

Protecting the Ozone Layer

Volume 2

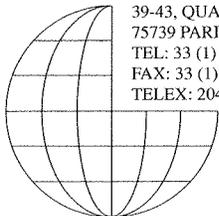
Solvents, coatings and adhesives



UNEP

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Foreword

In 1974, Sherwood Rowland and Mario Molina of the University of California claimed that the man-made chemicals known as chlorofluorocarbons (CFCs) were damaging the stratospheric ozone layer. Subsequent research supported the theory, and it is now established that the stratospheric ozone layer—which protects the earth from dangerously high levels of ultraviolet radiation from the sun—is being destroyed by human activity. Ozone-depleting substances are used in the manufacture of thousands of products.

The Montreal Protocol on Substances that Deplete the Ozone Layer was drawn up under the guidance of the United Nations Environment Programme (UNEP) in September 1987. The Protocol identified the main ozone-depleting substances, and set specific limits on their production levels in the future. By 1991, 71 countries had ratified the agreement.

It is intended that the Protocol be continually updated, as necessary. In June 1990 the Parties to the Protocol met in London to consider the implications of new scientific evidence that showed that the ozone layer was being depleted even faster than originally thought. The London meeting agreed to phase out the consumption and production of CFCs and halons by the year 2000, and to control certain other chemicals.

Signatories to the Montreal Protocol agreed to reduce and eliminate CFC usage even though substitutes and alternative technologies were not yet fully developed. Industries and manufacturers are starting to replace CFCs with less damaging substances, but a major obstacle in the conversion process is a lack of up-to-date, accurate information on issues relating to CFC substitutes and CFC-free technology.

The London Amendments to the Protocol acknowledged the financial and technical help that developing countries would need, and set up the Interim Multilateral Ozone Fund (IMOF) to provide them. UNEP was charged with specific responsibilities for implementing the IMOF, and it created an OzonAction Programme within UNEP's Industry and Environment Programme Activity Centre (IE/PAC) to carry out information exchange and training, and to act as an information clearinghouse.

One of the most important jobs of this programme is to ensure that all those who need to know understand clearly the issues involved in replacing CFCs and how to obtain the information and assistance they may need to do so. Hence the publication, in English, French and Spanish, of six plain language reports that summarize the major issues surrounding CFC replacement for decision makers in government and industry. This is the second in the series prepared by UNEP IE/PAC; others cover refrigerants; foams; aerosols and sterilants; and halons for fire fighting.

Each of these five publications summarizes the current uses of ozone-depleting substances within an industrial sector, the availability of CFC substitutes, and the technological and economic implications of converting to CFC-free production. A sixth volume summarizes the overall situation, provides examples of successful conversion to CFC-free technologies, and explains how to apply for assistance from the IMOF. Those requiring more detailed information should refer to the 1992 reports of the five UNEP Technical Options Committees (see Further Reading) on which this series is based.

Acknowledgements

This report is based on the *UNEP Solvents, Coatings and Adhesives Technical Options Report* (Nairobi, UNEP, 1992). Members of the Committee (see list below) gave freely of their time to ensure that this publication, while written in plain language, reflects accurately the much more detailed information available in the original report.

Thanks are also due for the assistance that was provided by Mr Steve Andersen, Chairman of the UNEP Scientific Options Committee on Solvents, and by the Industry Cooperative for Ozone Layer Protection.

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Executive summary

Until 1990 the use of ozone-depleting substances in industry has increased significantly and has led to the depletion of the ozone layer observed by scientists in the 1980s. New data have revealed that the hole in the Antarctic ozone layer which appears each spring is larger than was originally calculated, and there is evidence of a similar hole beginning to form over the Arctic. The serious implications for life on earth and human health have resulted in global action to protect the stratospheric ozone layer.

This action is contained in the Montreal Protocol which was developed under the guidance of the United Nations Environment Programme (UNEP) and by 1992 had 76 signatories. It aims first to limit, then to phase out completely the production and consumption of the man-made substances that have contributed to ozone depletion. If implemented, this action will prevent further damage to the ozone layer and—eventually—repair most of the damage already done.

The main ozone-depleting solvents in use today are CFC-113 and methyl chloroform. CFC-113 is a fully halogenated chlorofluorocarbon with a relatively high ozone-depletion potential. It is used because of its non-corrosive properties, chemical inertness, non-flammability, low viscosity and low surface tension. Its use is regulated under the Montreal Protocol and is due to be phased out by the year 2000. Methyl chloroform has also been used as a solvent; although its ozone-depletion potential is lower, it was included in the 1990 London revisions to the Montreal Protocol and its use is to be phased out by the year 2005. Carbon tetrachloride is now no longer used as a solvent in most developed countries because of its toxicity and potential carcinogenicity, but it is used as a feedstock to produce CFCs, and as a solvent in developing countries. Its use has been regulated under the protocol and must be phased out by 2000.

There is no one substitute for ozone-depleting solvents. Ozone-safe solvents and alternative technologies (or both) can be used, or the cleaning step eliminated by redesigning the production process. The substitutes being developed include organic solvents; the hydrochlorofluorocarbons HCFC-225ca, -225cb, -123 and -141b; alcohols such as isopropanol; solvent blends; and water with saponifiers. Alternative technologies include aqueous and semi-aqueous cleaning; no-clean options, such as using low-solids fluxes and pastes in electronics which eliminate the need for post-flux cleaning; and ice-particle and plasma cleaning. Improved conservation and recovery practices could initially reduce the emissions of CFC-113 and other ozone-depleting solvents by up to 90 percent, and in many cases could be implemented at minimal cost. Conservation measures include retrofitting and redesigning equipment, and introducing better operator, handling and storage practices.

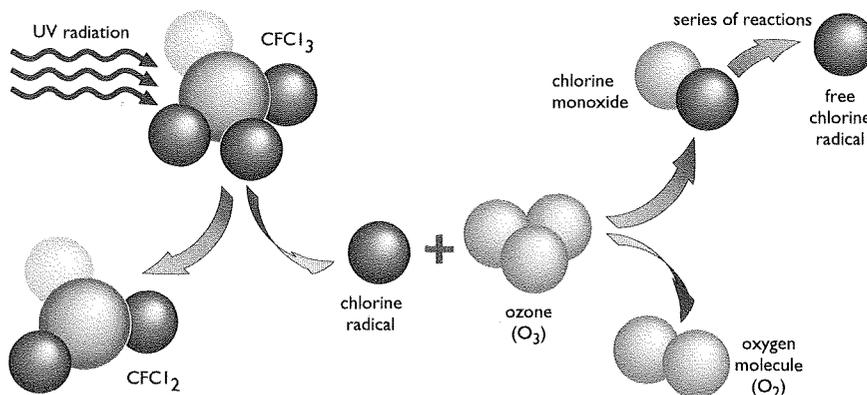
UNEP's Technical Options Committee is confident that the adoption of conservation and recovery measures, coupled with the use of alternative cleaning solvents and technologies, can phase out all uses of ozone-depleting solvents as early as 1995 in developed countries.

The science of ozone depletion

Ozone is a naturally occurring gas found in the earth's atmosphere that absorbs certain wavelengths of the sun's ultraviolet radiation. Ozone concentrations vary with altitude, peaking in the stratosphere approximately 25–30 km from the earth's surface. This concentration of the gas is known as the ozone layer, and it reduces the intensity of certain wavelengths of ultraviolet radiation reaching the earth's surface. High doses of ultraviolet radiation at these wavelengths can damage the human eye, cause skin cancers, reduce rates of plant growth, upset the balance of ecosystems, accelerate the degradation of plastics and, by suppressing the efficiency of the body's immune system, increase the risks of disease.

Solar radiation breaks down many of the gases in the stratosphere that contain chlorine and bromine. Chlorine and bromine radicals can then set off a destructive chain reaction,

Effects of CFCs on stratospheric ozone



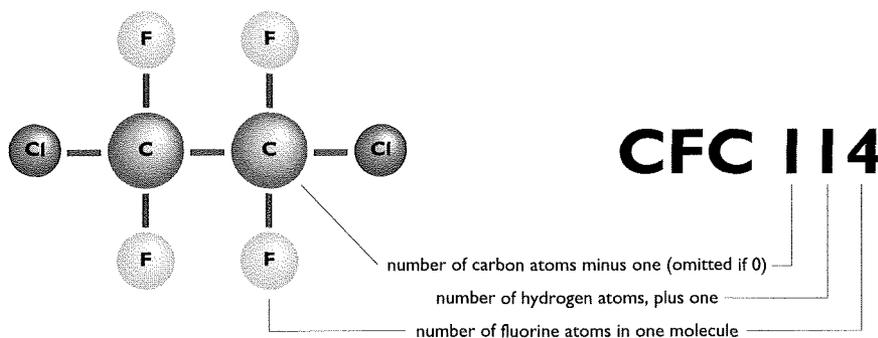
When gases containing chlorine, such as CFCs, are broken down in the atmosphere, each chlorine atom sets off a reaction that may destroy hundreds of thousands of ozone molecules

breaking down other gases in the stratosphere, including ozone. Ozone molecules are broken down into oxygen and chlorine monoxide (see above), thus reducing the concentration of atmospheric ozone. A single chlorine or bromine radical is left intact after this reaction, and may take part in as many as 100 000 similar reactions before eventually being washed out of the stratosphere into the troposphere.

During the past few decades, CFCs have been released into the atmosphere in sufficient quantities to damage the ozone layer. The largest losses of stratospheric ozone occur regularly over the Antarctic every spring, producing substantial increases in ultraviolet levels over Antarctica. A similar, though weaker, effect has been found over the Arctic. There is now evidence that ozone levels decrease by several percent in the spring and summer in both hemispheres at middle and high latitudes; they also fall during the winter at these latitudes in the southern hemisphere. Levels of ozone damage were generally higher during the 1980s than the 1970s.

HOW CFC NOMENCLATURE WORKS

CFC numbers provide the information needed to deduce the chemical structure of the compound. The digit far right provides information on the number of fluorine atoms, the digit second from the right provides information on hydrogen atoms, and the digit on the left provides information on carbon atoms. Vacant valencies are filled with chlorine atoms. Adding 90 to the number reveals the numbers of C, H and F atoms more directly.



- Note:
1. All spare valencies filled by chlorine atoms
 2. Different isomers are indicated by a suffix of lower case letters
 3. Bromine atoms are indicated by a suffix B plus number of atoms
 4. Hundreds number = 4 or 5 for blends (e.g. R502)

The second environmental impact of a gas is its contribution to global warming. Global warming potential (GWP) is related to the ability of a gas to absorb infrared radiation. GWP is an estimate of the atmospheric warming resulting from the release of a unit mass of gas, in relation to the warming resulting from the release of the same amount of carbon dioxide. Global warming, unlike ozone depletion, is not covered by the Montreal Protocol.

CFCs make a substantial contribution to global warming but there are indications that this effect is offset globally by the cooling that results from the destruction of ozone by CFCs in the lower stratosphere.

Fully halogenated chlorofluorocarbons (CFCs) contain only chlorine, fluorine and carbon, and have a high ODP. Similar compounds which are not fully halogenated, and contain hydrogen in addition to chlorine, fluorine and carbon, are called hydrochlorofluorocarbons, or HCFCs. The presence of hydrogen in HCFCs reduces their persistence in the atmosphere, and they have a less destructive effect on the ozone layer than CFCs. They are nevertheless classified as transitional substances under the Montreal Protocol, and their use is likely to be controlled in the future.

Chemicals containing fluorine, carbon and hydrogen, but no chlorine or bromine, are known as hydrofluorocarbons, or HFCs. The HFCs currently being developed as CFC substitutes do not damage the ozone layer, but may contribute to global warming.

Blends containing a combination of CFCs, HCFCs and HFCs have been developed for specific applications. Their ODPs are lower than that of the CFCs they contain—though they are more damaging to the environment than both HCFCs and HFCs.

The Montreal Protocol

The Montreal Protocol, developed under the management of the United Nations Environment Programme in 1987, came into force on 1 January 1989. The Protocol defined the measures that Parties must take to limit production and consumption of the controlled substances, originally five CFCs and three halons. In early 1992 there were 76 Parties to the Protocol, of which nearly 40 were developing countries.

New scientific information soon made it clear that the original Protocol would not protect the ozone layer adequately. A revision made in London in June 1990 adopted supplementary control measures, and provided for technical and financial assistance to be given to signatories from developing countries. The London revisions introduced controls on 10 more CFCs, carbon tetrachloride and methyl chloroform, and set deadlines for the elimination of the controlled substances.

The Montreal Protocol—and the Vienna Convention from which it was born (see box right)—are the first global agreements to protect the atmosphere.

How regulation works

Each of the controlled chemicals is assigned an ODP in relation to CFC-11, which is arbitrarily given an ODP of 1. These values are used to compute an indicator of the damage being inflicted on the ozone layer by each country's production and consumption of controlled substances. Consumption is defined as total production plus imports less exports, and therefore excludes recycled substances. Thus the relative ozone depletion effect of CFC production is computed by multiplying the annual production of each controlled CFC by its ODP. These totals are added together to produce an indicator of potential ozone damage. Parties are required to reduce this total by 50 percent by 1995, by 85 percent by 1997 and by 100 percent by the year 2000 (in relation to 1986 figures). Developing countries have a 'grace period' of 10 additional years in which to meet these requirements.

Parties* to the Montreal Protocol, February 1992



* countries that have formally ratified, acceded, approved or accepted the Protocol

- | | | | |
|----------------|----------------|--------------------|----------------|
| Argentina | European | Liechtenstein | Sweden |
| Australia | Community | Luxembourg | Switzerland |
| Austria | Fiji | Malawi | Syria |
| Bahrain | Finland | Malaysia | Thailand |
| Bangladesh | France | Maldives | Togo |
| Belarus | Gambia | Malta | Trinidad and |
| Belgium | Germany | Mexico | Tobago |
| Botswana | Ghana | Netherlands | Tunisia |
| Brazil | Greece | New Zealand | Turkey |
| Bulgaria | Guatemala | Nigeria | Uganda |
| Burkina Faso | Hungary | Norway | Ukraine |
| Cameroon | Iceland | Panama | United Arab |
| Canada | Iran | Philippines | Emirates |
| Chile | Ireland | Poland | United Kingdom |
| China | Italy | Portugal | United States |
| Costa Rica | Japan | Russian Federation | Uruguay |
| Czechoslovakia | Jordan | Singapore | Venezuela |
| Denmark | Kenya | South Africa | Yugoslavia |
| Ecuador | Korea, Rep. of | Spain | Zambia |
| Egypt | Libya | Sri Lanka | |

THE VIENNA CONVENTION

The Montreal Protocol details how signatories should reduce their production and consumption of ozone-depleting chemicals. The principle that countries would agree internationally to take steps to protect the ozone layer was established in the Vienna Convention for the Protection of the Ozone Layer, signed by

21 states and the European Economic Community in March 1985. The Convention pledges parties to protect human health and the environment from the effects of ozone depletion, and two annexes provide for participating states to cooperate in research, observation and information exchange.

Requirements of the Montreal Protocol, as amended in London 1990

Name	formula	ODP	reduction in production and consumption
<i>CONTROLLED SUBSTANCES</i>			
<i>chlorofluorocarbons</i>			
CFC-11	CFCl_3	1.0	relative to 1986: 1995: 50 percent 1997: 85 percent 2000: 100 percent
CFC-12	CF_2Cl_2	1.0	
CFC-113	$\text{C}_2\text{F}_3\text{Cl}_3$	0.8	
CFC-114	$\text{C}_2\text{F}_4\text{Cl}_2$	1.0	
CFC-115	$\text{C}_2\text{F}_5\text{Cl}$	0.6	
plus 10 other fully halogenated CFCs (see below)			
<i>halons</i>			
halon 1211	CBrClF_2	3.0	relative to 1986: 1995: 50 percent 1997: 85 percent 2000: 100 percent
halon 1301	CBrF_3	10.0	
halon 2402	$\text{C}_2\text{Br}_2\text{F}_4$	6.0	
carbon tetrachloride	CCl_4	1.1	relative to 1989: 1995: 85 percent 2000: 100 percent
methyl chloroform	CH_3CCl_3	0.1	relative to 1989: 1993: levels frozen 1995: 30 percent 2000: 70 percent 2005: 100 percent
<i>NON-CONTROLLED TRANSITIONAL SUBSTANCES</i>			
<i>hydrochlorofluorocarbons (HCFCs), such as</i>			
HCFC-22	CHClF_2	substances with low ODPs, to be phased out by 2020 if feasible and not later than 2040	
HCFC-123	CF_3CHCl_2		
HCFC-141	$\text{C}_2\text{H}_3\text{Cl}_2\text{F}$		
HCFC-142	$\text{C}_2\text{H}_3\text{ClF}_2$		
plus 33 other HCFCs (see below)			

Note: The 1990 London Amendments added the following CFCs with an ODP of 1.0 to the list of controlled substances: CFCs -13, -111, -112, -211, -212, -213, -214, -215, -216 and -217. The following HCFCs (and their isomers) were made transitional

substances, in addition to those shown by way of example above: HCFCs -21, -31, -121, -122, -124, -131, -132, -133, -151, -221, -222, -223, -224, -225, -226, -231, -232, -233, -234, -235, -241, -242, -243, -244, -251, -252, -253, -261, -262 and -271.

Ozone-depleting solvents

To conform to the terms of the Montreal Protocol, the consumption and production of two solvents—CFC-113 and carbon tetrachloride—must be phased out by the year 2000; consumption and production of methyl chloroform must be phased out by 2005.

CFC-113, methyl chloroform and carbon tetrachloride are ozone-depleting solvents controlled by the Montreal Protocol.

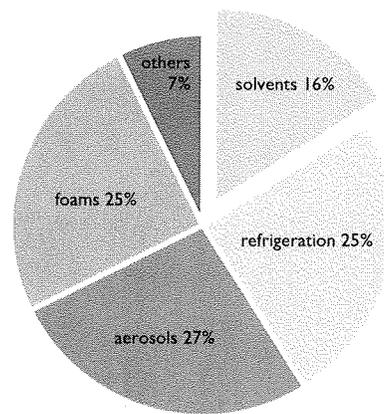
The CFC-113 currently used in the solvents industry represents 16.8 percent of the total world-wide use of controlled CFCs. Its use has in the past been essential in many industrial applications: in electronic assembly production processes, precision cleaning, general metal degreasing during manufacture, as well as in dry cleaning and other industrial applications. CFC-113 began to be used in the 1970s in metal degreasing and other areas due to concern, particularly in the United States and Japan, over the toxicity of the chlorinated solvents used previously. Its use in other sectors followed, contributing to a rapid growth of the CFC-113 market, which reached 178 000 metric tonnes a year in 1986.

But CFC-113 has an atmospheric retention time of 90 years and its relatively high ODP has contributed to an estimated 14 percent of total ozone depletion to date. It is included as a controlled substance under the Montreal Protocol (see pages 8/9).

Methyl chloroform, which at one time was considered a likely substitute for CFC-113, is now included as a controlled substance under the 1990 Montreal Protocol revisions and is therefore not an acceptable long-term substitute for CFC-113. Carbon tetrachloride is no longer used as a solvent in most countries due to its carcinogenicity, but it is used in some parts of the world. It too is a controlled substance, and should not be substituted for CFC-113. The three ozone-depleting substances used as solvents are shown in the table below.

North America, Europe and Japan are responsible for most use and emissions of CFC-113 and are taking the lead in reducing its use. Research is being carried out into CFC and methyl chloroform substitutes. HCFCs with low ODPs are being developed as CFC substitutes in some solvent uses, but are considered as transitional substances in a non-binding resolution of Parties to the Montreal Protocol, and their production is likely to be restricted in the future.

Distribution of industrial CFC use



Solvent uses currently account for about 16 percent of all CFC usage. About 45 percent of solvent use is in the electronics industry.

Ozone-depleting substances used as solvents

		formula	ODP	atmospheric lifetime (years)
CFC-113	1,1,2-trichloro-1,2,2-trifluoroethane	C ₂ Cl ₃ F ₃	0.8	90
methyl chloroform	1,1,1-trichloroethane	CH ₃ CCl ₃	0.1	
carbon tetrachloride	tetrachloromethane	CCl ₄	1.1	

Current uses

Electronics

The electronics industry is the largest users of the ozone-depleting solvent CFC-113, consuming about 45 percent of the total CFC-113 used globally. Most is used to remove flux from electronics assemblies; in 1988, an estimated 80 000 tonnes of CFC-113 were used to clean the printed circuit boards now used extensively in computers, satellites, avionic instruments, military equipment, telecommunications systems, domestic appliances, radios and televisions. The use of methyl chloroform has been limited in this sector because of its high solvent power (which can damage electronic components) but has been used more since manufacturers began switching to less solvent-sensitive circuit board materials; about 36 000 tonnes were consumed in 1989. In 1986 about 50 percent of circuits cleaned in the electronics industry were manufactured to stringent military cleaning specifications that encouraged or required the use of CFC-113. These military specifications retarded the adoption of ozone-safe cleaning methods throughout the industry (see page 13). However, in 1991 the US military revised its specifications to discourage the use of CFC-113 and to allow the use of materials that clean as well or better than solvent blends based on CFC-113.

Printed circuit assemblies consist of electronic components soldered onto electronic boards. Flux is used to increase solder adhesion. Removing the flux residues left after soldering is often essential to ensure subsequent electrical performance of the circuit, facilitate testing and inspection, minimize leakage currents and prevent corrosion.

Flux residues and other contaminants have traditionally been removed using a CFC-113/alcohol mixture. CFC-113 solvent removes flux residues effectively without damaging sensitive components such as the elastomers, polymers and coatings used on printed circuit boards. Cleaning methods include vapour cleaning, scrubbing, dipping (with or without ultrasonic agitation), high-pressure spraying, and a combination of spraying, immersion and vapour cleaning. A recent survey of US electronics firms showed that many (46 percent) are currently using CFC-113, slightly fewer rely on aqueous cleaning (36 percent), and the remainder use either other chlorinated solvents (13 percent) or do not clean at all (5 percent). The cleaning required depends on both the corrosivity of the flux residue and the final use: toys and domestic appliances need least; military, space and medical components must be cleaned to a critical degree. Small quantities of circuit boards may be cleaned by hand or small machines.

The quality of solvent needed is affected by the technologies chosen to assemble the circuit boards. Through-hole assembly is the traditional method of circuit board assembly, but a new surface-mount technology (SMT) is now being

Cleaning flux from printed circuit boards is one of the main uses of CFC-113, consuming an estimated 80 000 tonnes in 1988.

Available cleaning methods for different electronic flux types

	organic solvent	water	water and saponifier	terpenes/hydrocarbons and water
non-activated rosin*	●		●	●
mildly activated rosin*	●		●	●
activated rosin**	●		●	●
super-activated rosin	●		●	●
water soluble flux***		●	●	
activated synthetic resin***	●			●
low solids	no cleaning required			

* approved for US military use
 ** approved for UK and US military use
 *** approved for U K military use

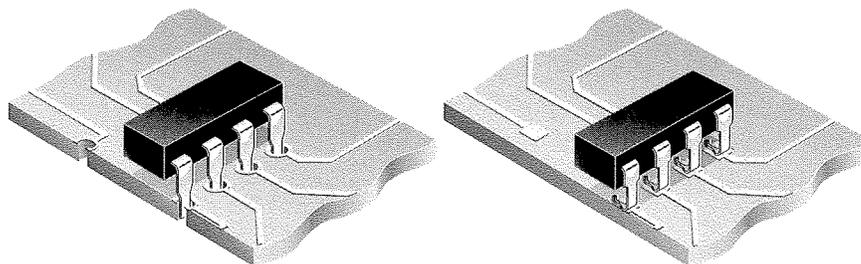
Current and future cleaning methods required for different electronics applications

<i>application</i>	<i>importance and methods of current cleaning</i>	<i>importance and methods of possible future cleaning</i>
satellites avionic instruments submarine telecommunications medical life-support	cleaning essential combination or solvent cleaning or saponification to military specifications for rosin fluxes	alcohol solvents saponifiers or water-soluble solvent or aqueous cleaning controlled atmosphere soldering
automotive (brakes and motor); land telecommunications	cleaning essential all cleaning methods, to clean all flux types and for ionic contaminants	alcohol solvents saponifiers or water-soluble solvent or aqueous cleaning controlled atmosphere soldering
sophisticated industrial computers; ordinary telecommunications; other automotive (not radio)	all cleaning methods, to clean all flux types and for ionic contaminants (to military specifications)	saponifiers or water-soluble solvent or aqueous cleaning no-clean controlled atmosphere soldering
Industrial medical non-life-support low-cost peripheral equipment	cleaning generally needed solvent cleaning for rosins	water soluble solvents aqueous cleaning no-clean controlled atmosphere soldering cleaning could be minimized
low-cost instruments office equipment TV EHT circuits	cleaning frequently needed solvent cleaning for rosin fluxes	cleaning frequently needed no-clean technologies (using low-solids rosin fluxes)
professional audio-visual equipment; quality consumer goods; automotive entertainment and public address systems	cleaning rarely needed rosin flux cleaning if required	no-clean technologies (using low-solids rosin fluxes)
Radio, television and other entertainment and home electronics (mass produced)	cleaning not required (fluxes of all types used)	no-clean technologies (using low-solids rosin fluxes)

implemented, enabling components to be densely packed on the circuit board. As fewer parts are required for attachment, board sizes can be reduced—one company claims a 40 percent board size reduction after adopting SMT instead of through-hole assembly. This has possible implications for the amount of solvent required for cleaning: less solvent may be able to clean more circuit boards, contributing to solvent conservation, as well as reducing cost. SMT is expected to be used more extensively during the 1990s.

Traditional and new circuit board technology

Traditional through-hole electronic assembly is shown immediately right. The new surface-mount technology (far right) allows components to be more densely packed, assembly boards to be made smaller, and the amount of cleaner used reduced (the assemblies are not shown to scale).



Key facts**typical electronic assembly contaminants****Category 1:**
particulate

resin and fibreglass debris from drilling and/or punching operations
 metal and plastic chips from machining and/or trimming
 dust
 handling contaminants
 lint
 insulation
 hair/skin

Category 2:
polar, ionic, inorganic

flux activators
 activator residues
 soldering salts
 handling contaminants such as sodium and potassium chlorides
 residual plating salts
 neutralizers
 ethanolamines
 surfactants
 flux rosin

Category 3:
non-polar, non-ionic, organic

oils
 grease
 waxes
 synthetic polymers
 soldering oils
 metal oxides
 handling contaminants
 polyglycol degradation by-products
 hand creams
 lubricants
 silicones
 surfactants (non-ionic)

Precision cleaning

Precision cleaning is the second largest application of CFC-113 and methyl chloroform solvents. CFC-113 is used in the electronics and other industries to clean delicate instruments and surfaces, which may be made of metal, plastic or glass. Computer disk drives, miniature bearings, optical components, telecommunication parts and aerospace instrumentation all require an extremely fine level of cleaning because their mechanical parts have very close fits. Some weapons also use gas control systems that require extreme cleanliness, as do military vehicle hydraulic control systems. Precision cleaning is also needed in some specialized forms of manufacture, maintenance, testing and assembly.

CFC-113 has been ideal for such applications due to its chemical inertness and non-corrosive properties which leave delicate surfaces intact; it is also non-toxic, non-flammable, has a low surface tension and low viscosity (both of which assist cleaning) and has a low water solubility. CFC-113 has been essential in cleaning sensitive metal surfaces because these are highly reactive in their fresh non-oxidized state; cleaning with substitute chlorinated solvents could be detrimental. CFC-113 is useful in cleaning medical equipment: not only is it highly volatile, capable of penetrating the most complex instrumentation, but it is also non-flammable allowing flushing solvent to be blown through without explosion risk.

Methyl chloroform, which has similar properties, has also been used in cleaning medical equipment and is appropriate for precision cleaning of heavy grease. Precision cleaning is carried out in 'clean room' conditions of very low contamination. Standard cleaning equipment is a vapour degreaser consisting of a boiling sump, hot clean rinse and a vapour blanket (see *next page*); mechanical handling equipment is sometimes attached for rapid transfer of goods to clean rooms. Smaller vapour degreasers using CFC-113 may be installed close to inspection and assembly areas. Bench-top ultrasonic cold cleaners are used in clean rooms; solvent losses from these may be very high because they have few vapour containment features. Processes chosen depend on applications: gyroscopes might require repeated cleaning at all stages of assembly using different fluids at different stages. (Though current gyroscope technology may gradually be superseded by solid-state optical systems for commercial and military uses, existing gyroscopes will remain in service for many years so there is a long-term need for alternative solvents compatible with existing machinery.)

Pressurized CFC-113 is used for removing dust and particles from high

MILITARY CLEANING REQUIREMENTS

Military applications account for half the CFC-113 used in the electronics assembly industry and are prominent in precision cleaning. Until recently, military specifications have set stringent cleaning requirements and have required the use of CFCs. These specifications established standards for civilian applications, resulting in unnecessary cleaning with ozone-depleting solvents and unnecessary vapour emissions.

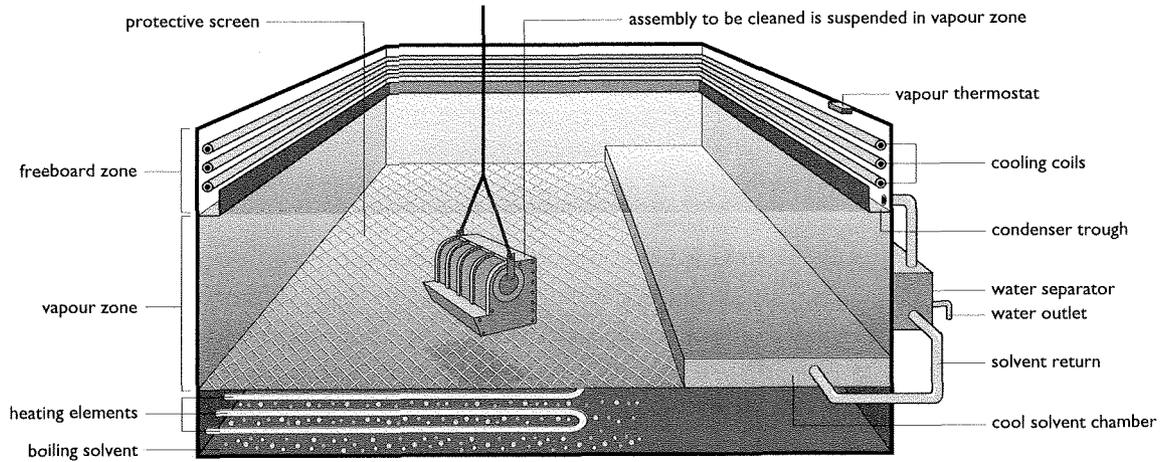
As a result of the Montreal Protocol, the US Secretary of Defense ordered the military to eliminate the use of CFCs and halons and to avoid the purchase of products that depend on these chemicals. In 1991, the United States Armed Forces adopted the MIL-STD-2000 (Revision A) standard, conditionally permitting the use of non-rosin fluxes and non-ozone-depleting solvents, cleaning agents and processes for all electronics assembly procedures.

Extensive research is currently being undertaken by the military to produce alternatives to CFC-113 and methyl chloroform. Isopropanol, alcohol, terpenes, HCFCs and other solvents have been demonstrated as effective cleaners for military purposes, and other alternative solvents and aqueous cleaning methods using ultrasonics, are being adopted.

Military requirements in the United Kingdom, Sweden and Germany are undergoing similar revisions.

Vapour degreasing system for precision cleaning

Vapour degreasing uses the hot vapour of a chlorinated or fluorinated solvent to remove contaminants, oils, greases and waxes. Vapour is generated by a boiling sump of liquid solvent at the bottom of the unit. Parts are lowered into the vapour zone; the temperature differential between the hot vapour below and the cold vapour above causes the vapour to condense on the cold parts, so dissolving and washing off the contaminants.



Key facts

precision cleaning applications

- aircraft controls
- auto-pilot inertial navigation systems
- auto-riveting
- gyroscopes
- maintenance cleaning
- medical equipment
- missile and satellite controls
- nuclear glove-box decontamination
- specialized manufacturing techniques
- underwater systems

definition cathode ray tubes and semi-conductors. CFC-113 is an excellent cleaner for micro-switches and connectors in sophisticated electronic equipment that requires absolutely clean contacting surfaces. This is particularly true in the defence industry, where some devices are designed for a long shelf-life and to be used only once, and must have absolute reliability.

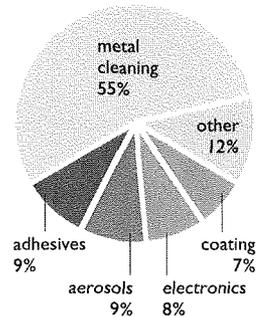
Significant quantities of CFC-113 are used by aircraft manufacturers for auto-riveting aircraft wings, which takes place in huge open assembly shops, causing high solvent consumption. The Industry Cooperative for Ozone Layer Protection (ICOLP) is investigating the elimination of this manufacturing procedure through the use of alternative materials.

General metal cleaning

Methyl chloroform and CFC-113 are used extensively in general metal part cleaning in a wide range of manufacturing and maintenance processes throughout industry. Solvent use is integral to many production processes, removing organic compounds such as grease and oils, particulate matter and inorganic contaminants from metal surfaces, and preparing parts for subsequent operations such as assembly, coating, electroplating, inspection, and packing. Machine parts are often complex and may need to be cleaned many times during manufacture; different alloys may need cleaning using the same system—in one case, the US Air Force cleans more than 15 different alloys during aircraft maintenance. Methyl chloroform was first used widely as a metal cleaner in the 1960s and the use of CFC-113 dates from the 1970s when concern arose about the effects of long-term, low-concentration exposure to chlorinated solvents. During 1974–83 CFC-113 use in the United States doubled from an estimated 26 000 to 52 000 tonnes.

There are a number of metal cleaning processes in which parts are dipped manually or hydraulically into a solvent solution. Soaking, mechanical agitation, ultrasonic cleaning, and vapour degreasing are used, and there is often a high solvent consumption because much equipment currently contains no vapour level controls or containment facilities. Small containers are used for maintenance cleaning of electronic parts; large containers for large machined parts, or large volumes of smaller parts in baskets. Vapour degreasing uses the hot vapour of a chlorinated or fluorinated solvent to remove contaminants, oils, greases and waxes.

US industrial uses of methyl chloroform



Metal cleaning accounts for the major share of methyl chloroform use in the United States. In western Europe and Japan, its share is even higher—about 75 percent.

Metal cleaning solvents and current cleaning processes

	cold immersion	vapour/hot liquid	conveyor	manual
CFC-113		●	●	●
Methyl chloroform	●	●		●
Trichloroethylene	●	●		
Methylene chloride	●			
Perchloroethylene		●		
Blends	●			●

Dry cleaning

The fabric and clothing dry cleaning industry is a relatively minor user of methyl chloroform and CFC-113, consuming less than 5 percent of all CFC-113. Organic solvents are ideal for dry cleaning because, unlike water, they do not distort fabrics. CFC-113 has been used because of its low toxicity, stability, mild solvency, non-flammability and relatively low boiling point, which minimizes energy requirements, and reduces risk of heat damage to sensitive fabrics. CFC-113 is used only in totally enclosed machines operating a dry-to-dry

process. These usually incorporate sophisticated recovery systems to purify solvent for reuse, minimizing solvent emissions; for every litre of solvent used, one of these machines can clean more than 50 kg of clothing. Dry cleaning machines are usually designed to operate with only one solvent and to last 12–15 years; they are not easily convertible to alternative solvents, though some new machines can operate with a choice of solvents. These machines represent the largest capital cost in setting up a dry cleaning operation and replacing with new machines that do not use CFC-113 may prove difficult for the small businesses that predominate in this sector. Conservation and recovery practices will be important in the short-term reduction of CFC-113 use.

Perchloroethylene, not CFC-113, is the most widely-used dry cleaning solvent, but has a higher boiling point. Its use is therefore energy intensive. Some animal tests indicate a degree of carcinogenicity but these findings are hard to assess and most authorities agree there is a low risk to humans under normal conditions of use.

Adhesives, coatings and aerosols

CFC-113 and methyl chloroform are also used as solvents in adhesives, coatings and aerosols. The quantities used are even less than in the dry cleaning industry, and represent less than 5 percent of total use. Methyl chloroform (not CFC-113) is used to improve adhesive performance, especially in foam, particle board, plywood and other contact-bonded materials. Its chief advantages are non-flammability and the speed with which it dries. It is used as an active solvent in solvent-based adhesives and a diluent in water-based adhesives.

In 1986, 48 percent of the US coatings market was solvent-based. In 1989, 21 000 tonnes of methyl chloroform were used in the production of inks and protective and decorative coatings to dissolve the main binding substance. Methyl chloroform is also used as a spray-coating thinner. CFC-113 use in this application is negligible. Methyl chloroform forms the active ingredient or solvent in the propelled liquid of many aerosols used in the motor industry, industrial products, pesticides and household goods. It increases product shelf-life and its small particle size results in a good spray pattern. CFC-113 is used only as a spray solvent for manual flux removal on delicate electronic components, or for contact cleaners.

Other industrial uses

Other applications use relatively small amounts of CFC-113 and methyl chloroform. CFC-113 acts as cleaner and lubricant in bearer media for coating and impregnation of metal parts to reduce friction damage. In vapour-phase soldering it enables both sides of a substrate to be soldered simultaneously. CFC-113 is used in component and semiconductor drying since any metal or other parts which contact water during processing must be dried immediately afterwards to prevent deterioration and rusting. CFC-113 and methyl chloroform are also used in miscellaneous testing; chemical analysis and analysis of CFC compounds; in wafer cleaning during semi-conductor manufacturing; in mould release agents; in cooling operations; in film and skin cleaning; and in fabric protection.

Key facts

other industrial solvent uses

bearer media for coating and impregnation
vapour soldering
component drying
riveting and machining
fabric protection
semiconductor manufacture
dielectric fluids
miscellaneous testing
mould release agents
film cleaning
skin cleaning
cooling operations

Substitute solvents and technologies

There is no single substitute for all uses of CFC-113 and methyl chloroform. Every solvent area has at least one or more available alternatives. CFC-113 has been so widely used as a solvent because it fits many different applications. Any substitute for CFC-113 or methyl chloroform should exhibit most, if not all of their useful characteristics—particularly in cleaning effectiveness. Substitutes should have a low ODP, GWP, and volatile organic content; they should not be toxic or carcinogenic; and recovery and recycling should be possible. They should be cost effective; and alternative processes should not generate other environmental hazards.

In any company replacement policy, there may be short- and long-term substitutes for CFC-113. In the short term, recycling and recovery may be the first step. In the long term, alternative processes and materials should be found since, because of losses, CFC-113 cannot be recycled indefinitely. Emissions should be minimized by the use of closed equipment.

Longer-term alternatives must be carefully monitored for environmental and health hazards. In applications where toxic chemicals are the only current substitutes, their use will be permitted only with strict workplace controls and until better substitutes are available.

Alternative solvent blends using HCFCs are currently being developed and marketed—HCFC-123, HCFC-141 and particularly HCFC-225 are possible substitutes but are only technically necessary for a very small portion of important CFC-113 applications. Their long atmospheric life and ozone-depletion potential mean that they are not long-term substitutes for CFC-113 or methyl chloroform.

The table overleaf lists the physical properties of the main ozone-depleting solvents and their main chlorinated alternatives.

Key facts

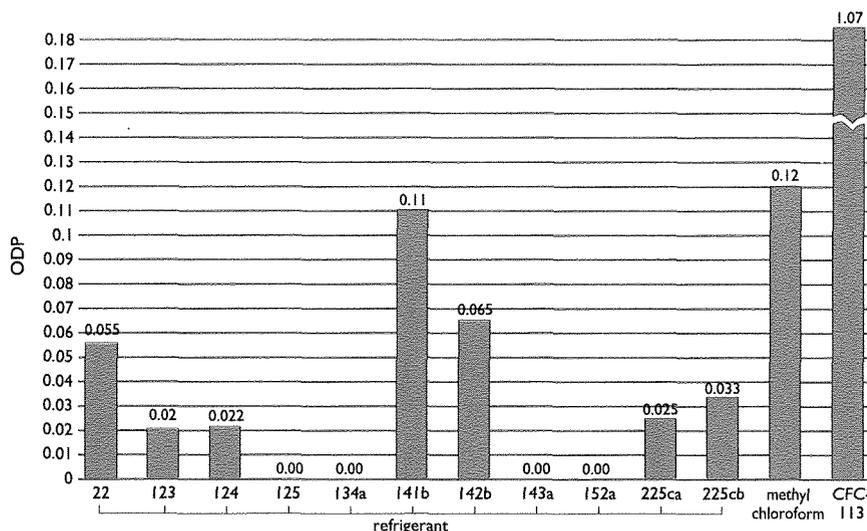
substitute CFC-113 and methyl chloroform solvent requirements

- zero or low ODP
- zero or low GWP
- effective cleaner
- non-toxic
- non-flammable
- non-explosive
- low viscosity
- non-reactive
- non-corrosive
- good recoverability
- low operating cost
- biodegradable

alternative processes

- semi-aqueous cleaning
- aqueous cleaning
- emulsion cleaning
- no-clean alternatives
- plasma cleaning

ODP of halogenated substitutes for CFC-113 and methyl chloroform



Graph right shows the ODPs of the major halogenated substitutes for CFC-113 and methyl chloroform. All the HCFCs included here, except HFC-125, -134a, -143a and -152a, are transitional substances and cannot be considered as substitutes over the long term.

Note: the values shown are revised figures based on the conclusions of the 1991 UNEP Scientific Assessment; they differ from those in the Montreal Protocol, and have not yet been accepted by Parties to the Protocol.

Properties of selected ozone-depleting solvents and their alternatives

	ODP	boiling point (°C)	surface tension (dyne/cm)	toxicity	carcinogenicity	flash point (°C)
CFC-113 C ₂ Cl ₃ F ₃	1.07	47.6	17.3	low	none	none
methyl chloroform CH ₃ CCl ₃	0.12	72–88	25.4	low	none	none
carbon tetrachloride CCl ₄	1.1	76.5	27	medium	yes	none
HCFC-225ca CF ₃ CF ₂ CHCl ₂	0.025	51.1	16.3	incomplete	unknown	none
HCFC-225cb CClF ₂ CF ₂ CHClF	0.033	56.1	17.7	incomplete	unknown	none
HCFC-141b/HCFC-123/ methanol blend CH ₃ CFCl ₂ /CF ₃ CCl ₂ H/CH ₃ OH	0.08-0.13	30–32	18.5-19	incomplete	unknown	none
Isopropanol CH ₃ CH ₂ CHOH	0	82	22.6	medium	none	12
methylene chloride CH ₂ Cl ₂	~0	39.4–40.4	n/a	medium	see note 1	none
pentafluoropropanol (5FP) CF ₃ CF ₂ CH ₂ OH	0	81	19	incomplete	unknown	none
perchloroethylene CCl ₂ CCl ₂	0	120–122	31.3	medium	see note 2	none
trichloroethylene CHClCCl ₂	0	86–88	29.3	medium	see note 3	none

KEY	
incomplete	toxicity testing in progress
unknown	unknown value
methyl chloroform	inconclusive toxicity tests
perchloroethylene	is regulated in most States of the United States as a VOC
blends	in addition to blends containing 90% CFC-113, some CFC manufacturers have introduced 'low' CFC-113 blends with 60-70% CFC-113 which are useful temporary substitutes
note 1	the IARC classification is Group 2B ('possibly carcinogenic to humans')
note 2	the IARC classification is Group 2B ('possibly carcinogenic to humans')
note 3	the IARC classification is Group 3 ('not classifiable as to its carcinogenicity to humans')



Electronics

Solvent losses in the electronics industry are often large, most occurring during cleaning, the rest during recovery and other handling operations. In a conventionally-maintained plant only 20 percent of the total solvents consumed may be recovered. Up to 90 percent of all solvent loss in the electronics industry could be eliminated through conservation, recovery and recycling at minimal net cost (see page 31). Such processes will be vital while longer-term solutions are developed and while equipment and procedures are modified. CFC-113's main advantage to the electronics industry as a non-corrosive solvent is less compelling now, due to the increasing use of more solvent-resistant assembly coatings. This has led to a greater use of methyl chloroform, but also allows the wider use of other, harsher substitutes. Electronic assemblies can be specifically designed with aqueous cleaning in mind and military specifications are currently being changed to allow use of non-rosin fluxes and aqueous cleaning. Replacement chemicals and technologies are already commercially available. The most environmentally sound alternative is the elimination of cleaning. A number of fluxes and flux application technologies exist which make this alternative viable.

Substitute solvents

Many alternative solvents could replace CFC-113 and methyl chloroform in electronics cleaning, either singly or in combination using different processes. Other chlorinated solvents such as trichloroethylene, perchloroethylene and methylene chloride have been used as effective cleaners for many years. They have been extensively tested. In some countries, the first two are regulated as volatile organic compounds (VOCs), which contribute to tropospheric ozone formation. These substances may be used providing their use does not contravene national regulations.

Hydrocarbon/surfactant solvents are mixtures of organic compounds and agents that reduce the surface tension of water and hence improve the efficiency of water cleaning. Organic chemicals used in conjunction with such surfactants include terpenes, alcohols, aldehydes and esters. They are non-corrosive, have low viscosity and foaming values, remove both polar and non-polar contaminants, and are useful for cleaning closely-spaced electronic assemblies at low temperatures. They require specially designed explosion-proof equipment because of their low flash points and potential room temperature flammability; because they are classified VOCs, their mists and vapours must be contained. These blends can be used to clean all types of soldered assemblies—most electronic assembly components are compatible with most hydrocarbon/surfactant blends. Terpene wastes may be hazardous and require proper disposal to prevent further environmental problems. A new hydrocarbon/surfactant blend, ethyl lactate, is an excellent non-toxic cleaner which mixes with water, but may deplete oxygen in discharged wastewater. Waste chemicals from these solvents have not yet been extensively tested.

Other organic solvents, such as ketones and alcohols, are effective in removing both solder fluxes and many polar contaminants. Being flammable and classified as VOCs, they can be used only in small quantities in well-ventilated areas. Isopropanol looks promising as a substitute and is an acceptable cleaner for activated rosin and other military-approved

Some 90 percent of all solvent loss in the electronics industry could be eliminated through conservation, recovery and recycling—at minimal net cost.

Key facts**substitute solvents**

chlorinated solvents
 hydrocarbon/surfactant blends
 organic solvents
 alcohol-derived solvents
 solvent blends

substitute technologies

aqueous cleaning
 aqueous cleaning and saponifier
 aqueous cleaning and hydrocarbon/surfactant blends
 light hydrocarbon solvent cleaning
 permitted halocarbon solvent cleaning
 no-clean technologies

fluxes. Special equipment required for flammable alcohol-based solvents is now commercially available including cold solvent cleaners, hot solvent cleaners, vapour-phase batch cleaners, in-line cleaners and immersion cleaners. Most use ultrasonic agitation and/or sprays to achieve a more thorough cleaning.

CFC-113 and methyl chloroform are non-polar and remove ionic contaminants only when blended with alcohols. New blends use significantly reduced amounts of ozone-depleting solvents and, while they are suitable short-term substitutes, they are not viable as long-term alternatives. Other partially or fully halogenated organic solvents such as pentafluoropropanol (5FP) and HCFC-225 could be substituted for CFC-113 and methyl chloroform. Their ODPs are low, though not zero. Toxicity testing (still incomplete) is promising for HCFC-225. A blend of HCFC-141b, HCFC-123 and methanol is available, and can be used in enclosed vapour degreasers; but HCFC-141b has a high ODP, and HCFC-123 has uncertain toxicity.

Alternative technologies

Aqueous cleaning requires no distillation equipment and often no water pretreatment, which can result in cost savings (though these may be offset if wastewater treatment and disposal is needed). Water is excellent for removing ionic contaminants and water-soluble fluxes; in combination with saponifiers, water can remove non-polar substances such as rosin flux residues, oils and activators. Water may also be combined with alcohol, neutralizers and detergents to maximize cleaning effectiveness. During cleaning, water may become too contaminated to remove fluxes effectively, in which case the water must be treated by deionization, reverse osmosis or carbon adsorption. Aqueous cleaning equipment includes mechanized brush cleaning machines, dishwasher-type batch machines, high-throughput batch machines, tank-immersion batch machines, and in-line conveyORIZED machines, each method being relevant to specific electronics applications.

Combination cleaning is used where no single solvent can remove all fluxes residues, as some contaminants are not water-soluble and some are not solvent-soluble. Substitute

Key facts

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

solvents can be used in conjunction with aqueous cleaning. Cost comparisons between aqueous and solvent cleaning favour aqueous methods by a small margin, particularly for large manufacturers, even taking into account the need for wastewater monitoring and disposal. New closed-loop aqueous cleaners minimize the discharge of contaminated water by recycling the water. They reduce operating costs and are commercially available.

No-clean options include the use of low-solids fluxes in printed circuit board manufacture. They can eliminate the need for cleaning altogether in numerous applications, particularly in consumer electronics where a relatively low level of cleanliness is required. However, in some military applications, where extremely high levels of cleanliness are required, all residues need to be removed.

Numerous new fluxes have been developed containing 2–10 percent solids as opposed to the traditional 15–35 percent solids. Many low-solid fluxes are non-corrosive and have high surface insulation resistance. It is unnecessary to remove the small residues that may be left, even for cosmetic purposes, resulting in material and operating cost savings—though existing soldering machines could need modification. Further testing is required to determine the relevance of this technology to different applications. High-solids fluxes requiring no post-soldering cleaning are also being used.

Controlled atmosphere soldering is another cost-efficient, no-clean option. Two options are involved: soldering in an inert or a reactive gas. In the former, an inert gas such as dry nitrogen fills the soldering chamber, displacing the air in preheated areas. Without oxygen, the solder leaves little oxide formation after soldering—solder dross can be reduced by as much as 90 percent compared to normal soldering. Maintenance time is greatly reduced. Reactive atmosphere soldering uses a reactive agent in an inert gas to reduce oxide layer formation on circuit boards.

Ice-particle cleaning is a new ozone-safe technology under development. Using ice-cleaning apparatus, a spray of ice particles, from 0.1–300 micrometres in diameter, is directed at a printed circuit board or precision parts; particle size and hardness, and spray pressure and angle, can be controlled as required to clean effectively.

Precision cleaning

Many companies have made significant progress in developing alternatives to CFC-113 and methyl chloroform in precision cleaning, including substitute solvents and new or improved technologies. Conservation methods could be implemented immediately in some applications (for example, clean-room assembly) to reduce current CFC-113 and methyl chloroform use and emissions in the short term. In large companies segregated solvent collection, coupled with training and investment, could reduce CFC-113 use by up to 85 percent (see page 31). Long-term prospects for switching to alternatives are excellent: ozone-depleting solvents could be replaced by 1997 in precision cleaning. Alternative materials have not yet achieved market penetration, but this is likely to change as the price of CFC-113 increases over the next few years. Major considerations in finding alternatives for precision cleaning solvents are ease of drying and material compatibility—due to the large range of materials and parts and the delicacy of instruments in this sector.

Substitute solvents

HCFCs have similar properties to CFC-113 and methyl chloroform, including compatibility with most metals and plastics. Regulated as transitional substances, their use is likely to be controlled in the future so they should be adopted only where other methods of cleaning are inapplicable. Performance evaluation and toxicity testing are still in progress for HCFCs. They present no drying problems but can be used economically and safely only in equipment designed to have very low emissions. HCFC-225 could be used for cleaning disk drives, gyroscopes, hydraulic control systems, optical components, electrical contacts, plastic assemblies and special lubricants. HCFC blends, such as constant boiling blends of HCFC-123 and HCFC-141b, can also be used in the medium term; they are compatible with the materials used in the flotation fluids of delicate gyroscopes.

Alcohols and ketones may be used in precision component cleaning, subject to material compatibility and use of explosion-proof or gas-blanketed equipment for low flash-point alcohols. With this equipment, and ultrasonic agitation, boiling isopropanol, combined with acetone, is a substitute in many applications—though not in large-scale clean-room operations, nor for polymers. HCFC/alcohol blends are also possible substitutes but the alcohols may damage metals such as beryllium.

Perfluorocarbons (PFCs), where all hydrocarbon hydrogen atoms have been replaced by fluorine, are compounds of great chemical stability, low toxicity, non-flammability and low ODPs. PFCs are suitable solvents for medical applications in which pure oxygen is used at high pressure, and for cleaning high accuracy gyroscopes—but equipment needs to be designed according to the application. However, PFCs are costly and have very high global warming potentials; they are unlikely to be acceptable as long-term substitutes. PFCs can be used as vapour blankets over alcohol cleaners to render them less flammable, providing an effective cleaning mix. Aliphatic hydrocarbons (such as mineral spirits, n-paraffin and kerosene) can be used as substitutes in processes similar to aqueous cleaning—with the advantage of not requiring water. Recovery processes such as carbon adsorption are essential as many aliphatics are classified as VOCs. They have been extensively tested. In some countries trichloroethylene and perchloroethylene are regulated as VOCs which

Long-term prospects for switching to alternatives are excellent: ozone-depleting solvents could be replaced by 1997 in precision cleaning. Alternative materials have not yet achieved market penetration, but this is likely to change as the price of CFC-113 increases over the next few years.

Key facts

substitute solvents:

- alcohols
- perfluorocarbons
- synthetic aliphatics
- HCFCs
- HCFC blends
- HCFC/alcohol blends
- other chlorinated/organic solvents

alternative technologies

- aqueous and semi-aqueous cleaning
- supercritical fluid cleaning
- UV/ozone cleaning
- pressurized gas cleaning
- plasma cleaning

contribute to tropospheric ozone formation. Trichloroethylene, perchloroethylene and methylene chloride may be used subject to national regulations.

Alternative technologies

Disk drive parts and gyroscope components are already being water cleaned by some major companies. Water is the most likely long-term precision cleaning substitute for CFC-113 and methyl chloroform. Water works better than CFC-113 in removing ionic contaminants, but is less effective in removing some organic contaminants, and dries slowly if special drying techniques are not used. Aqueous cleaning involves the use of spray, ultrasonic, hot-air and vacuum oven drying processes. Product design can affect cleanability and a rapid spot-free dewatering system is necessary. Semi-aqueous cleaning uses hydrocarbon/surfactant blends as emulsions in water solutions, or in concentrated form followed by water rinsing. It is effective and is compatible with most materials; however, safe worker exposure levels have not been established for some blends, and energy consumption may be high unless rinse water is recycled.

Plasma cleaning is a widespread method of cleaning gyroscopes. Electrically charged gases (such as oxygen, argon, helium and silicon tetrafluoride) are used to remove contaminants. Radio frequency discharges are used to produce the plasma, and these raise the energy levels of the charged particles in the plasma sufficiently to break the chemical bonds in organic contaminants. Volatile compounds are formed as a result which are swept out of the chamber by a gas. The process is non-toxic and has low operating costs, but the capital cost can be high and contaminant layers are not always cleaned at an even rate. Plasma cleaning is a viable option only for special circumstances since its use must always be preceded by solvent cleaning to achieve an ultra-clean, smooth surface.

Filtered, contaminant-free pressurized gas or air is increasingly used as a CFC-113/methyl chloroform substitute for cleaning cross hairs in surveying instruments, high definition cathode ray tubes and electron guns to remove non-metallic dust and particles.

Supercritical fluids are gases held above the critical temperature and pressure at which they would normally condense. Such gases are powerful solvents. They work rapidly to remove medium-molecular weight and low polar substances. They involve low operating but substantial capital costs.

Ultraviolet (UV) light combined with ozone can be used to remove organic films from a wide variety of surfaces—glass, quartz, sapphire, ceramics, metals, silicon and polyamide cement. Cleaning results from oxidation which is caused by a photosensitive chemical reaction. UV/ozone cleaning is simple, inexpensive and rapid. Concerns about worker and material exposure to UV light, and low workplace ozone limits (0.1 ppm), mean that specially designed equipment is needed, which entails further testing and development.



General metal cleaning

In recent years, the metal finishing industry has begun to use aqueous and semi-aqueous processes as alternatives to methyl chloroform and CFC-113. However, the industry is not formally organized in a manner which would allow the uniform phase out of these ozone-depleting solvents. The wide range of substrates being cleaned and the variety of processes used in metal cleaning and finishing mean that process-specific alternatives must be found for reducing CFC-113 and methyl chloroform use. Using all the alternatives mentioned here, CFC-113 and methyl chloroform use in metal cleaning applications could be replaced totally by the year 1997. A 90 percent reduction could be achieved within three to five years using these methods, and adoption of alkaline and emulsion cleaning could effect 75 percent of all short-term reductions.

As in other sectors, significant amounts of solvent can be recovered by improved operating practices and by using conservation processes specific to metal degreasing (see page 31). There are a few cleaning applications for which immediate substitution is limited to other chlorinated solvents, aliphatic hydrocarbons or aromatic hydrocarbons—oil-retaining bearings of power metallurgy products are the principal example.

Substitute solvents

Where metal substrates (such as mild steel parts) could be corroded by other solvent substitutes or where heavy contamination needs removing, trichloroethylene, perchloroethylene and methylene chloride may be short-term alternatives to methyl chloroform.

The United States Air Force has identified and tested six non-corrosive, biodegradable solvents to replace chlorinated and CFC solvents, including: petroleum distillate, ethyl ester, potassium hydroxide primed alcohol, 4-isopropenyl-1-methyl cyclohexene, alkyl acetate ester and dipropylene glycol/monomethyl ether. Other potential metal degreasing compounds have been developed, including hydrocarbon/surfactant blends, dibasic acid esters and n-methyl pyrrolidone. They are being tested for performance, toxicity, exposure limits, flammability, carcinogenicity, odour, recyclability and cost.

For cold immersion and manual cleaning, commercial solvent blends are already available, including mixtures of aliphatic and aromatic hydrocarbons (naphtha, toluene, xylene) and oxygenated solvents (ketones, esters and alcohols). Cold immersion in these blends removes heavy grease and other industrial contaminants. The new blends are being

CFC-113 and methyl chloroform use in metal cleaning applications could be replaced totally by the year 1997. A 90 percent reduction could be achieved within three to five years and adoption of alkaline and emulsion cleaning could effect 75 percent of all short-term reductions.

Alternative solvents and technologies for general metal cleaning

	<i>cold immersion</i>	<i>hot immersion</i>	<i>high pressure spray</i>	<i>manual</i>
alkaline cleaners	●	●	●	
emulsion cleaners	●	●	●	●
low vapour pressure solvent blends	●	●	●	●
hydrocarbon/surfactant blends	●			●
naphtha/hydrocarbons	●		●	
naphtha/terpene blends	●		●	
steam			●	

Key facts**substitute solvents**

aliphatic hydrocarbons
 aromatic hydrocarbons
 alcohol/azeotrope blends
 HCFC blends
 hydrocarbon/surfactant emulsions
 alkaline cleaners

alternative technologies

aqueous cleaning with ultrasonics
 semi-aqueous cleaning
 vacuum de-oiling
 no-clean options

developed to minimize flammability (their chief disadvantage) and toxicity. HCFC blends need improved recovery, handling and storage facilities due to their low boiling points which cause emissions during cleaning.

Alkaline cleaners are the most widely applicable substitutes for metal degreasing and could replace 75–90 percent of current methyl chloroform and CFC-113 solvent use. Their active ingredients include anionic and non-ionic surfactants, chelating and sequestering agents, and corrosion inhibitors. Hundreds of alkaline cleaners are available, and more are being developed for special applications. Qualification testing will be necessary for specific applications. The major aerospace manufacturers in the United States are in the process of replacing chlorinated and CFC solvents with alkaline and emulsion cleaners (hydrocarbon/surfactant blends). For example, General Dynamics' Fort Worth Division, a total integrated aircraft manufacturing facility, has replaced degreasing with an alkaline cleaner in metal forming and finishing processes. Acidic cleaners may be used to remove rust and scale, and to clean aluminium, which reacts with high alkalinity solutions, particularly those containing sodium hydroxide.

Alternative technologies

Aqueous cleaning uses immersion with mechanical agitation (impeller-type mixers or pumps) or spray processes. Ultrasonic agitation is applicable in small-scale systems. Each requires different equipment that may have optional features such as solution heaters, dryers, part-handling automation equipment, solution filtration, recycling and water treatment equipment. Proper waste disposal is important in aqueous cleaning, because some by-products are not biodegradable; this adds to cost.

Emulsion cleaners (hydrocarbon/surfactants) are used in semi-aqueous cleaning and have many different formulations. They are used with ultrasonic agitation and fluid circulation to clean metal parts. Their advantages are low vapour pressures, low evaporation loss, low flammability and low flashpoints, as well as being potentially less expensive than CFC-113. But they have associated recycling and disposal problems, low contaminant-saturation capacity and require special equipment. Aqueous immersion and solvent emulsions in semi-aqueous processes can be used in all metal-cleaning operations. Tubing, complex shapes, and sensitive materials all require specially designed equipment which has been tailored for that specific process. Additional research and system design work is needed when considering complex applications for aqueous/alkaline and emulsion cleaning technologies.

Thermal vacuum de-oiling can be used to clean parts after cutting, machining and stamping, and in preparation for coating and heat treatment. Oil is removed from parts by vaporization in a heated vacuum chamber to give a super-clean finish. The operation is simple, but contaminant specific.

No-clean options for metal degreasing include water-soluble, emulsifiable machining and metal forming lubricants (some non-chlorinated). They are much easier to remove with aqueous cleaners and not hazardous to workers. Dry lubricants and thin polymer sheeting which can be peeled from a metal surface after a metal forming operation are being developed. The technology is still in its infancy.

Dry cleaning

Prospects for Action

Key facts

Phase out option currently linked to replacement by perchloroethylene

Super-tight perchloroethylene dry cleaning machines are available

Short-term conservation is by improved operating practices and maintenance

The dry cleaning industry is a relatively minor user of CFC-113 and methyl chloroform. In some cases operation and maintenance techniques could be improved. Most solvent losses from the dry cleaning industry are due to poor recovery techniques, leaks, distillation losses and poor handling practices during refilling and servicing. Losses could be reduced by up to 90 percent but, although these figures seem potentially high, the industry is a frugal user of solvent. A typical machine uses only 5–10 litres a week. Recycling and recovery technology is already advanced, and all CFC-113 machines currently operate a dry-to-dry system incorporating solvent recovery technology. The only phase-out option currently available to most dry cleaners with machines using CFC-113 is to replace them with machines using perchloroethylene.

Capital costs of replacing dry cleaning machines are relatively high: machines which are designed to last up to 15 years represent a large capital investment for the small businesses that underpin the industry. Conservation is the best short-term measure to reduce usage. Two or three percent of the new CFC-113 dry cleaning machines can be retrofitted to accept different solvents. Garment manufacturers should be urged to produce clothes that can be cleaned only with CFC-113 with warnings stating that, at a future date, these garments may no longer be able to be dry cleaned.

Substitute solvents

Perchloroethylene is the most widely used dry cleaning solvent and has proven to be the only effective substitute for CFC-113 and methyl chloroform, though it is not suitable for all dry cleaning due to its strength. It can be safely used in new super tight machines which have been specially developed. These machines incorporate newly designed carbon adsorption systems which further reduce the already frugal solvent consumption. Some authorities consider it to be a possible human carcinogen but most agree that there is a low risk to humans under normal conditions of use (see page 16).

It is possible that HCFC-225 may be a suitable substitute for dry cleaning. This is defined as a transitional substance under the Montreal Protocol and should be used only with sophisticated recovery systems. It may be usable in the same machines as CFC-113.

Stoddard solvent or white spirit is too flammable for widespread use in commercial shops, its use is permitted by some authorities but its long-term toxicity has not been established and it also emits hydrocarbons into the atmosphere.

Alternative technologies

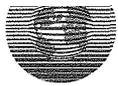
New features being introduced to dry cleaning machines include carbon adsorption systems to absorb solvent vapour prior to discharging air into the atmosphere. These can be retrofitted onto smaller machines, and can result in up to 90 percent solvent savings. Disc filtration can be used to remove contaminants from the solvent, and heat pumps can be used to pre-heat solvent before distillation.

BRAND SIZE 42

DRY CLEAN ONLY

WARNING: THE FLUID REQUIRED TO DRY CLEAN THIS GARMENT IS BEING PHASED OUT TO PROTECT THE OZONE LAYER FROM DAMAGE.

RESEARCH ON ALTERNATIVE PROCESSES IS UNDER WAY BUT IT MAY NOT BE POSSIBLE TO CLEAN THIS GARMENT IN THE FUTURE



Adhesives

Key facts

potential substitutes and technologies to improve adhesive performance

- water-based adhesives
- hot-melt systems
- radiation curing
- high-solids adhesives, powders
- reactive liquids

Methyl chloroform use as a solvent in adhesives can be reduced if existing substitutes are used or if the solvent is recovered in continuous operations. Emerging technologies to improve adhesive performance include radiation curing, high solids adhesives, powders and reactive liquids. The expense involved in adopting existing substitutes is affected by raw material costs and whether the alternative is a restricted VOC requiring expensive ventilation and vapour recovery equipment. However, the savings involved in using water-based adhesives have led a trend away from solvent-based adhesives. Most of these options can be used in developing countries and by smaller users.

Solvents and non-solvent substitutes

Rubber binders in methyl chloroform adhesives can be dissolved in other solvents such as acetone, ethyl acetate, heptane and toluene. Previous solvent formulations could also be used, but such solvent-based adhesives are expensive as they require flame-proof equipment (such as robots operating in enclosed areas) and are applicable only to large users.

Water-based adhesives can be solutions, latexes or emulsions. The latter are likely replacements for methyl chloroform and other solvent-based adhesives, because of their versatility and improved performance, though latexes require more complex formulation. The effectiveness of water-based adhesives in all applications has yet to be established, but they perform well on many surfaces, especially non-porous to porous bonding, and moist surfaces. They are not suitable for non-structural bonding of rubbers and many plastics, and require special handling, storage and transportation facilities.

Hot-melt adhesives are applied molten, forming a bond on cooling to a solid. They comprise 100 percent solid thermoplastic bonding materials and are used in bookbinding, packing, textiles and product assembly. They rely on polyolefin and polyamide/polyester rosins and thermoplastic elastomers for binding materials; the newer versions are clear and UV-resistant, which makes them suitable for outdoor use. Their applications are otherwise limited.

Alternative technologies

Radiation curing is a new technique which uses radiant energy (UV, infrared, electron beam, gamma and x-ray) to dry and preserve adhesives containing binding agents such as acrylic, epoxy, urethane, anaerobic material and polyester rosin. It is suitable for consumer products, transport, packaging, medical and dental uses, and particularly for electronics and communications applications where parts and glues must be resistant to environmental factors, electricity and ageing.

High solids adhesives use existing polyester and urethane technologies for laminating, at for example 68.5 percent solids, lowering the volatile content of adhesives. Powders of epoxy, urethane and rosins must be refrigerated to prolong their shelf-life.

A worldwide trend away from solvent-based adhesives—because of their low cost—is helping the adhesives industry reduce its consumption of methyl chloroform.

Coatings and inks

Methyl chloroform use as a solubilizer of binding substances in decorative coatings and inks has increased in recent years due to concern over the health risks of volatile solvents. CFC-113 use has remained very low in this sector. A number of suitable replacement solvents and formulations are available or under development. These may require improved handling and storage facilities as many are flammable. Solvent recovery systems such as carbon adsorption can effectively capture the emissions that result from evaporation during production.

Replacements

Water-based, high solids and powder formulations can be used in place of methyl chloroform and other solvents to produce coatings and inks. Water-based coatings now dry more quickly, are more durable and stable, have better adhesion and can be used for furniture, car electronics, hardboard, metal container, structural steel and heavy equipment coatings. Solvents can be added to coatings for better performance (such as improved wetting ability) at low concentrations which meet VOC regulations; an effective mixture might contain 80 parts water to 20 parts alcohol/ethyl acetate by volume.

High solids coatings contain less solvent and more rosin than conventional coatings. They can be used for appliances, metal furniture, and heavy construction equipment. They are applied using dipping, flow-coating, air or airless atomizing, air or airless electrostatic spraying, rotating disks and bells, rolling, continuous coating, centrifugal coating and tumbling.

Powder coatings contain no solvent and are applied by heating an object above the melting point of the powder, causing the rosin it contains to harden into a continuous film; the rosin forms a durable, corrosion-resistant finish. Powder coatings can be used on underground pipes, electrical components, cars, garden and farm equipment, steel shelving, some furniture and electrical transformer covers.

Methyl chloroform used as a solvent in coatings and inks can effectively be replaced by using water-based formulations, high solids coatings and powder coatings.

Aerosols

The global use of ozone-depleting substances solely as a solvent in aerosol liquids is relatively small (although use as a propellant or as a combination solvent and propellant is still very large). Most of the CFC-113 and methyl chloroform used in this way can be replaced with alternative compounds. The flammability and density of these alternatives must be evaluated. Switching to alternative delivery methods could eliminate the need for an aerosol package altogether. Alternatives are not yet available for all applications that require non-flammable substitutes—such as customer-applied water and oil repellents, spot removers and suede protectors; mould releasers; and electronics and brake cleaners.

Substitute aerosol liquids

Organic solvents such as petroleum distillates can be used to replace methyl chloroform and CFC-113 only in certain applications, because of their high flammability. Some formulations are now commercially available, particularly for the motor industry and for household goods. Petroleum-based solvents are less dense than methyl chloroform, so need larger containers to deliver a similar weight of product; this will result in a significant cost increase for aerosol manufacturers.

Water-based systems are applicable for certain fog-insecticides, but reduce the dispersability of the propelled liquid so may reduce overall effectiveness. Research and development is being undertaken to produce effective water-based solvent mixtures.

Alcohol, HCFCs and HCFC blends could be substituted for the largest current use of aerosol CFC-113 products, the repair of printed circuits.

Alternative delivery systems

The use of ozone-depleting solvents in aerosols products could be eliminated if alternative delivery methods are adopted. Some are already available, such as the use of brushes, vacuum enclosure cleaning for brakes and greater use of professional dry cleaners instead of aerosol spot-removers—for which there are no substitute aerosol formulations.

Methyl chloroform and CFC-113 used in aerosols can be replaced by using petroleum distillates, water-based formulations, HCFCs, HCFC blends and alternative delivery systems.

Performance factors and applications for aerosol solvent substitutes

	PERFORMANCE FACTORS		MAIN PRODUCT APPLICATIONS		
	flammability	density	automotive/ industrial	pesticides	household products
petroleum distillates	high	0.75	●	●	●
water systems	low/none	1.00	●	●	●
HCFC propellants	none	1-1.21	●	●	●
aromatic hydrocarbons	high	0.87	●		●
alcohols	high	0.80	●	●	
ketones	high	0.66	●	●	

Other industrial uses

Ozone-safe substitutes can be found for the remaining uses of CFC-113 and methyl chloroform.

Selected alternatives

Alternative lubricant bearers to reduce friction damage in machines are currently under development. They include mechanical methods, applying lubricant with emulsions, using alternative solvents that are compatible with fluorinated lubricants—such as HCFC-225— or using plastics-compatible alternative lubricants.

Vapour-phase soldering alternatives include avoiding the use of a secondary vapour blanket by using batch equipment that works without a vapour blanket, or using a secondary vapour blanket which is not ozone depleting. A perfluorocarbon liquid has now been developed with an atmospheric half-life of 1000 years which could meet this requirement.

Many electronic parts need drying immediately after production to prevent rust, staining and deterioration. Drying can be achieved without relying on CFC-113 by dipping wet circuits into two successive tanks filled with isopropanol fitted with dryers; or dipping them into a toluol-based water-displacement product. Mixtures of fluorocarbons and HFCs could be used in the medium-term for plasma etching in semiconductor manufacture in place of ozone-depleting solvents.

New lubricants are being tested to replace CFC-113 in aircraft wing riveting. A new cost-effective process has been developed for testing aircraft hydraulic systems, using inert gas and audio-inspection. Gas chromatography is a suitable substitute that replaces the use of CFC-113 in chemical analysis. Helium and other halocarbons can be used in miscellaneous testing, and CFC-113 alternatives should be commercially available by the end of 1994.

New agents for releasing products from moulds include either internal or water-based external release materials. Solvent recovery techniques could be used in the film cleaning industry until replacements have been identified and are available. In cooling operations—for example to shock-cool electrical components during diagnostic procedures—HCFC-22, carbon dioxide aerosols, mechanical cooling devices and liquid nitrogen have been found to be effective substitutes.

By the year 1997 all the CFC 113 and methyl chloroform used in miscellaneous solvent applications can be replaced by alternatives already available or now being developed.

Conservation and recovery

The Montreal Protocol covers only the consumption and production of ozone-depleting substances. Recovery and recycling is not included, and this is a major incentive for the solvents industry to improve conservation and recovery practices. Any reduction in current levels of consumption using such methods will contribute significantly to achieving the goals of the Protocol. Improved conservation and recovery protects the ozone layer, the local environment and the health of workers, and improves efficiency and saves money. Some countries are introducing specific measures to encourage better practices, over and above those required by the Protocol: the US Congress, for example, has placed an excise tax on ozone-depleting chemicals. Conservation and recovery practices are effective short-term solutions while longer-term solutions are being selected.

As much as 75 percent of the ozone-depleting solvents now being lost to the atmosphere could be conserved and recycled.

General steps

Some of the main sources of emissions in the major sectors of the solvents industry are: diffusive and convective losses of solvent vapour from equipment; leaks from equipment and connective piping; and liquid dragout on work being processed. Older equipment is generally less efficient and more likely to emit solvents, but can be retrofitted with containment devices. Five general steps can be taken by most companies to reduce solvent consumption and emission:

- **ELIMINATE** unnecessary cleaning; consolidate and centralize all cleaning processes, using fewer machines where possible;
- **ISOLATE** open sources of emissions, to give reductions of 50–80 percent. Open-top vapour degreasers can be retrofitted to include covers; vents can be turned off;
- **AUTOMATE** vapour degreasing and other processes—this can reduce solvent emissions by 20–30 percent;
- **EDUCATE** managers and operators about the financial and environmental costs of using ozone-depleting solvents, and about better procedures; these changes can reduce emissions by about 30 percent;
- **MAINTAIN** equipment according to manufacturers' specifications—thus reducing solvent loss by up to 20 percent.

Specific measures

In the electronics industry, solvent losses can amount to 90 percent of total consumption, so recovery measures should be adopted wherever possible. One US company estimated savings of up to \$250 000 per annum by recycling solvent wastes in-house.

Vapour degreasers used in electronics assembly (and general metal cleaning) can be fitted with covers or baffles to reduce diffusive and convective losses—on a warm day up to 20 litres of solvent can be evaporated just from an open container. Increasing the freeboard height can reduce evaporation losses. All machinery, and particularly batch cleaners, can be located in draft-free environments which reduce convective losses, and detectors can be used to monitor leakage from pipes and equipment.

Dragout losses contribute significantly to overall emissions. They can be reduced by

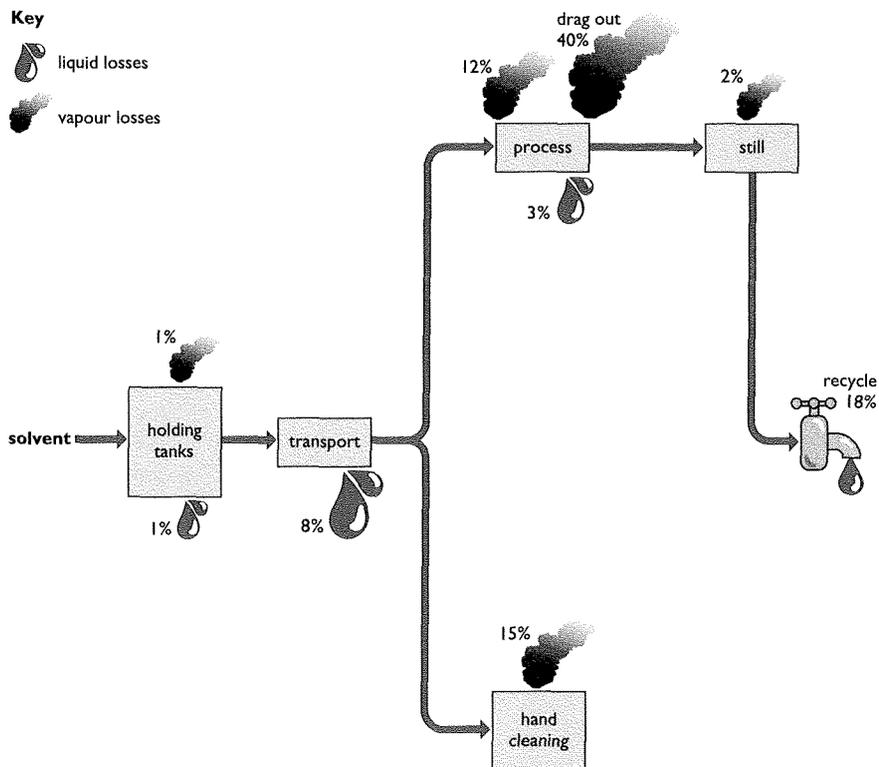
using automatic handling equipment programmed to feed parts into vapour degreasers at constant speed and for the correct length of time to produce an effective clean. Better basket and rack design can also reduce dragout in electronics cleaning. Fans used to cool parts after soldering can ensure that circuit boards enter cleaners at temperatures that minimize evaporation.

Dragout losses cannot be entirely eliminated so vapour capture systems—such as carbon adsorption—can be used. Solvent molecules are adsorbed on an activated carbon bed and are subsequently extracted by steam. After water separation, the solvent is rebled with additives for reuse.

Conservation and recovery are highly effective in precision cleaning during clean-room instrument assembly. Distillation at point-of-use is also possible. However, recycling the solvents used to clean complex military equipment is not practicable in the foreseeable future.

Good practices specific to general metal cleaning, including manual removal of large contaminants before degreasing with solvent and adding sophisticated filtration equipment,

Typical solvent losses during cleaning operations



Currently an average of less than 20 percent of solvent is recycled; this figure can be raised to nearer 75 percent with good recovery and recycling operations.

gravity separation, water adsorption, and single plate distillation. Vapour blanket collapse in general metal cleaning is often caused by introducing items with a large thermal mass. When the vapour blanket collapses, the air, saturated with solvent vapours, is expelled, causing a large solvent loss.

External reclamation and recycling services are often available to purify contaminated solvent and return it to the original customer or sell it to other users. On-site recycling is currently economical only if sufficient solvent wastes are generated.

Solvent recycling is advanced in the dry cleaning industry—many businesses have long had a financial incentive for frugal solvent use. Most existing machines have recovery equipment built in, and operator practices could be further improved by training to reduce solvent emissions by 25 percent. Ozone-depleting solvent use in adhesives, coatings, aerosols and other industrial applications is relatively small. In most instances they will be replaced by ozone-safe alternatives by 1997.

CASE STUDY: HOW A SWEDISH MANUFACTURER ELIMINATED CFC-113 USE

Saab Combitech Electronics produces simple and complex electronics for each of the Saab/Scandia groups and for outside clients. One-third of its solvent consumption is in automobiles; one-third in space, automation, transport control, and military applications; and the remaining third is for contract assembly. Solvents have been used with a combination of in-line vapour degreasers and aqueous cleaning processes.

One year before the Montreal Protocol, Saab took a corporate decision to reduce dependence on ozone-depleting chemicals, cancelling all orders to purchase new CFC vapour degreasers and freezing annual use of CFC-113.

The following reduction and elimination timetable emerged:

- 1986 corporate decision to freeze CFC use*
- 1987 vapour-phase CFC processes eliminated*
- 1988 carbon adsorption systems installed*
- 1989 low-solid fluxes adopted; controlled atmosphere soldering machines purchased*
- 1990 controlled atmosphere soldering implemented using low-solid fluxes*
- 1991 process simplified; further research into new fluxes*
- 1991 all manufacturing free of CFC-113 and methyl chloroform solvents.*

Saab now uses Lonco 25 flux in controlled atmosphere wave soldering machines, water-soluble flux in in-line aqueous/saponifier cleaning processes, and alcohol cleaning consisting of 90 percent ethanol, 10 percent isopropanol for rework and touch-up prior to adding conformal coatings, if needed. Alcohol is used for military products. The company is satisfied with the high quality of final products; in fact boards are cleaner now than they were when CFC-113 was used. Due to the early phase-out policy, the process was more expensive than it would be today, due to greater market availability of substitutes and advances in product research and development.

Reduction scenarios

The Montreal Protocol's Solvents, Coatings and Adhesives Technical Options Committee concluded in 1992 that the use of CFC-113 and methyl chloroform can be phased out by the dates shown in the table below. The phase out would use the combination of options described in this publication.

This reduction scenario is feasible only if there is a prompt worldwide response by governments, producers and user industries to the demands of the Montreal Protocol. Adequate engineering skills must be made available to develop alternative processes and materials. There must be sufficient impetus for industry to obtain market and regulatory approval for the use of selected alternatives, and sufficient capital must be available for their adoption.

Technically feasible phase-out schedule for developed and developing countries

	<i>CFC-113</i>	<i>methyl chloroform</i>
Developed 'head start' countries ¹	1990-1992	1992-1994
Other developed countries/ specific developing countries ²	1993-1997	1995-2000
Other developing countries	1995-2000	1997-2002

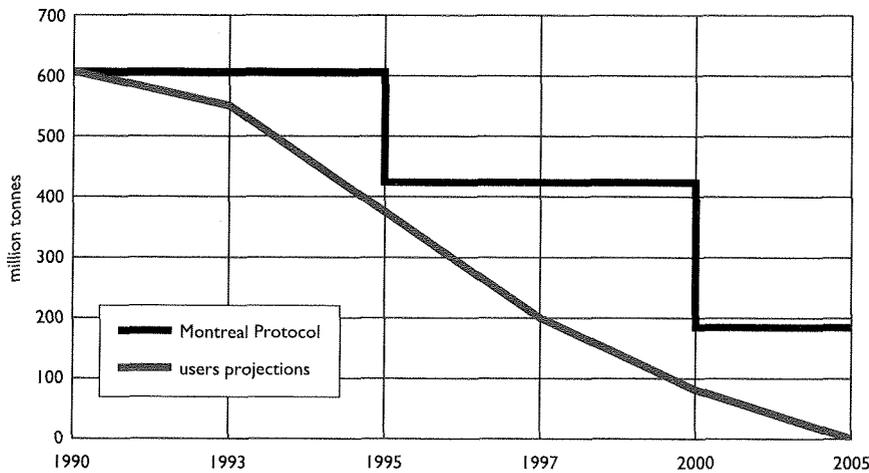
Notes:

1. Head start countries, including Austria, Germany, Norway, Sweden and Switzerland, have accelerated phase outs of ozone-depleting substances and have organized their industries to meet these goals.
2. Developing countries with strong technology transfer partnerships and/or aggressive regulatory regimes. They include Mexico, Singapore and Thailand.

With the freeze on production and the subsequent reduction in CFC availability in Montreal Protocol countries, the price of CFC-113 will increase, which will act as a catalyst to stimulate the use of those alternative solvents and technologies that are cost-competitive. Inevitable price increases may create a situation in which CFC-113 use becomes increasingly less economic and a more rapid phase-out may therefore occur.

A number of countries, including Austria, Germany, Norway, Sweden and Switzerland, plan to phase out the use of ozone-depleting solvents faster than the Protocol schedule. Considerable success has already been achieved. For example, by the beginning of 1991 the use of CFC-113 for electronics, metal and precision cleaning in Sweden had been reduced by 99.5 percent of its 1986 level. The use of CFC-113 in dry cleaning is to be permitted only until 1 January 1995, by which date methyl chloroform will be phased out. German legislation is even more ambitious, with phase out of both chemicals to be achieved by the end of 1992.

Forecasts of methyl chloroform use to 2005



Methyl chloroform phase out projections produced from a survey of solvent users are compared in the graph on the right with those of the Montreal Protocol. On the basis of this survey, the industry expects to phase out methyl chloroform faster than the requirements of the Protocol.

Financial help from the Interim Multinational Ozone Fund should enable some developing countries to achieve rapid results. Mexico, for example, is implementing a programme to eliminate the use of CFC-113 and methyl chloroform from manufacturing industry by the year 2000, with technical assistance from North American organizations. Similarly, US and Japanese government institutions have agreed to cooperate to help Thailand phase out the use of ozone-depleting solvents.

Protection of the ozone layer has become an important policy objective for companies still using CFC-113 and methyl chloroform. The commitment of large multinational companies and military establishments to phasing out use of CFC and other ozone-depleting substances means that large markets will soon exist for substitutes. This is also creating an example for corporate managers not yet sufficiently motivated to begin phase-out measures.

Similarly, many major manufacturers believe that their own phase-out plans will preempt those laid down by the Montreal Protocol. A survey of solvent users, for example, revealed that their expectations were considerably in advance of Protocol dates for methyl chloroform (see graph above). Many major manufacturers have also pledged to phase out the use of ozone-depleting solvents well before the year 2000 (see list right).

Many large companies offer technical assistance in transferring technology to developing countries. Some industries have already tested new alternatives but the information is not yet widely available. Smaller companies will follow the example of larger companies which will set trends in developing the markets for alternative solvents and cleaning processes.

Phase out target dates for CFC solvents in selected companies

Apple Computer	1992
Asahi Optical	1997
AT&T	1994
Boeing (90 percent)	1995
Canon	1995
Copal	1996
Digital Equipment	1995
Ericsson	1991
Fujitsu	1997
Hitachi	1995
Honda	1996
Honeywell	1997
IBM	1993
Intel (all ODS)	1992
Konica	1994
Litton Guidance	1996
Matsushita	1995
Mazda	1996
Minolta	1996
Mitsubishi	1996
Motorola	1992
Nikon	1996
Nippon (NEC)	1994
Northern Telecom	1991
Olympus	1996
Raytheon	1992
Sanyo	1995
Seiko Epson	1993
Sharp Corporation	1995
Shiseido	1991
Texas Instruments	1994
3M Corporation	1990
Toshiba	1995
Toyota	1995

Resources

The OzonAction Programme under the IMOF

The 1990 London Amendments to the Montreal Protocol created an Interim Multilateral Ozone Fund to help developing countries party to the Protocol meet the specified control measures. As one of the Fund's three implementing agencies, UNEP has responsibility for research, data gathering and an information clearinghouse function. In 1991 UNEP IE/PAC in Paris established the OzonAction Programme to discharge these duties. The programme includes three activities: information exchange, workshops/networking, and country programmes.

Information exchange includes an on-line information exchange system known as the OzonAction Information Clearinghouse (see box), the quarterly *OzonAction* newsletter, and a series of publications aimed at providing developing countries with technical and policy information needed to comply with the requirements of the Protocol. This document is part of that series.

Workshops/networking activities provide decision makers in government and industry with the latest scientific, technical and policy information on ozone-depletion control measures. The OzonAction Programme conducts a series of regional workshops, sponsors national information campaigns to help raise public awareness of the issues involved, and publishes technical papers, workshop proceedings and training manuals.

Country programmes are designed to help low CFC-consuming developing countries to establish their own baseline surveys, and draw up replacement and control strategies.

OzonAction Information Clearinghouse (OAIC)

The OAIC is an on-line data system that contains technical, policy and scientific information on a wide range of issues concerning the phase out of ozone-depleting substances controlled under the Protocol. It contains:

- descriptions of alternative technologies and product listings for each industrial use sector, including refrigeration and air conditioning;
- an international directory of experts;
- a database of technical literature abstracts, and information for ordering documents;
- descriptions of national and corporate policies and programmes to phase out the controlled substances;
- a listing of workshops, conferences and meetings concerning ozone-depletion issues;
- bulletins containing news on phase-out initiatives.

In addition to providing information directly through these databases, the OAIC also refers users to more specialized information held by other organizations. The clearinghouse's electronic mail feature allows users to pose queries and exchange information with UNEP IE/PAC and with one another.

There is no charge for using OAIC. Anyone with a personal computer, a modem, and communication software can access the system via the methods indicated below.

Access via normal telephone lines

Set communication software to 1200 or 2400 baud, 8 data bits, 1 stop bit, no parity, emulated terminal to VT 100 (if necessary) and dial (33-1) 40 58 88 78.

Access via SprintNet™

Set communication software to same settings as above, and dial your local SprintNet™ access number. Once connected, type D<enter> if you are using 1200 baud, @D<enter> if you are using 2400 baud. If you are using an IBM PC, type <enter> when asked for a terminal identifier. At the system @ prompt, type the OAIC access code: 76200604. Enter your SprintNet™ password when requested to do so.

Access via national packet switching networks (PSNs)

The OAIC can be accessed by numerous PSNs that connect with SprintNet™. Contact UNEP IE/PAC for more information (see inside front cover).

Contact points

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Interim Multilateral Ozone Fund (IMOF)

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Industry Cooperative for Ozone Layer Protection (ICOLP) membership includes:

AT&T
Boeing Company
British Aerospace
Compaq Computer Corporation
Digital Equipment Corporation
Ford Motor Company
GEC
Hitachi Ltd
Honeywell
IBM
Matsushita
Mitsubishi
Motorola
Northern Telecom
Sunstrand
Texas Instruments
Toshiba

ICOLP industry affiliates

American Electronics Association
City of Irvine, California
Electronics Industries Association
Japan Electrical Manufacturers' Association
Halogenated Solvents Industry Alliance
National Academy of Engineering

ICOLP government affiliates

Swedish Environmental Protection Agency
USSR State Institute of Applied Chemistry
United States Air Force
United States Environmental Protection Agency

Equipment and trade names

The following categories of ozone-safe equipment and solvents are now commercially available. A full list of manufacturers and vendors for each sector can be obtained from ICOLP or from the Thomas Register in the United States (see page 37).

Conservation and recovery

Licensed solvent recycling equipment
Carbon adsorption equipment
Emissions monitoring equipment
Vapour degreasing equipment

Precision cleaning

Alcohol cleaning equipment
Alternative solvents
Aqueous cleaners
Aqueous cleaning equipment
Hydrocarbon/surfactants
Plasma cleaning systems
Supercritical carbon dioxide
Ultraviolet light/ozone cleaners

Electronics assembly defluxing

Aqueous cleaners
Aqueous cleaning equipment
Hydrocarbon/surfactant cleaners
Hydrocarbon/surfactant equipment
Wastewater treatment equipment

General metal cleaning

Alcohol cleaning equipment
Alternative organic solvents
Aqueous cleaners
Aqueous cleaning equipment
Hydrocarbon/surfactant cleaners

The following are common generic trade names for CFC 113, and diluted CFC 113 blends.

Arklone
CG Triflon
Daiflon
Delifrene
Flon Showa Solvent
Flugene
Fluorisol
Freon
Frigen
Fluorisol
Fronsolve
Genesolve
Kaltron
Magidry
Nanofron

The following are common generic trade names for methyl chloroform and diluted methyl chloroform blends.

Aerothene
Asahitriethane
Baltane
Chlorothene
CG Triethane
Dowclene
Genklene
Kanden Triethane
Propaklone
Shine Pearl
Solvethane
Three One
Toyoclean
Triethane
1,1,1-Tri

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Glossary

adsorption	surface phenomenon in which substances form physiochemical bonds with other materials	neutralizer	substance added to balance the acid/alkaline content of water
alcohol	hydrocarbon derivatives with at least one hydrogen atom replaced by -OH.	non-ionic	uncharged
aliphatic	organic compound not based on the benzene ring—opposite of aromatic	ODP	ozone-depletion potential
aromatic alcohol	derivative of aromatic series in which a hydroxyl group appears in the side chain replacing a hydrogen atom	organic	compound containing carbon and hydrogen
azeotrope	chemical mixture where vapour and liquid composition are identical	ozone	gas formed from three oxygen atoms
biodegradable	products easily broken down by living organisms	PCB	printed circuit board
CFC	chlorofluorocarbon	polar	molecule in which electric charges are unbalanced
carcinogen	causing cancer in animals and humans	rosin	solid rosin made from pine-tree resin
ester	fruity smelling acid derivative obtained by exchanging replaceable hydrogen for alkyl radicals; used as solvents or artificial fruit essences	saponifier	chemical that reacts with organic fatty acids (such as rosin), oils and greases to form water-soluble alkaline soaps, mineral- or organic-based
flux	chemical employed in soldering to facilitate solder joint production, usually rosin-based	SMT	surface mount technology of printed circuit boards
flash point	temperature at which a substance ignites on contact with a flame	surfactant	chemical that reduces water surface tension to enable cleaning
GWP	global warming potential	terpene	any homocyclic hydrocarbon with a formula $C_{10}H_{16}$
HCFC	hydrochlorofluorocarbon	vapour phase cleaning	cleaning process where final rinse is achieved by condensing solvent vapour on parts being cleaned
HFC	hydrofluorocarbon	ultrasonic cleaning	immersion cleaning to maximize cleaning efficiency using high frequency sound waves to create cavitation implosions close to parts
hydrocarbon	organic substance made of hydrogen and carbon	VOC	volatile organic compound—constituents will evaporate at temperature of use, and may react photochemically with atmospheric oxygen to produce toxic and smog-producing tropospheric ozone.
hydrocarbon/surfactant blend	less volatile hydrocarbon solvents are mixed with surfactants that can be used in two-phase cleaning, with water (semi-aqueous cleaning)	wave soldering	mass soldering electronics assemblies after fluxing by passing them through a wave of molten solder
ion	electrically charged particle	water-soluble flux	flux where post-solder residue can be removed by water—usually very active—also known as organic acid fluxes
ketone	very reactive compound containing carbonyl group, that may be formed by oxidation of secondary alcohols		
low-solid flux	flux containing little solid matter, eliminating the need for cleaning		
naphtha	hydrocarbon mixture, usually a cut between gasoline and kerosene		