3	0.05	0.870
n-Hexane	-27.8	6.9	1.25	0.01	0.678
Methyl Ethyl Ketone	-5.6	11.5	1.81	11.80	0.804
Ethyl Acetate	-2.2	11.0	2.25	3.3	0.900

^a NF - No Flash Point.

Source: Dow 1984.

In addition, 1,1,1-trichloroethane evaporates faster than other solvents which allows increased throughput in applications where drying time contributes to the overall process yield (e.g., in pressure-sensitive tape manufacturing). The density of chlorinated solvents is greater than that of the conventional solvents used in adhesives. According to Bashford (1983), the solids/viscosity relationship of the diluted adhesive is different than the relationship obtained with conventional solvents. When selecting solvent alternatives these differences have to be taken into account with regard to application cylinders, machine speeds, etc.

1,1,1-Trichloroethane has a mid-range solvency when compared to the conventional adhesive solvents. 1,1,1-Trichloroethane is an active solvent for alkyl, acrylic, chlorinated rubbers and many phenolic resins; it is a diluent for nitrocellulose, vinyl, and epoxy resins (Dow 1984). 1,1,1-trichloroethane can be mixed with other solvents to adapt its solubility strength to the needs of a specific resin system. This task is usually performed by the adhesive formulator who customises solvent blends to specific solubility needs.

In the U.S., 1,1,1-trichloroethane is exempt from volatile organic compound (VOC) regulations in most states and, therefore, some adhesive manufacturers and users consider the use of the solvent as a viable alternative to other organic (VOC) solvents. Several sources indicate the use of 1,1,1-trichloroethane as a replacement for organic solvents (Bashford 1983, Wood 1984, Deitch 1984, Gniecko and Helm 1987). Specific examples include:

- manufacture of styrene-butadiene latex adhesives (Adhesion 1984),
- formulation of polyurethane adhesives (Frisch and Xiao 1988),
- replacing extremely flammable solvents in pressure-sensitive tape and label, and in industrial and consumer adhesives (Fragiacomo 1988),

- substituting flammable solvents in PVC flooring adhesives (Adhesives Age 1988), and
- replacing ethyl acetate solvents in laminating adhesives used in packaging (PFFC 1985).

In general, 1,1,1-trichloroethane is used as active solvent in solvent borne-adhesives and as a diluent in water-borne adhesives. Table VI-4 shows the specific binding substances (i.e., adhesive type) where 1,1,1-trichloroethane is used.

There is a general trend in the U.S. and Western European adhesives industries towards replacing solvent-based adhesives with solvent free types, such as water-based and hot melt adhesives (O'Driscoll 1988). According to one market survey conducted in the U.S., volatile organic compound (VOC) regulations provided the initial impetus for moving away from solvent-borne technologies; however, for some industry sectors such as tapes, this shift would continue in the absence of regulations because alternative technologies are more competitive on a cost/performance basis (Ellerhorst 1982). The use of solvent-based adhesives is costly because this type of adhesive warrants flame proof equipment and extraction systems (O'Driscoll 1988). Solvent-diluted (as opposed to solvent-based) adhesives have also been on the decline for economic reasons (Kimel 1988). Two paths are available for solvent reduction in adhesives: established technologies and emerging technologies. Established technologies are water-based adhesives, hot melt systems, and solvent recovery systems in continuous operations. Emerging technologies include radiation cured adhesives, "high solids" adhesives, powders, and reactive liquids. These technologies are discussed in further detail below.

Table VI-4. ESTIMATES OF 1,1,1-TRICHLOROETHANE
CONSUMPTION BY USE SECTOR

Use Sector	Binding Substance
As Active Solvent in Solvent-Borne Adhesives	Styrene-Butadiene Rubber (SBR) Neoprene Natural Rubber Rubber Cement Other
As a Diluent or Coalescent in Water- Borne Adhesives ^a	

^a No data is currently available on the specific binding systems that employ 1,1,1-trichloroethane as a diluent and or coalescent.

Source: Based on Skeist 1987.

6.7.1 Water-Based Adhesives

Water-based adhesives use water, in lieu of organic solvents, as the primary solvent. Water is a logical substitute for organic solvents in 11 adhesives. A water-based adhesive can be a solution, a latex, or an emulsion. Solutions are made from materials that are soluble in neutral or alkaline water. Most natural adhesives are water solutions. Latexes are stable dispersions of solid polymeric material in an essentially aqueous medium (Landrock 1985). An emulsion is a stable dispersion of immiscible liquids. Emulsions usually appear milky white in the liquid state, and they dry to a clear film. In industry, the terms latex and emulsion are generally synonymous. Latex adhesives are more likely to replace solvent-based adhesives than solution adhesives because their synthetic binders provide more versatility and higher performance (Landrock 1985). However, latexes require more extensive formulation because they are produced from polymers that were not designed for use as adhesives.

The binding substances that are candidates for water-borne adhesives are natural binding substances including natural rubber; synthetic elastomers such as styrene butadiene rubber, neoprene, and isoprene; vinyl resins like polyvinyl acetate (PVAc) and polyvinyl chloride (PVC); acrylics; and epoxies (Landrock 1985). Some of these binding substances require additional formulation and additives like emulsifiers, surfactants, or additional resins. Water-based binding substances use the traditional methods for adhesive application. These include brush, spray, roll coat, curtain, flow, and knife coat (Landrock 1985).

Water-based adhesives have many advantages. Water meets clean-air goals, is non-toxic and nonflammable, is readily available, cuts inventory requirements, uses the same equipment (with minor modifications) as solvent-

based adhesives, and cleans easily during manufacturing (Manino 1981). In addition, water-based adhesives can be stored in less costly plastic or phenolic-coated containers (Manino 1981). Recent literature on water-based adhesives suggests that there is still much debate about the overall effectiveness of water-based adhesives in many end use sectors. In general, water-based adhesives show good durability, water resistance, and adhesion to a wide variety of substrates, especially in the area of nonporous to porous bonding (Chao and Hernisch 1986). Problems still exist in the bonding of non-porous to non-porous substrates because the water is difficult to evaporate from such substrates. Water-based adhesives can bond moist surfaces better than solvent-based adhesives. One inherent advantage of water emulsions is that viscosity is independent of molecular weight of the resin (Fries 1984). The higher initial molecular weight provides greater internal cohesive strength to the freshly made bond. This initial bond (or "green bond") is important to avoid uneven stress to the bond and blisters in laminating applications (Fries 1981 and Fries 1984). Poor initial bond strength has been a criticism of low molecular weight water-borne adhesives. Unlike solvent-borne adhesives and hot melts, there are no restrictions on the initial molecular weight of the resin for water emulsions.

The direct replacement of solvents by water is not feasible in all sectors. Selecting water as the vehicle in adhesives demands totally new concepts in raw materials and formulation as discussed above. Water-based adhesives often require special handling in manufacturing, storage, and application. They must be kept from freezing during shipment and storage (Landrock 1985). Problems with corrosion require that all storage and transfer pipes are corrosion-resistant. Some manufacturers, however, maintain that corrosion is not a factor if additives which prevent corrosion are

included in the formulation. In addition, one set of laboratory tests found water-borne adhesives not to be more prone to corrosion than solvent-borne adhesives (Manino 1981). The problem has not been resolved conclusively; more research and development is needed in this area. Another problem with storing water-based adhesives is that agitation is needed to maintain consistency of the dispersed materials in the adhesive solution. Yet agitation can cause foaming, and anti-foaming agents compromise performance.

Water-based adhesives reportedly have other performance disadvantages when compared with solvent-based adhesives. During application, water-based adhesives do not "wet" surfaces as well as their solvent-based counterparts due to water's inherent polarity and high surface tension. Minor contamination of the surface (i.e., oil, mould release, fingerprints) can lead to bonding problems.⁴ Water-based adhesives do not have the versatility of application provided by solvent-based adhesives. Although polar substrates such as natural rubber bond well with water-borne adhesives, nonpolar elastomer substrates such as ethylene propylene copolymers are difficult to bond (Manino 1981). Silicones and fluoroelastomers provide a greater challenge, and water-borne adhesives still cannot compete with solvent-borne systems in these areas (Manino 1981).

Drying ovens currently used for solvent-based systems are generally adequate to handle water-based adhesives. The argument that more energy is needed to dry water, which has a slower evaporation rate than most solvents, has not been established. On the contrary, drying water-borne adhesives in practice requires less total energy than solvent-borne adhesives. Water-borne

⁴ A solvent-based primer can boost performance by ensuring a clean substrate for the water-based adhesive. A primer uses less than half as much solvent as solvent-borne adhesives. 1,1,1-Trichloroethane has been used as a primer to degrease many substrates (Landrock 1985).

adhesives do not require an excess volume of heated air to dilute the concentration of solvent vapour under the lower explosive limit (LEL) (Fries 1981). With these air volume adjustments, less process energy is required and faster coating speeds can result (Fries 1981).

6.7.2 Hot Melt Adhesives

The Committee D-14 of the American Society for Testing and Materials (ASTM) defines a hot melt adhesive as one that is applied in a molten state and forms a bond upon cooling to a solid state (Fullhart and Mottershead 1980). Hot melts are primarily 100 percent solids thermoplastic bonding materials which achieve a solid state and resultant strength upon cooling. The major applications of hot melt adhesives are bookbinding, packaging, textiles, and product assembly including construction glazing and automotive door panel and carpet installation (Fullhart and Mottershead 1980). Application methods include melt-reservoir and pressure-feed systems (Landrock 1985). The binding substances that provide the foundation for hot melt adhesives are ethylene vinyl acetate (EVAc) and other polyolefin resins; polyamide (or nylon) and polyester resins; polyester/amide resin alloys; and thermoplastic elastomers (Landrock 1985). Foamable hot melts (e.g., polyethylene) form a superior bond with metals, plastics and paper (Landrock 1985).

Hot melts have several advantages. No solvents are used in hot melts, and therefore, they reduce air pollution. The hot melt equipment saves space and energy (Lipiec 1982). Using hot melt technology permits automation, lowering manufacturing costs and increasing productivity. With hot melts, the 100 percent solids shipments eliminates the excess freight costs involved in storing and shipping either water- or solvent-based adhesives (Lipiec 1982). Hot melts can be applied faster and more efficiently than water-borne

adhesives because there is no delay for evaporation (Kimel 1988). Hot melts are inherently water resistant. In part because no oven capacity is needed, hot melt pressure sensitive adhesives (PSAs) require far less energy to process than any other adhesive types (Maletsky and Villa 1981).⁵ Although earlier hot melt PSAs had unacceptable colour retention and UV resistance, present hot melt PSAs are clear and UV resistant (Maletsky and Villa 1984). Hot melt PSAs now compete with water-based acrylics in outdoor applications (Maletsky and Villa 1984). They have been used on paper labels for indoor applications since 1978.

Hot melts are, however, limited in several key performance characteristics. They have poor specific adhesion to a number of substrates. Performance problems with hot melt adhesives include material creep under load over time and at high temperatures, limited strength, and limited heat resistance (Landrock 1985). A specific hot melt acrylic used for pressure-sensitive applications has poor tack for many applications (Lipiec 1982). Room temperature shear resistance and elevated temperature shear resistance are also deficient in hot melt acrylic PSAs (Lipiec 1982). Any hot melt system requires the installation of an expensive equipment which does not use existing solvent system coating/drying equipment. In addition, the presence of hot equipment may be a danger to workers (Fullhart and Mottershead 1980). Finally, hot melts are more expensive per unit of formulated weight.

⁵ One case shows a reduction of about 3.165×10^7 Joules from a toluene solution at 60 percent solids to 100 percent solids hot melt. Even water-based emulsions require comparable energy at 50 percent solids, although they use slightly less energy than the 60 percent solvent system (Maletsky and Villa 1981). The percent solids directly influences the amount of energy saved, and this percentage varies depending on the application.

6.7.3 Radiation Cured Adhesives

Radiation curing is a production technique for drying and curing adhesives through the use of a form of radiant energy (i.e., UV, IR, electron beam (EB), gamma and x-rays). In essence, radiant energy becomes chemical energy in the forming of the adhesive bond. The binding agents cured with radiant energy are acrylics, epoxies, urethanes and other elastomers, anaerobic adhesives, and polyester resins (Adhesives Age 1988). Pressure-sensitive or 100 percent non-volatile formulations of adhesives are applied by conventional techniques between one or two plastic films and then cured by exposure to radiant energy (Chemical Week 1987). Application areas include electronics, communications, consumer products, transportation, packaging, and medical and dental uses (Bluestein 1982). Radiation cured adhesives are especially well adapted for the electronics and communications industries for encapsulating applications with end use requirements of resistance to environment, electricity, and aging. Pressure-sensitive tapes are another major application of radiation cured adhesives. High growth is anticipated for UV and EB curing adhesives.

The advantages of radiation cured adhesives are low energy costs, reduction of waste effluents and polluting gases and liquids, a longer shelf life of the adhesive, and the production of a more reliable product (Bluestein 1982). The elimination of product waste includes lower rejection rates, lower labour costs, and reduced cleanup and inspection times (Moreau 1988). Radiation cured adhesives are an option for new production facilities due to the simpler, space-saving equipment (Bluestein 1982). Among the radiation curable technologies, UV and EB curing have separate applications. UV curing works more cost effectively for smaller applications; whereas, EB curing is better adapted for large scale operations.

Radiation curable adhesives have some disadvantages. Existing capital equipment cannot be used for this type of adhesive without the addition of a cure unit (Bluestein 1982). In addition, the applications are limited for radiation cured adhesives.

6.7.4 High Solids Adhesives

One way to lower volatile organic compound (VOC) emissions is to increase the percent solids in an adhesive. In the specific example of polyester urethane laminating adhesives, high solids/low solvent adhesives are a viable alternative to solvent-borne adhesive systems. Using the existing technology for polyesters and polyester urethane systems, high solids have been very successful in laminating uses (Bentley 1983). One manufacturer supplies a 68.5 percent solids polyester urethane laminating adhesive which meets VOC regulations by lowering the amount of solvent used (Wood 1984). By lowering the amount of solvent used, high solids adhesives provide good performance characteristics, including initial bond strength, comparable to 30 percent solvent-based performance in medium and high demand applications (Wood 1984). High solids can be applied using existing equipment at normal line speeds with minor modifications.⁶

In other application areas high solids adhesives have not been as successful as in polyurethane laminating adhesives. For bonding rubber assemblies, high solids adhesive films are too thick, which results in limited versatility and generally poor performance (Manino 1981). In general, high solids adhesives cost more and perform worse than their solvent-borne

⁶ A metering device and a specially etched gravure cylinder are recommended with the 68.5 percent high solids but are not needed at 50-60 percent solids levels (Wood 1984).

counterparts at lower solids levels. This technology is being developed; wider application may be possible in the near future.

6.7.5 Powders

One-part epoxies, urethanes, and natural resins are often supplied as powders which require heat to cure (Frisch and Xiao 1988). Powders are only used for non-pressure-sensitive applications. They are generally applied in three ways: by sifting the powder onto pre-heated substrates, by dipping a preheated substrate into the powder, and by melting the powder into a paste or liquid and applying it by conventional means (Landrock 1985). One advantage of the powder form is that no mixing or metering is necessary; however, to maximise shelf life, powders must be refrigerated (Landrock 1985). No data are currently available comparing performance and cost with solvent-borne adhesives.

6.7.6 Non-Volatile Solids and Liquids and Reactive Liquids

Moisture cure adhesives and reactive liquids can be applied as 100 percent non-volatile solid and liquid systems. These adhesives are composed entirely of binding substances, modifiers, and fillers (i.e., they have no carrier or solvent). Moisture cure adhesives cure upon exposure to the humidity in the ambient air; this type of adhesive might not work well in dry climates. Moisture cure adhesives are available in 100 percent non-volatile liquids and solids, hot melts, solvent-borne formulations, and other technologies (Frisch and Xiao 1988). The 100 percent non-volatile moisture cure systems are of interest to this discussion because they offer another alternative to the solvent-based systems. The two primary binding substances used in moisture cure adhesives are isocyanates and polyurethanes (D'Autilio 1983). They are available as single and multiple component adhesives. The two-part system physically separates the binding agent from the curing agent

during storage. Although it requires metering and mixing to cure, the two-part system exhibits a longer shelf life. The two-component system also achieves higher performance. Both systems achieve compliance with volatile organic compound (VOC) regulations because they contain no solvents. Because moisture cure systems need no driers, they save energy (D'Autilio 1983). The application equipment is more compact than that of solvent-based systems, but moisture cure adhesives cannot use the existing equipment (Morphy et al. 1987). A two-component solvent-free isocyanate adhesive that does not require moisture to cure nor precise metering has appeared on the market. A thin coat of one component is applied to one part and a thin coat of the other to the second part. The two are brought together to form a rapid and strong bond (in a few seconds). As it is anaerobic, it is useful for joining metallic and other non-porous parts. Tests have shown that the electrical properties exclude this type of adhesive from electronics applications, such as bonding surface mounted components to substrates prior to wave soldering.

Reactive liquids are two-component adhesives that contain no solvents. Reactive liquids consist of one solution of an elastomer colloiddally dispersed in a monomer and a second solution which cures the first (via a free radical chemical polymerisation) to create the bond (Prane 1980). The binding substances for reactive liquid adhesive systems include epoxies, urethanes, polyesters, silicones, polysulphides, acrylics, modified phenolics, and resin compounds (Prane 1980). Reactive liquids are used for high performance structural applications. Application methods are similar to those used in contact adhesives, namely, brush, roller, or spray (Prane 1980). No information is currently available on the relative performance attributes of this emerging technology.

Substitution costs for the established alternative technologies are driven primarily by raw material costs because no major capital investments are required to implement these technologies (ICF 1989). Although research and development resources are also required to develop and test these alternative technologies (water-based adhesives, hot melt adhesives, and solvent recovery) for specific adhesive systems, reductions in 1,1,1-trichloroethane use are possible in the near to mid-term.

6.8 USE OF CFCs IN AEROSOLS

Small quantities (probably a few tens of tonnes per year) of CFC blends as the propelled liquid (not to be confused with the propellant, which is not the subject of this report) are used in the electronics industry. CFC-113/alcohol blends are popular in service establishments for localised defluxing after hand reworking of an assembly. This is a convenient method but is obviously limited to small-volume work for cost reasons. If no major toxicological obstacles appear, it is probable that an HCFC formulation would be able to replace the CFC-113. It is essential that such a formulation have as low an ODP as possible as it is evident from the nature of the usage that it all evaporates.

Another similar application is blended five percent CFC-113 with CFC-11/12. This blend provides local shock refrigeration of electronics components for diagnostic purposes. One company provides a substitute in the form of liquid carbon dioxide which forms solid gas as it is sprayed, at -73°C. Another company has offered a spray filled with pure LPGs (butane and propane) for this application, but this spray could provide a severe fire or explosion hazard if used on live equipment employing more than a few volts.

Other formulations which may contain CFC-113 or similar solvents are switch and contact cleaners, and lubricants.

6.9 USE OF 1,1,1-TRICHLOROETHANE IN AEROSOLS

Aerosol packaging is a popular method for storing and dispensing consumer and industrial products ranging from insecticides to hair sprays. In 1986, the worldwide aerosol industry produced an estimated 6.8 billion units. Western Europe is the largest producer, followed by the United States and Asia. 1,1,1-Trichloroethane consumption in the U.S. was approximately 41 million pounds (ICF 1989). It is estimated that Western Europe and Japan consumed 27.4 and 23.8 million pounds of 1,1,1-trichloroethane in 1984, respectively (ICF 1989). No data are available for the rest of the world. No information is currently available on current chlorinated solvent consumption trends in Western Europe, Japan, and the rest of the world, therefore, the discussion that follows focuses on the U.S. market for aerosols.

The major aerosol product end-uses where 1,1,1-trichloroethane is used includes automotive and industrial products, pesticides, and household products (ICF 1989). To address the substitution of 1,1,1-trichloroethane in aerosols, it is important to understand the function and properties of this solvent in the various product areas. 1,1,1-Trichloroethane functions as the active ingredient, not just the carrier, in various aerosol products (e.g., automotive degreasers and household cleaners). It is generally difficult to substitute this solvent in these applications because few non-chlorinated solvents have the desired properties. In comparison with non-chlorinated solvents, for example, the higher solvency and non-flammability of 1,1,1-trichloroethane make it an excellent solvent for aerosol applications. 1,1,1-Trichloroethane's high density adds to container weight while its high stability translates to a long shelf life. Other properties that make 1,1,1-trichloroethane especially well-suited for aerosol applications are its high evaporation rate and its ability to generate a spray of small particle size.

Quick evaporation allows 1,1,1-trichloroethane to deliver the active ingredient efficiently and small particle size results in a good spray pattern. Non-chlorinated solvent substitutes (e.g., petroleum distillates, toluene, and mineral spirits) are flammable and lack these combination of desirable properties.

1,1,1-Trichloroethane can be replaced with a number of non-chlorinated organic solvents in several applications. Table VI-5 lists substitute solvents and the major product application areas. From a number of properties determining product performance, two performance factors are considered of most importance: flammability and density. Except for water, all of the substitute solvents considered are more flammable than 1,1,1-trichloroethane.

Industry considers flammable solvents a significant hazard at both, the manufacturing and end-use levels. Flammable solvents in the workplace are considered undesirable because of the fire hazard and the associated liability. The aerosols industry generally prefers to manufacture non-flammable (Johnson 1987). Since the 1978 U.S. ban on CFC propellants and subsequent bans in Sweden, Canada, Norway, and Denmark, the aerosol industry has adapted its manufacturing processes to utilize flammable hydrocarbon propellants. Non-flammable water-based systems and HCFC-propellants represent an opportunity to address these concerns.

The density of 1,1,1-trichloroethane and other chlorinated solvents is higher than the density of water and most other organic solvents. A higher mass/volume ratio indicates that for a given weight, 1,1,1-trichloroethane takes up a smaller portion of the can's volume. According to industry sources, consumers single out weight for price comparisons because most aerosol products are labelled with the contents' net weight. Therefore, a high density is desirable in solvents used for aerosol applications.

Table VI-5. SUMMARY OF SUBSTITUTE SOLVENTS FOR
1,1,1-TRICHLOROETHANE IN AEROSOLS

	<u>Major Product Applications</u>		
	A&I	Pest	HH
1,1,1-Trichloroethane	*	*	*
<u>Substitute Solvents:</u>			
Petroleum Distillates	*	*	*
Aromatic Hydrocarbons	*		*
Alcohols	*	*	
Ketones	*		*
Water Systems	*	*	*
DME		*	
HCFC Propellants	*	*	*

* Denotes that the substitute solvent can be used in the product application indicated.

A&I : Automotive and Industrial Products.

Pest : Pesticides.

HH : Household Products.

HCFC Propellants: Includes HCFC-22, HCFC-142b, and HFC-152a.

Source: Based on ICF 1989.

Solvent substitution in aerosol formulations affects variable and fixed production costs. Variable costs include ingredients, labour and overhead; fixed costs include additional research and development, marketing, and capital investment associated with product reformulation. In the event that use of 1,1,1-trichloroethane was reduced, certain products would require high investment in research and development (primarily products adopting new HCFC propellant or water). For example, a complete reformulation and testing program may be required. Other products would require relatively little development work, such as replacement of 1,1,1-trichloroethane with mixtures of organic solvents.

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APPENDIX A

Members of the UNEP Solvents Technical Options Committee for Technical Assessment Under Article 6 of the Montreal Protocol

Dr. Stephen O. Andersen
Chief, Technology and Economics Branch
Global Change Division
Office of Air and Radiation
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, DC 20460
United States
Tel: 202-475-9403
Fax: 202-382-6344

Dr. H. Ahmadzai, C. Eng.
Head of Section
National Environmental Protection Board
STATENS NATURVARDsverk
Smidesvagen 5
Box 1302
S-171 25 Solna, Sweden
Tel: +46-8-7991145
Fax: +46-8-292382

Mr. B.H. Baxter
Chief Materials Scientist
British Aerospace (Dynamics) Ltd.
Six Hills Way
Stevenage
Herts SG1 2DA
United Kingdom
Tel: +44-438-312422 Ext. 3222
Fax: +44-438-753572

Mr. Mike Clark
Sketchley Plc.
Hinckley
Leicestershire LE10 2NE
Tel: +44-455-38133
Fax: +44-455-619056

Mr. Brian Ellis
Protonique S.A.
P.O. Box 78
CH-1032 Romanel-sur-Lausanne
Switzerland
Tel: +41-21-38 23 34
Fax: +41-21-38 24 11

Mr. Stephen Evanoff, P.E.
Engineer Specialist
Environmental Resource Management
General Dynamics (Fort Worth Division)
Mail Zone 5984
P.O. Box 748
Fort Worth, TX 76101
United States
Tel: 817-777-3772
Fax: 817-777-2115

Mr. Joe R. Felty
Senior Member Technical Staff
Manager, Process Engineering -- Electro-Optics Systems
Defense Systems & Electronics Group
Texas Instruments
8505 Forest Lane
P.O. Box 660246
MS 3125
Dallas, TX
United States
Tel: 214-480-1037
Fax: 214-480-1197

Mr. Art FitzGerald, P.Eng.
Director, Environmental Affairs
Northern Telecom Limited
3 Robert Speck Parkway
Mississauga, Ontario
Canada L4Z 3C8
Tel: 416-566-3048
Fax: 416-275-1143

Dr. Leslie Guth
Member Technical Staff
AT&T Bell Laboratories
P.O. Box 900
Princeton, NJ 08540
United States
Tel: 609-639-3040
Fax: 609-639-2898

Alternates: Dr. Ruth Anderson
Dr. John Fisher
(same address)

Mr. Hitoshi Hirano
Senior Manager
Semiconductor Materials Engineering
Department
(c/o Toshiba Horikawa-Cho Works)
Toshiba Corporation
72, Horikawa-cho, Saiwai-Ku
Kawasaki, 210, Japan
Tel: +81-44-549-3067
Fax: +81-44-522-6440

Alternate: Mr. Shigeo Matsui
(same address)

Mr. Sudhakar Kesavan
Vice President
ICF Incorporated
9300 Lee Highway
Fairfax, VA 22031-1207
United States
Tel: 703-934-3052
Fax: 703-934-9740

Mr. Leo Lambert
Digital Equipment Corporation
1925 Andover Street
Tewksbury, MA 01876
United States
Tel: 508-858-2324
Fax: 508-858-2839

APPENDIX B

Expert Advisors to UNEP Solvent Technical Options Committee

Mr. Paul Cammer
President
Halogenated Solvents Industry Alliance
1225, 19th Street N.W.
Suite 300
Washington D.C. 20036
Tel: 202-223-5890
Fax: 202-223-5979

Mr. Chris Hartley
Association of Fluorocarbon
Consumers and Manufacturers
484 St. Kilda Road
Melbourne, Victoria 3004
Australia
Tel: +61-3-820-9180
Fax: +61-3-820-0872

Mr. Peter G. Johnson
Product Manager
Solvents Marketing Department
ICI Chemicals & Polymers Limited
P.O. Box 19
Runcorn, Cheshire WA7 4LW
United Kingdom
Tel: +44-928-512556
Fax: +44-928-580742

Mr. S.G. Rawlings
Director ABL, CRS
7 Churchill Court
Station Road
North Harrow
Middlesex
United Kingdom
Tel: +44-1-863-7755
Fax: +44-1-861-2115

Mr. Bernard Underwood
EEA/ECTEL
Leicester House
London WC2H 7BN
United Kingdom
Tel: +44-1-437-0678
Fax: +44-1-434-3477

Mr. H. Umeki
DuPont-Mitsui Fluorochemicals Co. Ltd.
Assistant Division Manager
Corporate Planning Division
Mitsui Seimei Building
2-3, Ohtemachi 1-Chome, Chiyoda-Ku
Tokyo, Japan
Tel: +81-3-216-8452
Fax: +81-3-285-0358

Mr. Anders Bergstrom
Manager
Production Technology
ABB Automation AB
S-721 67, Vasteras
Sweden
Tel: +46 21 10 92 68
Fax: +46 21 11 48 44

Mr. Jorgen Svensson
Manager
Research and Development
Printed Circuit Board and Electronic Packaging
Ericsson Telecom
Alvsjo Electronic Factory
S-126 25, Stockholm
Sweden
Tel: +46 8 719 8028
Fax: +46 8 749 2136

Dr. John F. D. Mills
c/o ICI Chemicals and Polymers Ltd.
P O Box 13, The Heath
Runcorn, Cheshire WA7 4QF
England

Dr. Kirk Bonner
Allied-Signal Incorporated
2001 North Janice Ave
Melrose Park, IL 60062
Tel: 312-450-3880

Dr. Bill Kenyon
DuPont
Chestnut Run Location, Bldg. 711
Wilmington, DE 19898
Tel: 302-999-2880
Fax: 5340

Mr. Bill Fisher
International Fabricare Institute
Columbia, MD
Tel: 301-622-1900

Mr. John F. Russo
Separation Technologists
32 Granger Avenue
Reading, MA 01867
Tel: 617-942-0023

Mr. Richard Szymanowski
Northern Telecom Inc.
4001 E. Chapel Hill- Nelson Hwy.
Research Triangle Park, NC 27709
Tel: 919-992-5000

Mr. Bill Rhoades
U.S. EPA AEERL
Research Triangle Park, NC
Tel: 919-541-2157

Mr. David Bergman
IPC
7380 North Lincoln Ave
Lincolnwood, IL 60646
Tel: 312-677-2850
Fax: 312-677-9570

Dr. Michael Hayes
Director- Research & Development
Petroferm Inc.
5400 First Coast Highway
Fernandina Beach, FL 32034
Tel: 904-261-8286
Fax: 803628

Mr. Charles Carpenter
Environmental Research Engineer
U.S. Air Force Engineering Center
Tyndall AFB, FL 32403-6001
Tel: 904-283-2942
Fax: 904-523-2942

Mr. Joel Rodgers
Vice President and General Manager
Allied-Signal Inc.
Engineered Solvents Systems
Morriston, NJ 07960
Tel: 201-455-4848

Mr. David Doniger
NRDC
1350 New York Ave, NW
Washington, D.C.
Tel: 202-783-7800