

2001  
UPDATE



Protecting the  
**Ozone Layer**

V o l u m e 2

Solvents, coatings  
and adhesives

This booklet is one of a series of reports prepared by the OzonAction Programme of the United Nations Environment Programme Division of Technology, Industry and Economics (UNEP DTIE). UNEP DTIE would like to give special thanks to the following organizations and individuals for their work in contributing to this project:

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## Foreword

When the Montreal Protocol on Substances that Deplete the Ozone Layer came into force, in 1989, it had been ratified by 29 countries and the EEC, and set limits on the production of eight man-made chemicals identified as ozone-depleting substances (ODS). By July 2001 there were more than 170 Parties (i.e. signatories) to the Protocol, both developed and developing countries, and production and consumption of over 90 substances were controlled.

Linking these two sets of figures, which attest to the success of the Montreal Protocol, is a process of elimination of ODS in which ratification of the Protocol was only a first step. It was recognized from the start that the Protocol must be a flexible instrument and that it should be revised and extended to keep pace with scientific progress. It was also recognized that developing countries would face special problems with phase out and would need assistance if their development was not to be hindered. To level the playing field, the developing countries were given extra time to adjust economically and to equip. A Multilateral Fund (MLF) was also set up early in the process to provide financial and technical support for their phase out efforts.

Exchanges of information and mutual support among the Parties to the Montreal Protocol – via the mechanisms of the MLF – have been crucial to the Protocol's success so far. They will continue to be so in the future. Even though many industries and manufacturers have successfully replaced ozone-depleting solvents with substances that are less damaging to the ozone layer or with ozone depleting free technology, lack of up-to-date, accurate information on issues surrounding ODS substitutes continues to be a major obstacle for many Parties, especially developing country Parties.

To help stimulate and support the process of ODS phase out, UNEP DTIE's OzonAction Programme provides information exchange and training, and acts as a clearinghouse for ozone related information. One of the most important jobs of the OzonAction programme is to ensure that all those who need to understand the issues surrounding replacement of ODS can obtain the information and assistance they require. Hence this series of plain language reports – based on the reports of UNEP's Technical Options Committees (TOC) – summarizing the major ODS replacement issues for decision makers in government and industry. The reports, first published in 1992, have now been updated to keep abreast of technological progress and to better reflect the present situation in the sectors they cover: refrigerants; solvents, coatings and adhesives; fire extinguishing substances; foams; aerosols, sterilants, carbon tetrachloride and miscellaneous uses; and methyl bromide. Updating is based on the 1998 reports from the TOCs and includes further information from the TOCs until 2000.

Updating of the reports at this point is particularly timely. The 'grace period' granted to developing countries under the Montreal Protocol before their introduction of a freeze on CFCs came to an end in July 1999. As developing countries now move to meet their Protocol commitments, accurate and up-to-date information on available and appropriate technologies will be more important than ever if the final goal of effective global protection of the ozone layer is to be achieved.

The publications in this series summarize the current uses of ODS in each sector, the availability of substitutes and the technological and economic implications of converting to ODS-free technology. Readers requiring more detailed information should refer to the original reports of the UNEP Technical Options Committees (see Further Reading) on which the series is based.

## Acknowledgements

This report is based on the UNEP Solvents, Coatings and Adhesives Technical Options Report (Nairobi, UNEP, 1998). Several members of the Committee contributed specific sector input (\*) and peer reviewed (\*\*) this document to ensure that the plain language reflects accurately the much more detailed information available in the original report. The report was written by Darrel Staley, Boeing.

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## Executive summary

Industries in non-Article 5 countries have successfully complied with the production phase out of ozone-depleting solvents that came into effect in 1996, with minor exceptions for solvent use allowed under Essential Use Exemptions<sup>1</sup>. Carbon tetrachloride (CTC) was not used as an industrial solvent and the 1,1,1-trichloroethane produced in 1995 has reached the end of its shelf-life, although there may still be some recycled solvent in use. Stockpiled CFC-113 is still being relied on for some applications but users are feeling increasing pressure to find alternatives as stockpiles run out. A very small quantity of ozone-depleting solvents authorized for essential use is still produced. Aqueous and semi-aqueous processes have successfully replaced ozone-depleting solvents in many applications. It is estimated that a large percentage of users (about 50–60 per cent) have made the transition to these alternatives. In electronics, “no-clean” methods have taken over a large part of the solvents market.

Although the phase out effort is going well in Article 5 countries, many challenges remain, including:

- identification of producers, importers and vendors of ozone-depleting solvents;
- identification of products that contain ozone-depleting solvents;
- identification of and assistance to users from many small and medium size enterprises in selecting and converting to the most appropriate alternative (most difficult in the solvent sector);
- affordability of alternatives, including new or retrofit equipment and, in some cases, higher operating expenses for the converted process.

The multitude of applications in a number of diverse industries has slowed phase out in the solvents sector in Article 5 countries. A major effort remains for small and medium size enterprises which, when taken collectively, consume the greatest volume of ozone-depleting solvents.

CTC, considered toxic and carcinogenic by environmental authorities in most non-Article 5 countries, is widely used for various cleaning processes in developing countries. Often, cleaning with carbon tetrachloride is done in inadequately sealed vapour degreasing machines or in open containers. Use of CTC in emissive operations presents a serious threat to the health of workers due to its proven toxic effects. There is an urgent need to prevent its use under such conditions.

Recently, two ozone-depleting brominated solvents have been commercially introduced: bromochloromethane (CBM) and n-propyl bromide (nPB). These two substances are also blended into solvent mixtures that are sold under many trade names. They are being marketed as substitutes for ozone-depleting solvents (CFC-113, 1,1,1-trichloroethane, and HCFCs) as well as non-ozone-depleting solvents (methylene chloride, trichloroethylene and perchloroethylene). CBM has high toxicity and is now also a controlled substance under the Montreal Protocol. A TEAP Task Force has recently (2001) recommended that nPB not be used pending further data on its toxicity and its effect on the ozone layer. The UNEP Solvents Technical Options Committee does not recommend nPB as a substitute for other ozone-depleting solvents. Environmentally preferable non-ozone-depleting solutions exist for all of the cleaning applications for which nPB is being promoted.

<sup>1</sup> Essential use exemptions currently allow the use of small quantities of 1,1,1-trichloroethane for manufacture of solid rocket motors, CFC-113 for maintenance of torpedoes, and for laboratory and analytical uses. In 2001, the Secretariat granted an emergency exemption for the use of OD solvents in testing of oil in water.

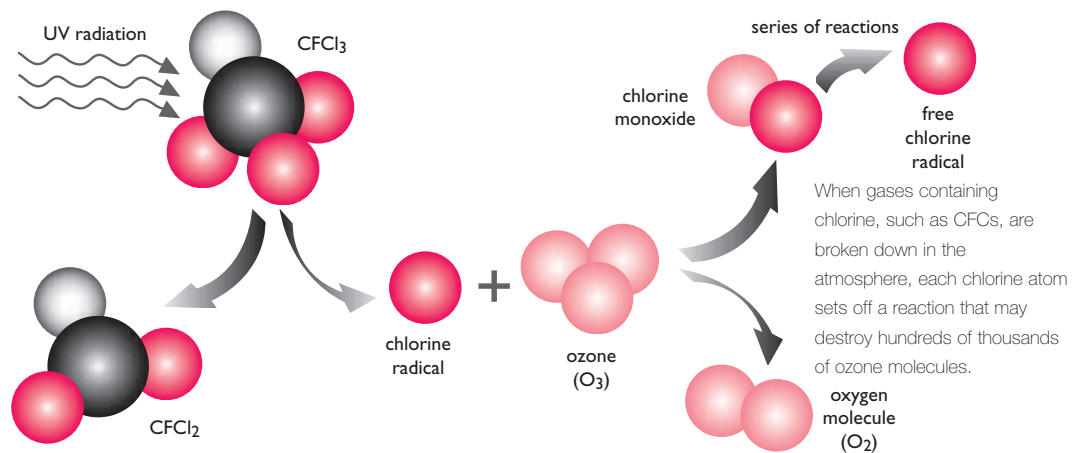
## Ozone depletion: an overview

Most of the oxygen in the Earth's atmosphere is in the form of molecules containing two oxygen atoms, known by the familiar chemical symbol  $O_2$ . In certain circumstances, three atoms of oxygen can bond together to form ozone, a gas with the chemical symbol  $O_3$ . Ozone occurs naturally in the Earth's atmosphere where its concentration varies with altitude. Concentration peaks in the stratosphere at around 25–30 kilometres from the Earth's surface and this region of concentration of the gas is known as the ozone layer.

The ozone layer is important because it absorbs certain wavelengths of ultraviolet (UV) radiation from the Sun, reducing their intensity at the Earth's surface. High doses of UV radiation at these wavelengths can damage eyes and cause skin cancer, reduce the efficiency of the body's immune system, reduce plant growth rates, upset the balance of terrestrial and marine ecosystems, and accelerate degradation of some plastics and other materials.

A number of man-made chemicals are known to be harmful to the ozone layer. They all have two common properties: they are stable in the lower atmosphere and they contain chlorine or bromine. Their stability allows them to diffuse gradually up to the stratosphere where they can be broken down

### Effects of CFCs on stratospheric ozone



by solar radiation. This releases chlorine and bromine radicals that can set off destructive chain reactions breaking down other gases, including ozone, and thus reducing the atmospheric concentration of ozone. This is what is meant by ozone depletion. The 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.

### How CFC Nomenclature Works

**CFC 114**

number of carbon atoms minus one (omitted if 0)

number of hydrogen atoms, plus one

number of fluorine atoms in one molecule

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. R-502)

Another important environmental impact of a gas is its contribution to global warming. Global Warming Potential (GWP) is an estimate of the warming of the atmosphere resulting from release of a unit mass of gas in relation to the warming that would be caused by release of the same amount of carbon dioxide. Some ODS and some of the chemicals being developed to replace them are known to have significant GWPs. For example, CFCs have high GWPs and the non-ozone-depleting hydrofluorocarbons (HFCs) developed to replace CFCs also contribute to global warming. GWP is an increasingly important parameter when considering substances as candidates to replace ODS.

During past decades, sufficient quantities of ODS have been released into the atmosphere to damage the ozone layer significantly. The largest losses of stratospheric ozone occur regularly over the Antarctic every spring, resulting in substantial increases in UV levels over Antarctica. A similar though weaker effect has been observed over the Arctic.

At present, scientists predict that, *provided the Montreal Protocol is implemented in full*, ozone depletion will reach its peak during the next few years and will then gradually decline until the ozone layer returns to normal around 2050.

## 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 defines measures that Parties must introduce to limit production and consumption of substances that deplete the ozone layer. The Montreal Protocol and the Vienna Convention – the framework agreement from which the Protocol was born – were the first global agreements to protect the Earth’s atmosphere.

The Protocol originally introduced phase out schedules for five CFCs and three halons. However, it was designed so that it could be revised on the basis of periodic scientific and technical assessments. The first revisions were made at a meeting of the Parties in London, in 1990, when controls were extended to additional CFCs and halons as well as to carbon tetrachloride and methyl chloroform. At the Copenhagen meeting, in 1992, the Protocol was amended to include methyl bromide and to control HBFCs and HCFCs. A schedule for phase out of methyl bromide was adopted at the Vienna meeting in 1995, and this was later revised in 1997, in Montreal. In 1999, the Parties met in Beijing, where they extended control to bromochloromethane. By July 2001, there were 177 Parties to the Montreal Protocol and more than 90 chemicals are now controlled.

### Ozone-depleting substances (ODS) covered by the Montreal Protocol and their ozone-depletion potential (ODP)\*

Ozone-depleting substance (ODS)	Major uses	Ozone-depletion potential (ODP)
Chlorofluorocarbons (CFC)	Refrigerants; propellants for spray cans, inhalers, etc.; solvents, blowing agents for foam manufacture	0.6–1
Halons	Used in fire extinguishers	3–10
Carbon tetrachloride (CTC)	Feedstock for CFCs, pharmaceutical and agricultural chemicals, solvent	1.1
1,1,1-trichloroethane (methyl chloroform)	Solvent	0.1
Hydrobromofluorocarbons (HBFCs)	Developed as 'transitional' replacement for CFCs.	0.01–0.52
Hydrochlorofluorocarbons (HCFCs)	Developed as 'transitional' replacement for CFCs.	0.02–7.5
Methyl bromide	Fumigant, widely used for pest control	0.6
Bromochloromethane (CBM)	Solvent	0.12

\* Where ranges of ODP are given, readers requiring the exact ODP for a given CFC, halon, HBFC or HCFC should refer to the *Handbook for the International Treaties for the Protection of the Ozone Layer*, published by the UNEP Ozone Secretariat, or other accredited sources.

## How regulation works

All ODS do not inflict equal amounts of damage on the ozone layer. Substances that contain only carbon, fluorine, chlorine, and/or bromine – referred to as fully halogenated – have the highest potential for damage. They include CFCs and halons. Other substances, including the hydrochlorofluorocarbons (HCFCs), developed as replacements for CFCs, also contain hydrogen. This reduces their persistence in the atmosphere and makes them less damaging for the ozone layer. For the purposes of control under the Montreal Protocol, ODS are assigned an ozone-depletion potential (ODP).

Each controlled chemical is assigned an ODP in relation to CFC-11 which is given an ODP of 1. These values are used to calculate 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. The relative ozone-depleting effect of production of a controlled ODS is calculated by multiplying its annual production by its ODP, results are given in ODP tonnes, a unit used in this series of publications and elsewhere. The ODS currently covered by the Montreal Protocol are shown, with their ODPs, in the table on page 8.

## Developing countries and the Montreal Protocol

From the outset, the Parties to the Montreal Protocol recognized that developing countries could face special difficulties with phase out and that additional time and financial and technical support would be needed by what came to be known as 'Article 5' countries. Article 5 countries are developing countries that consume less than 0.3 kg per capita per year of controlled substances in a certain base year. They are so called because their status is defined in Article 5 of the Protocol<sup>1</sup>.

Financial and technical assistance was provided under the 1990 London Amendment which set up the Multilateral Fund (MLF). Activities and projects under the MLF are implemented by four implementing agencies: UNDP, UNEP, UNIDO and the World Bank.

Article 5 countries were also granted a 'grace period' of 10 years to prepare for phase out. 1999 marked the end of that period for production and consumption of CFCs. Article 5 countries have, since 1999, entered the 'compliance' period in which they will have to achieve specific reduction targets.

The requirements of the Montreal Protocol as of December 2000 for both developed and Article 5 countries are shown in the table on page 10.

1 This is often written Article 5(1), indicating that status is defined in paragraph 1 of Article 5 of the Protocol. 'Article 5 Parties' is also used.

## Requirements of the Montreal Protocol including amendments and adjustments to the end of 1999\*\*

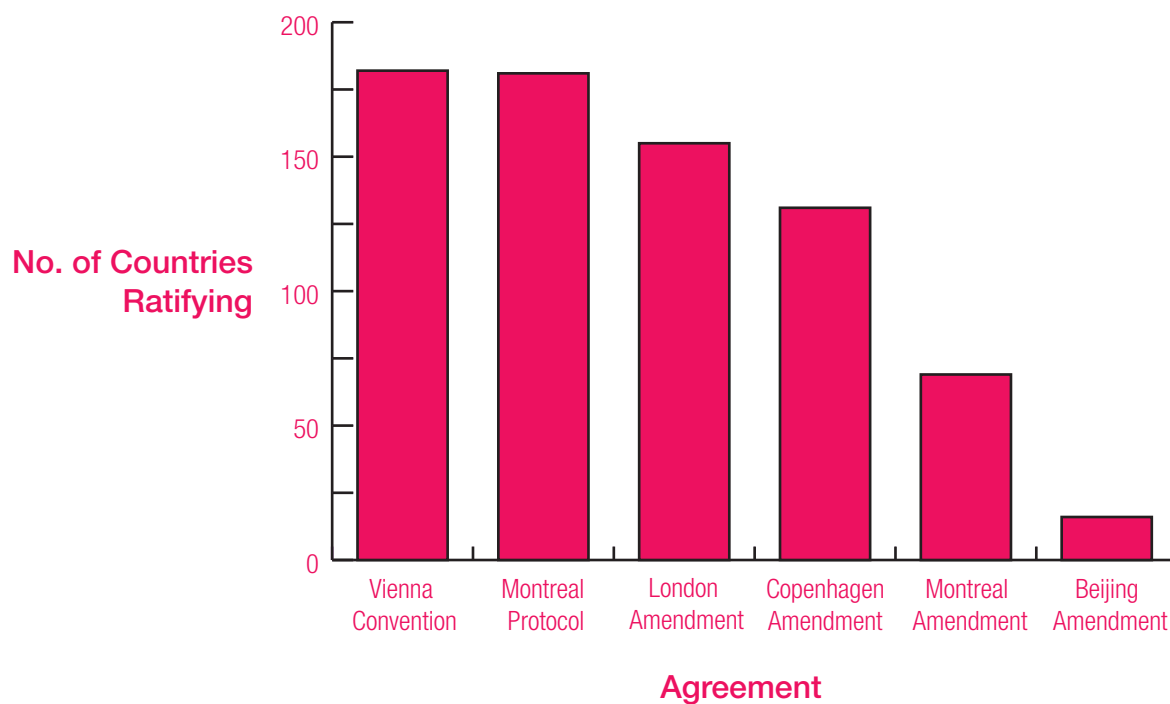
Controlled Substance	Reduction in consumption and production for developed countries	Reduction in consumption and production for developing (Article 5) countries
CFC-11, CFC-12, CFC-113, CFC-114, CFC-115	<i>Base level: 1986</i> 1989: Freeze 1994: 75 per cent 1996: 100 per cent	<i>Base level: Average of 1995–1997</i> 1999: Freeze 2005: 50 per cent 2007: 85 per cent 2010: 100 per cent
Halon 1211, halon 1301, halon 2402	<i>Base level: 1986</i> 1992: 20 per cent 1994: 100 per cent	<i>Base level: Average of 1995–1997</i> 2002: Freeze 2005: 50 per cent 2010: 100 per cent
Other fully halogenated CFCs	<i>Base level: 1989</i> 1993: 20 per cent 1994: 75 per cent 1996: 100 per cent	<i>Base level: Average of 1998–2000</i> 2003: 20 per cent 2007: 85 per cent 2010: 100 per cent
Carbon tetrachloride	<i>Base level: 1989</i> 1995: 85 per cent 1996: 100 per cent	<i>Base level: Average of 1998–2000</i> 2005: 85 per cent 2010: 100 per cent
1,1,1-trichloroethane (methyl chloroform)	<i>Base level: 1989</i> 1993: Freeze 1994: 50 per cent 1996: 100 per cent	<i>Base level: Average of 1998–2000</i> 2003: Freeze 2005: 30 per cent 2010: 70 per cent 2015: 100 per cent
HCFCs	<p><b>Consumption</b> <i>Base level: 1989 HCFC consumption + 2.8 per cent of 1989 CFC consumption</i> 1996: Freeze 2004: 35 per cent 2010: 65 per cent 2015: 90 per cent 2020: 99.5 per cent 2030: 100 per cent</p> <p><b>Production</b> <i>Base level: 1989 HCFC consumption + 2.8 per cent of 1989 CFC consumption</i> 2004: Freeze</p>	<p><b>Consumption</b> <i>Base level: 2015</i> 2016: Freeze 2040: 100 per cent</p> <p><b>Production</b> <i>Base level: 2015</i> 2001: Freeze</p>

## Requirements of the Montreal Protocol including amendments and adjustments to the end of 1999\*\*

Controlled Substance	Reduction in consumption and production for developed countries	Reduction in consumption and production for developing (Article 5) countries
HBFCs	1996: 100 per cent	1996: 100 per cent
Bromochloromethane	2002: 100 per cent	2002: 100 per cent
Methyl bromide	<i>Base level: 1991</i> 1995: Freeze 1999: 25 per cent 2001: 50 per cent 2003: 70 per cent 2005: 100 per cent	<i>Base level: Average of 1995-1998</i> 2002: Freeze 2005: 20 per cent 2003: review of reduction schedule 2015: 100 per cent

\*\* The Protocol allows some exemptions, e.g. for "essential uses." Readers requiring full details of phase out for a given substance should refer to the *Handbook for the International Treaties for the Protection of the Ozone Layer*, published by the UNEP Ozone Secretariat, or other accredited sources.

## Progress in the ratification of the Montreal Protocol and its amendments



\*Source: Caleb Management. Senics, U.K.

## Ozone-depleting solvents

CFC-113, 1,1,1-trichloroethane, carbon tetrachloride (CTC), and bromochloromethane (CBM) are ozone depleting solvents controlled by the Montreal Protocol.

In the past, CFC-113 use was essential in many industrial applications: in electronic assembly production processes, precision cleaning and 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 owing 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 tonnes a year in 1986. CFC-113 has an atmospheric residence time of 85 years and a relatively high ODP. It is a controlled substance under the Montreal Protocol.

For many years 1,1,1-trichloroethane was the solvent of choice to replace other more toxic chlorinated solvents for general metal cleaning. Early on in the phase out effort, it was considered a likely substitute for CFC-113. However, it has been included as a controlled substance under the Montreal Protocol since the 1990 revisions.

CTC is no longer used as a solvent in most countries because of its toxicity, but it is still used in some parts of the world. It, too, is a controlled substance, and should not be substituted for CFC-113 or 1,1,1-trichloroethane. The ozone-depleting substances used as solvents are shown in the table below.

Ozone-depleting substances used as solvents				
	Formula	ODP	GWP (100y)	Atmospheric lifetime (years)
CFC-113	$C_2Cl_3F_3$	0.8	5,000	85
1,1,1-trichloroethane	$CH_3CCl_3$	0.1	140	4.8
CTC	$CCl_4$	1.1	1,400	35
HCFC 141b	$CH_3CFCl_2$	0.11	700	9.2
HCFC 225ca	$CF_3CF_2CHCl_2$	0.03	180	2.1
HCFC 225cb	$CClF_2CF_2CHClF$	0.03	620	6.2
Bromochloromethane (CBM)	$CH_2BrCl$	0.12		
n-propyl bromide**	$CH_3CH_2CH_2Br$	*	< 1	< 1

\* Unknown at this time but > 0. Currently under study.

\*\* N-propyl bromide is not yet controlled by the Montreal Protocol.

CBM has been promoted as a precision cleaning solvent. The high toxicity of CBM is well known and it has an ODP of 0.12. For these reasons alone, CBM should not be considered for any cleaning application.

In recent years, HCFCs with lower ODPs have been developed as ozone-depleting solvent substitutes in some uses. However, they also deplete the ozone layer and are now controlled under the Montreal Protocol. HCFCs have later phase out dates than the three primary ODS. They are currently used in some applications as a temporary solution and are therefore sometimes referred to as transitional substances. As can be seen in the table on the previous page, 1,1,1-trichloroethane and HCFC-141b have similar ODPs. For this reason, experts strongly advise against this conversion.

## Current status

### 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
- underwater systems

This section gives a baseline description of current ozone-depleting solvent use and an update on remaining phase out challenges (usually in Article 5 countries). A more complete description of ozone-depleting solvent applications can be found in the 1998 Assessment Report of the Solvent, Coatings and Adhesives Technical Options Committee.

#### **Electronics**

The phase out of ozone-depleting solvents began much earlier in non-Article 5 countries, with the production ban that came into effect on 1 January 1996. Both substitute solvents and not-in-kind technologies have been implemented to replace CFC-113 and 1,1,1-trichloroethane-based solvent formulations for post-soldering rosin and synthetic activated flux residue removal. Industry-wide initiatives were undertaken to ensure that the new alternatives were compatible with the vast array of metals, plastics, elastomers, adhesives and marking inks used. Industry trade organizations undertook comprehensive studies of many technologies to ensure that the alternatives would provide the same high level of electrical performance expected by electronics users.

#### **Precision cleaning**

Use of CFC-113 and 1,1,1-trichloroethane for precision cleaning applications has been essentially eliminated in all non-Article 5 countries either by substitute solvents (e.g. HCFC, HFC, HFE and PFC) or other not-in-kind technologies. HCFCs are relied on most heavily in this sub-sector because they have properties very similar to the solvents previously used for these crucial cleaning operations, and because they are more affordable than the other alternatives. For example, HCFC-225 has been used with great success in military programme applications. However, as transitional substances, phase out of these alternatives will ultimately be required as well.

HCFCs are also a popular alternative for precision cleaning applications in Article 5 countries because they are much less expensive than the non-ozone depleting HFCs and HFEs. Where possible it is always advisable to convert to a non-ozone depleting alternative and avoid the need for a future conversion. Many not-in-kind alternatives exist for the Article 5 effort, but the equipment to support these options tends to be expensive. Affordability will continue to be a concern for the Article 5 phase out, especially for conversion projects in the precision cleaning sub-sector.

**Current and future cleaning processes required for different electronics applications**

Class	Application	Current importance of cleaning	Current non-ODS cleaning processes	Future importance of cleaning	Possible future non-ODS cleaning processes
3	satellites avionics instruments avionics guidance systems submarine telecommunications medical life-support	cleaning essential	solvent or co-solvent or combination solvents  semi-aqueous or saponification cleaning (to military specifications for rosin fluxes)	cleaning essential	alcohol or various halogenated or speciality solvents  saponifiers or water-soluble solvent or aqueous cleaning controlled atmosphere soldering
3	automotive anti-lock braking systems automotive engine control systems land telecommunications high frequency & RF circuits	cleaning essential	all cleaning methods to clean all flux types and for ionic contaminants	cleaning essential	alcohol or various halogenated or speciality solvents  saponifiers or water-soluble solvent or aqueous cleaning controlled atmosphere soldering
3	sophisticated industrial computers other automotive (except radio)	cleaning essential	all cleaning methods to clean all flux types and for ionic contaminants (to military specification requirement levels)	cleaning essential	saponifiers or water-soluble solvent or aqueous cleaning no-clean controlled atmosphere soldering
2	industrial machinery controls medical non-life-support	cleaning generally needed	solvent cleaning for rosin or resin fluxes semi-aqueous or saponification cleaning for rosin or resin fluxes	cleaning generally needed  cleaning could be minimized	water soluble solvents aqueous cleaning  no-clean controlled atmosphere soldering
2	low-cost instruments office equipment desktop and laptop computers customer premise telecommunications automotive radio TV EHT circuits	cleaning sometimes needed	solvent or semi-aqueous or saponification cleaning for rosin or resin fluxes	cleaning sometimes needed	no-clean technologies using low-solids rosin fluxes
1	professional audio-visual equipment quality consumer goods automotive entertainment public address systems	cleaning rarely needed	rosin or resin flux cleaning if required	cleaning not required	no-clean technology using low-solids rosin fluxes
1	radio, television and other entertainment and home electronics (mass produced)	cleaning not performed	none	cleaning not required	no-clean technology using low-solids rosin (or other) fluxes

Note: Class 3, 2, or 1 denotes product classification by intended end-item use:

Class 3: Continued high performance on demand where equipment must function when required

Class 2: Continued, extended performance is desired but not critical

Class 1: Continued performance desired; non-function is an inconvenience

### **General metal cleaning**

In the late 1990s, the metal forming and finishing industry of non-Article 5 countries completed replacement of 1,1,1-trichloroethane and CFC-113 by substitute solvents or by aqueous and semi-aqueous processes. Some Article 5 countries have also switched from ozone-depleting solvents in general metal cleaning, but many challenges remain.

There is no single replacement method. Alternatives must be carefully selected and optimized for each application, depending on the varying substrate materials, soils, cleanliness requirements, process specifications and end uses.

While many alternatives reduce worker exposure to potentially harmful chemicals, the total cost – including environmental concerns and socio-economic impact – should also be considered. Furthermore, it has become clear that a significant use of CTC as a low cost, non-flammable solvent for cleaning applications in Article 5 countries still remains.

### **Dry cleaning**

The dry cleaning industry was never a large user of CFC-113, consuming less than 5 per cent of all CFC-113. Its use has largely been eliminated as a result of replacement of CFC-113 dry cleaning machines with new machines using perchloroethylene or hydrocarbon solvents. Only tail-end use of residual stocks of CFC-113 in dry cleaning machines and some hand application of 1,1,1-trichloroethane for stain removal remain. However, CTC is used for dry cleaning in some Article 5 countries.

Organic solvents are ideal for dry cleaning textiles because, unlike water, they do not distort fabrics. CFC-113 was perfect 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 dry-to-dry processes. The machines invariably incorporate sophisticated recovery systems to purify solvent for reuse and to minimize solvent emissions.

Modern dry cleaning machines typically clean more than 50 kg of clothing for each litre of solvent used. They 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. A machine represents the largest capital cost in setting up a dry cleaning operation. Replacement with new machines that do not use CFC-113 may prove difficult for the small businesses that predominate in this sector. For those machines remaining in use, improved operator training, better housekeeping and maintenance practices will help maximize solvent mileage.

Perchloroethylene is the most widely used dry cleaning solvent, accounting for about 90 per cent of the world's dry cleaning. It has been used in this application for over 60 years and, although it has a higher boiling point than CFC-113, the introduction of advanced heat exchange technology and airflow dynamics has provided significant energy savings. Although some testing on rodents has indicated a degree of carcinogenicity, it was concluded that the method of development was not replicable in humans. Most authorities agree there is a very low risk to humans under normal conditions of use.

**Adhesives and coatings**

1,1,1-trichloroethane has been the primary ozone-depleting solvent used in adhesive, coating, and aerosol formulations. It is non-flammable, dries rapidly, does not significantly contribute to local air pollution and performs well in many applications.

The total use of 1,1,1-trichloroethane in adhesives and coatings was always relatively small and has now mostly been eliminated in the non-Article 5 countries. In Article 5 countries it is still being used, but at a declining rate. A partial list of applications where 1,1,1-trichloroethane adhesives are used includes packing, non-rigid bonding, rigid bonding, construction, tapes, transportation, and consumer adhesives.

**Aerosols**

Solvents in aerosol product formulations function as either an active ingredient (e.g. degreaser or cleaner) or as a solvent or carrier of other active substances. Though most ozone-depleting solvent aerosol applications traditionally used 1,1,1-trichloroethane as their solvent, some products made use of CFC-113, CFC-11, and CTC as well. Most uses of these four substances for aerosol products have been replaced with alternative compounds, although considerable amounts are still used in some Article 5 countries. Work is still underway to improve safety and flammability, to alleviate health concerns, and to replace transitional alternatives such as HCFCs. There has also been success in switching to alternative delivery methods that eliminate the need for an aerosol package altogether.

**Miscellaneous uses**

There are a number of miscellaneous industrial and laboratory applications where some amounts (relatively small quantities in most cases) of CFC-113, 1,1,1-trichloroethane, and CTC are employed.

In most cases, including cleaning of oxygen systems and detection of latent fingerprints, alternatives are readily available and pose little further challenge. In other areas, such as laboratory testing and space vehicle manufacturing, significant progress has been made but a complete phase out is still not possible.

**KEY FACTS**

Miscellaneous ozone-depleting solvent uses include:

- Oxygen systems cleaning
- Detection of latent fingerprints
- Laboratory testing
- Space vehicle manufacturing
- Bearer media
- Semiconductor manufacturing
- Component drying
- Riveting and machining
- Aeroplane hydraulic system testing
- Leak detection
- Fabric protection and coating
- Mould release agents
- Motion picture film cleaning
- Military applications
- Vapour phase soldering

**Article 5 countries**

Phase out of ozone-depleting solvents is already initiated in Article 5 countries. A planned reduction of consumption of the three controlled solvents has been initiated based on the total production in respective countries. The phase out target is 2010 for CFC-113 and CTC. For 1,1,1-trichloroethane it is 2015.

Phase out in developing countries has gone fairly well in the solvent sector, given the widespread use of ozone-depleting solvents and the variety and complexity of the applications. Of the various sub-sectors within the solvents sector, electronics and general metal cleaning have faced the greatest challenge. The electronics industry has already made significant progress. This may be due to the large number of electronics joint venture companies that have received assistance from their experienced non-Article 5 partners. The large number of small users, many of whom are undercapitalized, hampers the effort for metal cleaners.

Because of its low cost, non-flammability and good degreasing properties, CTC is widely used in various general metal cleaning processes by large numbers of small users in Article 5 countries. Typically, it is used in simple open containers where it presents not only a serious threat to the ozone layer but, because of its proven toxic effects, a threat to the health of workers. Users have minimal resources for change. Nevertheless, cleaning with CTC in open containers should not be allowed to continue. Immediate substitution of trichloroethylene or perchloroethylene seems the most appropriate short-term solution. Countries where CTC is still being used as a solvent need to develop plans to assist users with the proper methods of use and disposal.

## Substitute solvents and not-in-kind technologies

There is no single substitute for all uses of CFC-113 and 1,1,1-trichloroethane. Every solvent sub-sector has at least one or more available alternatives. CFC-113 has been so widely used as a solvent because it is suitable for many different applications. Any substitute for CFC-113 or 1,1,1-trichloroethane 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, as low toxicity as possible, and not be carcinogenic. Recovery and recycling should also be possible. Alternative processes should be cost effective and should not generate other environmental hazards.

An enterprise's conversion strategy may include both short- and long-term plans for ozone-depleting solvents. In the short term, recycling and recovery may constitute the first step. In the long term, alternative processes and materials should be found since, because of losses, ozone-depleting solvents 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.

A short description is given below of the general classes of alternatives available to replace ozone-depleting solvents. Sector specific details follow this section.

### Substitute solvents

Conventional non-ozone-depleting organic solvents (both halogenated and non-halogenated) are excellent alternatives for many ozone-depleting solvent applications. Improved equipment and other technical advances in recent years have extended the list of feasible applications for these well-known solvents. Many of them are also attractive from a financial perspective. However, most non-halogenated organic solvents that are useful for cleaning are also flammable or combustible. It is also important to bear in mind that many of these solvents are classified as volatile organic compounds (VOCs), which may restrict their emissive use in some geographic areas. In addition, vapour recovery systems may be required to reduce worker exposure and environmental emissions. For these reasons, this class of familiar alternatives requires careful consideration.

**KEY FACTS****Ozone-depleting solvent alternative requirements**

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

**Select substitute solvent classes**

- non-ozone-depleting halogenated organic
- non-ozone-depleting non-halogenated organic
- HFCs & HFEs
- HCFCs
- PFCs

**Select not-in-kind technologies**

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

Hydrofluorocarbon (HFC) and Hydrofluoroether (HFE) formulations are now available to replace ozone-depleting solvents. These solvents are an attractive solution because their physical properties are similar to CFC-113 but they have no ODP. Because they are relatively weak cleaners, they are typically combined with any of a number of other solvents to adjust their cleaning power and facilitate soil removal. At this time, solvent blends containing HFC or HFE are still expensive. They also have high GWPs.

Alternative solvent blends using HCFCs should be considered carefully. HCFC-141b and particularly HCFC-225 are possible substitutes for CFC-113. However, they are only technically necessary for a very small portion of CFC-113 applications. Although HCFC-141b is a possible substitute for 1,1,1-trichloroethane, this substitution is strongly discouraged. The two solvents have the same ODP so this switch offers no benefit. In general, the long atmospheric life and ODP of HCFCs mean that they are not long-term substitutes for ozone-depleting solvents.

Perfluorocarbon (PFC) solvents are virtually inert and therefore have extremely long atmospheric lifetimes and associated high GWPs. PFCs are extremely expensive and cleaning power is very low except for a small range of soils. This class of substitute solvent should only be used as a last resort in unique applications where emissions can be kept at or near zero.

The table overleaf lists some of the physical properties of the ozone-depleting solvents and their halogenated substitute solvents.

**Not-in-kind technologies**

Although smaller, the list of not-in-kind alternatives is shorter than that of possible substitute solvents, knowledge of proven not-in-kind technologies is extensive. Aqueous, semi-aqueous and emulsion processes have successfully replaced ozone-depleting solvents in many applications. It is estimated that a large percentage of users (about 50–60 per cent) have made the transition to these alternatives. Aqueous processes, in general, use surfactants and additives with water. The semi-aqueous and emulsion processes use hydrocarbon and surfactants plus additives followed by aqueous rinsing.

"No-clean" methods have also taken a large percentage of the solvents market, particularly in the electronics sector. The alternative is different for each sector, but generally it has meant production of a new product (not maintenance) and usually requires significant changes to the manufacturing process.

### Properties of ozone-depleting solvents and selected halogenated solvent alternatives

Properties	Formula	ODP	GWP (100y)	Boiling point C	Flash point C	Surface tension (dyne/cm)	Kauri- Butanol value	Toxicity
<b>Halogenated solvent</b>								
<b>1,1,1-trichloroethane &amp; carbon tetrachloride substitutes</b>								
1,1,1-trichloroethane	CH <sub>3</sub> CCl <sub>3</sub>	0.1	100	80	None	25	124	Low
carbon tetrachloride (CTC)	CCl <sub>4</sub>	1.1	1,400	77	None	27	113	High
methylene chloride	CH <sub>2</sub> Cl <sub>2</sub>	0	9	40	None	28	136	Med
perchloroethylene	CCl <sub>2</sub> CCl <sub>2</sub>	0	~ 9	121	None	31	90	Med
trichloroethylene	CHClCCl <sub>2</sub>	0	< 9	87	None	29	129	Med
bromochloromethane (CBM)*	CH <sub>2</sub> BrCl	0.12		68	None		132	High
n-propyl bromide	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Br	**	< 1	71	None	26	125	***
<b>CFC-113 substitutes</b>								
CFC-113	C <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub>	0.8	6,000	48	None	17	32	Low
HCFC 141b	CH <sub>3</sub> CFCl <sub>2</sub>	0.1	700	32	None	18	58	Low
HCFC 225ca	CF <sub>3</sub> CF <sub>2</sub> CHCl <sub>2</sub>	0.03	180	54	None	16	34	Med
HCFC 225cb	CClF <sub>2</sub> CF <sub>2</sub> CHClF	0.03	620	54	None	17	30	Low
HFC-43-10mee	CF <sub>3</sub> CHFCHFCF <sub>2</sub> CF <sub>3</sub>	0	1,300	55	None	14	10 ****	Low
HFE-449s1	C <sub>4</sub> F <sub>9</sub> OCH <sub>3</sub>	0	480	60	None	14	10 ****	Low
PFC	C <sub>6</sub> F <sub>14</sub>	0	7,400	56	None	12		Low

\* CBM is not considered an alternative to 1,1,1-trichloroethane & carbon tetrachloride as it has high toxicity and is also a controlled substance under the Montreal Protocol. It is included for reference.

\*\* Unknown at this time but > 0. Currently under study.

\*\*\* Currently under study.

\*\*\*\* Cleaning power increased with blends.

## Prospects for action

### 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

### Electronics

#### Substitute solvents

Chlorinated solvents such as trichloroethylene (TCE) were used as a rosin flux residue cleaning agent prior to the advent of 1,1,1-trichloroethane. TCE blends may be used, provided their use complies with applicable regulations.

Brominated solvents such as n-propyl bromide (nPB) have been found to be good replacements for 1,1,1-trichloroethane, since the physical and chemical properties are almost an exact match. However, this solvent is not recommended until its ozone-depleting and toxicity data are known.

Hydrochlorofluorocarbons (HCFC) such as HCFC 225 ca/cb and HCFC-141b are used in certain applications as alternatives to CFC-113. HCFC-225 ca/cb has physical and chemical properties almost identical to CFC-113. However, the commercially available HCFC-225 ca/cb mixture now has a higher toxicity than CFC-113. The new blend ratio, which will greatly facilitate applications such as cleaning of oxygen lines and electronics components, has about the same toxicity level as TCE. Both solvents are considered transitional as they have finite ODPs and thus will be phased out in the future.

Hydrofluorocarbon (HFC) and Hydrofluoroether (HFE) formulations are used to replace CFC-113 formulations. However, the zero ODP HFC-43-10mee and HFE 7100 are relatively weak cleaners when used alone. These partially fluorinated solvents can be blended with various low molecular weight alcohols (methanol, ethanol, propanols) as well as trans-dichloroethylene. This provides the user with a wider selection of cleaning agents that can be tailored to the cleaning task. Typically, they are combined with a number of other solvents to adjust their cleaning power to facilitate efficient flux residue removal. They are also expensive and have GWP.

Non-ozone-depleting organic solvents used for electronics cleaning include terpenes, alcohols, ketones, aldehydes and esters. These materials 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 in appropriate equipment. 2-Propanol (iso-propanol or IPA) is an acceptable cleaner for some activated rosin fluxes. Special equipment required for flammable alcohol-based solvents is 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 more thorough cleaning.

Co-solvent systems are made up of a high-boiling ester and HFE combination in the washing stage, followed by HFE in the rinsing and drying stage(s). The composition of the washing stage tank controls the boiling point of the mixture, allowing the user to 'mimic' the boiling point of a number of chlorinated solvents such as 1,1,1-trichloroethane, TCE and PCE.

Siloxanes contain silicon, oxygen and carbon. Such materials can be made with a range of boiling points to meet specific needs. Although this has been achieved, many of the siloxanes are flammable, requiring suitable equipment and cleaning procedures.

**Not-in-kind technologies**

Aqueous cleaning for water-soluble fluxes and pastes has now been used successfully for many years in electronics manufacturing, so this technology is well accepted.

Aqueous cleaning, where alkaline organic or non-organic ‘saponifiers’ are mixed with water for residue removal, has been in use for over 25 years. Recently, new saponifier formulations have improved the process and now permit cleaning of some types of “no-clean” flux residues. This is useful for companies wishing to standardize on using the same soldering chemistry for both cleaned and uncleaned assemblies. Problems in using both types of aqueous technology are well known to users. Some treatment of waste water may be required prior to discharge or disposal.

Semi-aqueous or Hydrocarbon/Surfactant (HCS) solvents are used to clean electronics assemblies to remove rosin or synthetic activated flux residues, followed by water washing, rinsing and conventional aqueous process drying. This process was first implemented in Article 5 countries when its capability for cleaning surface mount technology was demonstrated. HCS are non-corrosive, have low viscosity and foaming behaviour, remove both polar and non-polar contaminants, and are useful for cleaning closely-spaced electronic assemblies at low temperatures. These materials are compatible with a wide range of electronic materials of construction and have a neutral pH. Early formulations had fairly

**KEY FACTS**

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

Available cleaning agent options for different electronic flux types								
Flux type	Brominated solvent	Chlorinated solvent	Partially fluorinated solvent	Organic solvent	Speciality solvent & co-solvent	Water	Water and saponfire	Terpenes/ hydrocarbons and water
Non-activated rosin*	●	●	●	●	●	-	●	●
Mildly activated rosin*	●	●	●	●	●	-	●	●
Activated rosin**	●	●	●	●	●	-	●	●
Super-activated rosin	●	●	●	●	●	-	●	●
Water soluble***	-	-	-	-	●	●	●	-
Synthetic activated***	****	****	●	****	****	-	-	●
Low solids no cleaning required	-	-	-	-	-	-	-	-

\* approved for US military use  
 \*\* approved for UK and US military use  
 \*\*\* approved for UK military use  
 \*\*\*\* not demonstrated

Notes:

- a) It is assumed the halogenated cleaning agents will be formulated with low molecular weight alcohol(s) for improved ionic residue removal.
- b) While the chlorinated solvent family includes MC, TCE, and PCE solvents, it is anticipated TCE will have the widest use for flux residue removal.
- c) The ‘partially fluorinated solvent’ family includes HCFCs, HFCs and HFEs

low flash points, but the current formulations have high flash points, eliminating the need for some fire suppression measures. These materials are classified as VOCs, thus their mists and vapours must be properly contained. Waste streams from such processes may be hazardous and require proper treatment or disposal. As this process combines both solvent and aqueous cleaning, capital and operating costs are higher than for straight aqueous processes.

Aqueous emulsions of semi-aqueous cleaning agents have recently proven to be extremely effective in cleaning electronics. Such emulsions can remove both rosin and synthetic activated flux residues with the same effectiveness as other cleaning agents, although contaminant loading may be lower than with other methods.

Low residue (“no-clean”) options include the use of low-solid fluxes and pastes in printed wiring assembly (PWA) manufacture. These soldering materials can eliminate the need for cleaning altogether in numerous applications, particularly in consumer and office electronics where a relatively low level of cleanliness is acceptable. However, in high reliability applications, where extremely high levels of cleanliness are required, all residues usually need to be removed.

Numerous new fluxes have been developed for wave soldering, containing 2-10 per cent solids as opposed to the traditional 15-35 per cent solids. Many low-solid fluxes are non-corrosive and have high surface insulation resistance. It is unnecessary to remove the minimal residues that may be left, even for cosmetic purposes, resulting in material and operating cost savings – though existing soldering machines may need modification. Further testing is required to determine the relevance of this technology to the newest designs in different applications. High-solid fluxes requiring no post-soldering cleaning have also been used. Low residue solder pastes for surface mount products, based on ‘no clean’ flux technology, are also widely available. Their use is focused on the consumer and business class of products where life is not at risk if the product fails in use.

Controlled atmosphere soldering is another cost-efficient, “no-clean” option. Two options are involved: soldering in an inert gas or in 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 forms minimal amounts of oxides after soldering, so solder dross can be reduced by as much as 90 per cent 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.

## Precision cleaning

### Substitute solvents

The fluorinated substitutes for CFC-113 are HCFCs, HFCs, HFEs and PFCs. They all have similar properties including excellent compatibility with most metals and plastics.

HCFCs (225 and 141b) were available at the time of CFC-113 phase out in non-Article 5 countries and were readily adopted for some applications. However, these compounds have finite ODP and are now scheduled for phase out, although not until 2030 for non-Article 5 countries and 2040 in Article 5 countries. In most cases, HCFCs will be replaced with HFCs, HFEs and their formulations.

Hydrofluorocarbons (HFC-43-10mee) and Hydrofluoroethers (C4F9OCH3 and C4F9OC2H5) were introduced in the mid 1990s as substitutes for CFC-113 in precision cleaning applications. These compounds have zero ODP, low toxicity and excellent material compatibility, but are expensive. HFCs and HFEs do have GWP but it is lower than CFC-113 and PFCs. They are also commercially available in many blends (azeotropes) with alcohols, hydrocarbons and chlorocarbons to increase cleaning power for specific soils.

Perfluorocarbons (PFCs) were introduced in some CFC-113 applications before HFCs and HFEs became available. PFCs have very high GWP, are very expensive and should only be considered where other available substitutes cannot be used. PFCs are now being replaced with lower GWP, HFCs, and HFEs in some applications.

Chlorocarbons (perchloroethylene, methylene chloride and trichloroethylene) are used as a substitute for 1,1,1-trichloroethane in some precision cleaning applications. However, these compounds have higher toxicity and could also raise compatibility issues. In some countries, trichloroethylene and perchloroethylene are regulated as VOCs that contribute to tropospheric ozone formation, although the effect of trichloroethylene is very small compared with most other volatile solvents.

Trichloroethylene, perchloroethylene and methylene chloride may be used, subject to applicable regulations regarding operator exposure levels and environmental hazards.

Aliphatic hydrocarbons (such as mineral spirits, n-paraffin and kerosene) can be used as substitutes in some processes involving hydrocarbon oils and greases. However, these compounds require flammable rated equipment. Also, recovery processes such as carbon adsorption may be required to reduce their emission as many aliphatics are classified as VOCs.

Alcohols and ketones can also be used in precision component cleaning, subject to material compatibility and use of flammable rated equipment.

n-Propyl bromide (nPB) was recently introduced as an alternative to 1,1,1-trichloroethane for precision cleaning. The physical and cleaning properties of this compound are comparable. However, it has questionable toxicity and ODP and, until these issues are resolved, its use is discouraged.

## KEY FACTS

**Substitute solvents for CFC-113:**

- HCFCs and Blend
- PFCs
- HFC-43-10mee and blends
- HFEs (C<sub>4</sub>F<sub>9</sub>OCH<sub>3</sub> and C<sub>4</sub>F<sub>9</sub>OC<sub>2</sub>H<sub>5</sub>) and blends

**Substitute solvents for 1,1,1-trichloroethane:**

- Chlorocarbons (PCE, MH<sub>2</sub>Cl<sub>2</sub>, and C<sub>2</sub>HCl<sub>3</sub>)
- Hydrocarbons (aliphatic and oxygenated)
- n-propyl bromide

**Not-in-kind technologies:**

- Aqueous and semi-aqueous cleaning
- Supercritical fluid cleaning and CO<sub>2</sub> snow
- Plasma cleaning
- UV/ozone cleaning

**Not-in-kind technologies**

The most popular not-in-kind technologies for precision cleaning are aqueous and semi-aqueous processes. Aqueous processes, in general, use surfactants and additives with water. The semi-aqueous and emulsion processes use hydrocarbon and surfactants plus additives followed by aqueous rinsing. Both, aqueous and semi-aqueous processes involve the use of spray, mechanical agitation and/or ultrasonics. Additional equipment such as heaters, filters, automation equipment, recycling, and water treatment may be required. The cleaned parts are generally hot-air and/or vacuum-oven dried. Such a rapid, potentially energy-intensive drying or de-watering process is necessary. Most aqueous and semi-aqueous processes also require more floor space than solvent processes.

Supercritical fluids (CO<sub>2</sub>) are gases held above the critical temperature and pressure at which they would normally condense. Such gases are good solvents but can only be used in speciality applications because they involve high-pressure systems and require substantial capital funds.

Plasma cleaning is used in a very selective cleaning application: that of precision instruments. Plasma cleaning is only a viable option in special circumstances since it must often be preceded by solvent cleaning to achieve an ultra-clean surface. It should therefore be considered a second step or 'polishing' cleaning process.

Ultraviolet (UV) light combined with ozone is also used in some speciality applications, to remove organic films from surfaces (glass, quartz, sapphire, ceramics, metals, silicon and polyamide cement).

## General metal cleaning

### Substitute solvents

Where metal substrates (such as aluminium or mild steel parts) could be corroded by acidic or alkaline not-in-kind technologies or where parts are heavily contaminated, trichloroethylene, perchloroethylene and methylene chloride are the most obvious alternatives to 1,1,1-trichloroethane. They have similar physical and chemical properties, are inexpensive, and require only minor modifications of the cleaning process.

Other commercially available substitute solvents for CFC-113 include HCFCs, HFCs, HFEs and their blends. HCFC blends need improved recovery, handling and storage facilities due to their low boiling points. This increases emissions during cleaning. Most non-Article 5 countries are phasing out HCFCs because of their ODP. HFCs and HFEs are expensive, have low solvency and need the addition of a more potent co-solvent. Many of these products are being regulated because of their GWP and/or as VOCs in some countries.

Low cost hydrocarbon solvents and their oxygenated derivatives are increasingly used in specialized equipment designed to prevent potential flammability and explosion hazards. These systems allow the use of a large number of solvents. However, hydrocarbon and oxygenated solvents are often

Viable alternatives to metal cleaning ozone-depleting solvents							
Substitute	Cold immersion <sup>c</sup>	Hot immersion <sup>c</sup>	Vapor decreasing	High pressure spray	Manual	Airtight	Low flash point
Alkaline Cleaners	•	•		•	•		
Alternative Chlorinated Solvents	•	•	•	•	• <sup>d</sup>	•	
Co-Solvent Cleaners		•	•	•		•	
Emulsion Cleaners	•	•		• <sup>b</sup>	•		
Hydrocarbon/Surfactant Blends	•				•		
HCFCs	•	•	•		•		
HCFCs & HFEs	•	•	•	•	•	•	
Low Flash Point Solvents	• <sup>b</sup>	• <sup>b</sup>	• <sup>b</sup>	• <sup>b</sup>	• <sup>b</sup>		• <sup>b</sup>
Low Vapour Pressure Solvent Blends <sup>a</sup>	•	• <sup>b</sup>		• <sup>b</sup>	•		
P-Chlorobenzotrifluoride	• <sup>b</sup>						• <sup>b</sup>
Media Blasting				•			
Steam				•			
Volatile Methyl Siloxanes	• <sup>b</sup>				• <sup>b</sup>		• <sup>b</sup>

a) Non-halogenated mixtures   b) With appropriate flammability protection   c) Includes agitation such as ultrasonics, mechanical, etc.  
 d) With reasonable containment

## KEY FACTS

**Substitute solvents:**

- chlorinated solvents (trichloroethylene, perchloroethylene, methylene chloride)
- aliphatic and aromatic hydrocarbons
- oxygenated hydrocarbon derivatives
- HCFC blends

**Not-in-kind technologies:**

- aqueous cleaning
- semi-aqueous cleaning
- mechanical cleaning
- vacuum de-oiling
- "no-clean" options

regulated as VOCs. Many hydrocarbon solvents are toxic, especially those with an aromatic molecular structure. Some are carcinogenic or mutagenic. The toxicology of oxygenated derivatives is very complex: some are very toxic, others much less so.

Many solvent blends are available for manual cleaning and for cold immersion cleaning.

**Not-in-kind technologies**

Aqueous cleaners are potential substitutes for CFC-113 and 1,1,1-trichloroethane in metal degreasing. The process involves washing, rinsing and drying. Aqueous cleaning uses immersion with mechanical agitation, ultrasonic or spray processes. Each requires different equipment with optional features such as heaters, dryers, automation equipment, filtration, recycling and water treatment. Proper waste disposal is important in aqueous cleaning, because some by-products are not biodegradable. Aqueous cleaning is more energy-intensive than solvent cleaning and thus has a larger global warming impact. Ultrasonic cleaning is appropriate only for small parts and becomes inefficient if the water contains dissolved gases.

Emulsion cleaners and 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 high flash points. However, they have associated recycling and disposal problems, low contaminant-saturation capacity and require special equipment. Also, they are frequently highly alkaline, imposing strict health and safety measures. 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 tailored for that specific process.

Various mechanical cleaning methods have been used for metal surface preparation and have been proposed as possible alternatives for CFC-113 and 1,1,1-trichloroethane. Brushing, wiping with rags or sponges, use of absorbent materials, media blasting and pressurized gases are generally best suited for lower grade cleaning requirements or as a pre-cleaning operation in the removal of solid and semi-solid soils. Pressurized gas (air, rare earth gases, carbon dioxide, and nitrogen) may be used for particulate contamination. The compressed air typically found in workshops is totally unsuitable for this application because – unless a suitable filter and drier are used – it is frequently heavily contaminated with entrained water and compressor oil. Specific technologies under development include wheat starch, sodium bicarbonate, and solid carbon dioxide blasting.

So called "no-clean" options for metal degreasing include water-soluble, emulsifiable machining and metal forming lubricants (chlorinated or not). They are much easier to remove with aqueous cleaners and not hazardous to workers. The true "no-clean" methods are rarely used and consist of volatile pressing and cutting oils (so-called "vanishing oils").

## Dry cleaning

### Substitute solvents

The new generation of higher flash point hydrocarbon solvents (HCs) that have lower odour and toxicity are the most suitable substitute for CFC-113 dry cleaning.

A small number of machines using HCFC-141b and HCFC-225 are in use and are effective substitutes for dry cleaning. These solvents are, however, defined as transitional substances under the Montreal Protocol and should only be used with sophisticated recovery systems.

Perchloroethylene is the most widely used dry cleaning solvent in the world, although it is not suitable for all dry cleaning due to its solvency power. It can be used safely in specially developed new super tight machines. These incorporate newly designed carbon adsorption systems that 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. Perchloroethylene is also the most suitable substitute for 1,1,1-trichloroethane for hand application to remove machine oil stains caused during garment manufacture.

Gentle wet cleaning is a useful adjunct to dry cleaning but, due to its tendency to shorten the life of structured wool jackets and coats, it is only suitable for a proportion of the cleaning classifications.

### Article 5 countries

There are no known CFC-113 machines installed in Article 5 countries, but CTC and 1,1,1-trichloroethane are used. Depending on the level of soiling of the articles requiring cleaning, perchloroethylene or hydrocarbon solvents are the recommended substitutes. For medium to heavily soiled work perchloroethylene should be used. Hydrocarbons are suitable for lightly soiled work, delicate colours and beaded garments. Many dry cleaning machine manufacturers produce basic machines suitable for developing countries.

Large quantities of CTC are being used in Article 5 countries. Use of CTC in non-Article 5 countries was ended some 30-40 years ago on health and safety grounds. CTC is a probable human carcinogen as well as having high ODP. Substitution with perchloroethylene or hydrocarbon should be arranged as soon as practicable. This will require replacement of CTC machines, as they will be unsuitable for safe conversion.

### KEY FACTS

- Phase out option currently linked to replacement by hydrocarbon
- Super-tight perchloroethylene dry cleaning machines are available for more soiled fabrics
- Short-term conservation is by improved operating practices and maintenance
- Phase out of carbon tetrachloride (CTC) in developing countries should be expedited
- Suitable lower cost hydrocarbon or perchloroethylene models are available for developing countries
- Waste residues should be contained for recycling/incineration according to local regulations

## Adhesives

### Substitute solvents

The solvents used for adhesives are of following types:

- Toluol, xylol and other aromatic hydrocarbons;
- Aliphatic hydrocarbons, such as white spirit, hexanes;
- Ester, ketone, glycol ethers;
- Hydrochlorocarbons, mainly methylene chloride;
- Hydrobromocarbons, essentially n-propyl bromide.

They are suitable for dissolving polymers such as polyvinylacetate and co-polymers, natural and synthetic rubbers, nitrocellulose, acrylics and polyurethane. Almost all conventional organic solvents are VOCs and their use is restricted in several countries, requiring expensive ventilation and vapour recovery equipment. Some of the above mentioned solvents are flammable and require flameproof equipment and extraction systems for safe handling. Some aromatic hydrocarbons are toxic. The hydrohalocarbons are used to replace 1,1,1-trichloroethane. While n-propyl bromide is considered a 'drop in' alternative, the faster evaporation rate of methylene chloride requires significant formulation adjustment to achieve the same adhesive application level. This is especially true with sprayed adhesives.

### Not-in-kind technologies

Water-based adhesives: a large number of adhesives use water instead of organic solvents. A water-based adhesive can be a solution, latex or an emulsion. Latex adhesives are more likely to replace solvent-based adhesives than solution adhesives because their synthetic binders provide more versatility and higher performance. Water-based adhesives perform well on many surfaces especially non-porous to porous bonding and moist surfaces.

Hot melt adhesives: hot melts are primarily 100 per cent solid thermoplastic bonding materials that achieve a solid state and resultant strength upon cooling. The major applications are bookbinding, packaging, textiles and product assembly including construction glazing and automotive door panel and carpet installation. Hot melt adhesives applications are, however, limited. They have poor adhesion to a number of substrates, creep under load over time and, at elevated temperatures, have limited strength and heat resistance.

Radiation cured adhesives: radiation curing is a production technique for drying and curing adhesives through the use of radiant energy: ultraviolet (UV), infrared (IR), electron beam (EB), gamma and x-rays. The binding agents that can be cured include acrylics, epoxies, urethanes, anaerobic adhesive and polyester resins. Applications include electronics, communications and consumer products, transportation, packaging, medical and dental uses, and pressure sensitive tapes. One drawback is that adhesive curing is only possible in the "line of sight" of the radiant energy, unless the adhesive is designed to release free radicals on irradiation, starting a chain reaction to the "hidden" areas.

High solids adhesives: high solids have good performance characteristics, including initial bond strength, comparable to that of 30 per cent solids adhesives in medium and high demand applications and can be applied using existing equipment at normal line speeds with minor modifications. In other application areas, such as bonding of rubber assemblies, high solids adhesives have not been as successful. High solids adhesive films are too thick for bonding of rubber assemblies, resulting in limited versatility and generally poor performance.

Powders: one-part epoxies, urethanes, and natural resins are often supplied as powders that require heat to cure. Powders are used only for non-pressure-sensitive applications. One advantage of the powder form is that no mixing or metering is necessary. However, powders must be refrigerated to maximize shelf-life.

Non-volatile solids and liquids and reactive liquids: moisture-cured adhesives and reactive liquids can be applied as 100 per cent non-volatile solid and liquid systems. These adhesives are composed entirely of binding substances, modifiers, and fillers (i.e. they have no carrier or solvent). Some two-component adhesives use reactive solvents that form part of the cured mass and thus do not depend on evaporation. Reactive liquids are used for high performance structural applications.

#### KEY FACTS

- Complete elimination of ozone-depleting solvents is possible
- Several substitutes
- Water-based adhesives
- Hot melts
- Radiation cured adhesives
- High solids and powders
- Non-volatile solids and reactive liquids

## Coatings and inks

Use of 1,1,1-trichloroethane as a solvent for binding substances in decorative coatings and inks increased in the late 1980s, as it was used to replace VOC solvents in coating and ink formulations. However, even at its peak, 1,1,1-trichloroethane use in this sector was not more than 1 per cent of total consumption. CFC-113 use has always been much less and is considered negligible. The trend towards increased use of 1,1,1-trichloroethane has reversed in recent years as the solvent came under the Montreal Protocol. A number of suitable replacement solvents and formulations are now available.

### Substitute solvents

Many different conventional non-halogenated linear or cyclic hydrocarbon solvents can be used in place of 1,1,1-trichloroethane for coatings and inks, for example, alcohols, esters, xylol, terpenes or ketones. These solvents or blends of them are very capable of dissolving the binding resin systems. However, there are significant drawbacks. From a safety perspective, these solvents require warning labels for users accustomed to the non-flammable 1,1,1-trichloroethane products. Storage and distribution methods may also have to be altered to complete a conversion to flammable solvents/products. Because of both VOC and flammability concerns, there is a trend towards an increased use of water-based products.

### Not-in-kind technologies

Water-based: Water-based, high solids and powder formulations can be used in place of 1,1,1-trichloroethane and other solvents to produce coatings and inks. Recent advances in water-based coating technology have improved the dry-time, durability, stability, adhesion, and application of water-based coatings.

High solids: Although high-solid coatings resemble conventional solvent coatings in appearance and use, high-solid coatings contain less solvent and a greater percentage of resin. They are applied using methods similar to those used for water-based coatings. High-solid coatings 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: Powder coatings contain the resin only in powder form and thus have no solvent. They are applied using fluidized beds, electrostatic spray, and electrostatic fluidized beds. The object to be coated is heated above the powder's melting point, so that when the object is removed from the presence of heat, the resin fuses into a continuous film. The resin then hardens to form a finish that has excellent durability and corrosion resistance.

UV/EB-cured: UV/EB-cured coatings and inks have been used in very limited applications over the last 20 years, but their use has seen a dramatic increase in recent years. There are several factors that contribute to the growing popularity of UV/EB-cured coatings and inks. These include high quality, rapid cure times, and low energy use. One major limitation to the use of UV/EB-cured coatings and inks is outdoor durability.

## Aerosols

### Substitute solvents and carriers

Replacement technologies include petroleum distillates, non-ozone-depleting chlorinated solvents, HCFCs, HFCs and HFEs, alcohols, other organic solvents, and water-based formulations. When evaluating the alternatives, three performance factors are considered of most importance: toxicity, flammability and density. Flammability is a major concern for petroleum distillates, alcohols, and other non-halogenated organic solvents. The lower density of these same solvents increases the tendency of solid ingredients to settle and requires larger containers to deliver a similar weight of product. It is also important to consider the flammability of the aerosol propellant and bear in mind that many alternative solvents are classified as VOCs, which may restrict their use in some geographic areas.

Petroleum distillates and other non-halogenated organic solvents are used for various automotive products such as tyre cleaners, lubricants, spray under-coatings, and in household products such as water repellents/shoe water-proofers, glass frostings, and insecticides. These and other flammable organic solvents, including alcohols, ketones, and terpenes, are attractive alternatives due to their strong cleaning power, coupled with an ability to dissolve other active ingredients.

Non-ozone-depleting chlorinated solvents including trichloroethylene, perchloroethylene, and methylene chloride may be used in limited applications. Their primary benefits are non-flammability and high solvency. However, potential formulators and users of aerosols containing these solvents must be aware of their associated human health risks.

HCFC solvents have much the same properties as CFC-113 and 1,1,1-trichloroethane, making them ideal replacements from a technical standpoint. However, both HCFC-141b and HCFC-225 have low, but finite, ODPs and have a phase out date that will limit their future use. Some countries already forbid their use in aerosol products.

HFC and HFE compounds are non-flammable and have low toxicity, good stability and compatibility with many metals and synthetic materials. However, HFCs and HFEs have relatively low solvency, are more expensive than other options and have GWP. Aerosol packagers often blend these compounds with hydrocarbons, alcohols, chlorocarbons, and ketones to enhance their cleaning and carrier performance. These partially fluorinated solvents are used for cleaning of operating electrical contacts, because of their non-flammability.

Available water-based products include shoe polishes, insecticide foggers, mould release agents, and fabric protectors. Some of these products may have reduced overall effectiveness due to reduced dispersion of the propelled liquid, long drying time, and inability to sufficiently wet the surface being sprayed.

### Alternative delivery systems

The use of ozone-depleting solvents in aerosol 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. In some cases – where the ozone-depleting solvent is used only as a solvent or carrier and not as an active ingredient – it may be possible to reformulate the aerosol product to function without the use of a solvent. Such formulations are available for tooling release agents, with improved performance in some applications. However, it is also possible that performance may be lower, primarily because of uneven dispersion of the active ingredient.

### KEY FACTS

1,1,1-Trichloroethane and CFC-113 used in aerosols can be replaced by petroleum distillates, non-ozone depleting chlorinated solvents, HCFCs, HFCs and HFEs, alcohols, other organic solvents, water-based formulations, and alternative delivery systems.

## Miscellaneous uses

Alternatives for selected applications (A full discussion of more 'exotic' miscellaneous uses can be found in the latest 1998 STOC manual).

Oxygen system cleaning: the use of oxygen involves a degree of risk because oxygen vigorously supports combustion when in contact with many substances. A high level of cleanliness is therefore a prerequisite for oxygen system components. Examples of alternatives to CFC-113 include aqueous cleaning with certain parts requiring ethanol, and solvent blends containing HFEs, HFCs, and HCFCs.

Detection of latent fingerprints: several alternatives have been evaluated for the ninhydrin reagent fingerprint detection technique. Some alternatives such as HCFC-141b, HCFC-225ca/cb, hydrocarbons and alcohols can be used, but they are not as effective as CFC-113. The most common problems have been fading of ink, toxicity or flammability. Recently, HFC and HFE blends have been used with excellent results. Similarly, UV-sensitive fingerprint detectors have successfully converted from CFC-113 to HFC/HFE products.

Laboratory testing: CFC-113, 1,1,1-trichloroethane, and CTC are used for analyses in laboratories or investigations. Many uses of ozone-depleting solvents in laboratory applications have been granted global exemption. However, alternatives have been found for testing of oil, grease, and total petroleum hydrocarbons in water and testing of tar in road paving materials.

Semiconductor manufacturing: FCs (and possibly some CFCs) used in plasma etching may be able to be replaced with an HFC or HCFC while potential newer process alternatives include mixtures of various fluorocarbons and HFCs with non-ozone-depleting chlorine sources. Most of these materials are destroyed during the plasma generation process, which greatly limits their impact on the environment.

Fabric protection and coating: alternative non-aerosol fabric protection products applied at the mill or by the retailer include organic solvents that extend the dry time and are flammable. These products may require additional capital expense if solvents are to be handled and used safely. A water-based fluorocarbon resin system has been introduced recently that will replace solvent-based fluorocarbon products currently used for this application. The system will require the purchase of special equipment for the application of the water-based product.

## Article 5 Countries

### Choosing the best alternative

The previous sections have provided an outline of the many substitute solvents and other not-in-kind cleaning technologies available to enterprises in Article 5 countries. Fortunately, alternatives now exist for all but a tiny number of extremely high-tech uses. In fact, there are so many options for most applications that choosing the best available alternative can be challenging. Even within a given solvent sub-sector, many different advantages and disadvantages exist between the options.

The selection of the alternative should be based on five primary factors given below (in order of importance). The alternative:

- (1) should not be an ozone-depleting substance;
- (2) should enable the enterprise to maintain a product reliability level at least equal to the past methods;
- (3) should be economical;
- (4) should not create significant environmental impact; and
- (5) should not compromise worker or consumer health and safety.

To assist Article 5 country enterprises with their decision, the following hierarchy of alternative classes (in order of preference) has been assembled, taking account of these five primary factors :

- "No-clean", keep-clean;
- Aqueous cleaning;
- Hydrocarbon-surfactant ("semi-aqueous") cleaning;
- Organic solvent cleaning (with solvents less toxic than non-ozone-depleting conventional halogenated solvents);
- Non-ozone-depleting conventional halogenated solvents (TCE, MC, PCE);
- Organic solvent cleaning (with solvents more toxic than non-ozone-depleting conventional halogenated solvents);
- HFCs and HFEs;
- HCFC-225;
- HCFC-141b;
- PFCs.

Experience thus far has shown that most conversions involving new equipment have been to aqueous or hydrocarbon-surfactant cleaning. However, for enterprises considering retrofits of existing equipment, conventional chlorinated solvents offer the only economical solution. Although HCFCs, HFCs, and HFEs may work technically, the solvent cost remains prohibitive for use in a typical retrofit vapour degreaser. Retrofits to aqueous and hydrocarbon-surfactant cleaning are also possible. Degreaser tanks are sometimes retrofitted for water based cleaners, but this requires extensive engineering redesign and should not be attempted without direct consultation with a qualified equipment supplier. For hydrocarbon-surfactant processes, the chemical manufacturer must also be consulted.

## Conservation and recovery

The Montreal Protocol controls only the importation and production of ozone-depleting substances. Recovery and recycling are not included, and therefore provide 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, as well as improving efficiency and saving money. Some countries are introducing specific measures to encourage better practices, over and above those required by the Protocol. Conservation and recovery practices are effective short-term solutions while longer-term solutions are being selected.

### 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 drag-out on work being processed. Older equipment is generally less efficient and more likely to emit solvents, but can sometimes be retrofitted with containment devices. Seven general steps can be taken by most companies to reduce solvent consumption and emission:

- eliminate unnecessary cleaning; consolidate and centralize all cleaning processes, and use fewer machines where possible;
- isolate open sources of emissions, to give reductions of 50–80 per cent. Open-top vapour degreasers can be retrofitted to include covers and hoists;
- eliminate all sources of draughts over the vapour-air interface of the machines, turn off all “lip vent exhausts”;
- match the workload size and weight to the cross-sectional area of the tanks and heating capability of the cleaning equipment;
- automate vapour degreasing and other processes – this can reduce solvent emissions by 20–30 per cent;
- 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 per cent;
- maintain equipment according to manufacturers’ specifications and eliminate all leaks – thus reducing solvent loss by up to 20 per cent.

**Specific measures**

In the electronics industry, solvent losses can account for 90 per cent of total consumption, so recovery measures should be adopted wherever possible. Drag-out losses contribute significantly to overall emissions. Using automatic handling equipment to feed parts into the vapour degreasers at a constant rate to produce an effective cycle can reduce solvent losses. Better basket and rack design can also reduce drag-out in electronics cleaning. Fans used to cool parts after soldering can ensure that circuit boards enter cleaners at temperatures that minimize evaporation.

Good practices specific to general metal cleaning include: manual removal of large contaminants before degreasing with solvent and adding sophisticated filtration equipment; 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 re-forms, air saturated with solvent vapours is expelled, causing 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. An example of such downstream reuse would be selling solvent from an electronics cleaning process into the dry cleaning industry. On-site recycling is especially economical if the soiled solvent from several machines is piped to a single still for recycling. This is viable only when all the cleaners are removing the same soil with the same solvent formulation.

## Reduction scenarios

### Non-Article 5 countries

Non-Article 5 countries have phased out ozone-depleting solvents since the beginning of 1996. CTC was not used as an industrial solvent and 1,1,1-trichloroethane produced in 1995 has reached the end of its shelf life, although there may still be some recycled solvent in use. Minor use of stockpiled CFC-113 continues. However, users are feeling increasing pressure to find alternatives as stockpiles run out. A very small quantity of ozone-depleting solvent, authorized for Essential Use Exemptions, is still produced. Use of transitional solvents HCFC-225 and HCFC-141b may continue until as late as 2030. The recent availability of HFCs & HFEs has made it technically feasible to phase out HCFCs in all but a small number of applications. However, the higher price of these alternatives may delay conversion from HCFCs until later years.

### Article 5 Countries

Many Article 5 countries have made impressive progress in phasing out ozone-depleting solvents. Some countries have been phasing out solvents for several years. Conversely, others have continued to increase production and use right up to the mid 1999 freeze.

The primary phase out challenge is no longer technical in nature. The technology was developed and implemented to support the 1996 phase out in non-Article 5 countries. For Article 5 countries it is a matter of identifying, informing and, where necessary, assisting the many thousands of ozone-depleting solvent users. Excellent coordination between government and industry will be required to ensure a smooth transition from CFC-113 and CTC (by 2010) and TCE (by 2015) to the multitude of possible alternatives.

Specific challenges for Article 5 countries and their industries include the following:

- identification of producers, importers and vendors of ozone-depleting solvents;
- identification of products that contain ozone-depleting solvents;
- identification of and assistance to users from many small and medium size enterprises in selecting and converting to the most appropriate alternative (most difficult in the solvents sector);
- affordability of cost of alternatives, including new or retrofit equipment and, in some cases, higher operating expenses for the converted process.

It is generally recognized that, compared to other sectors, phase out in the solvents sector is slower due to a multitude of applications over about 16 sub-sectors in a number of diverse industries. Large international companies in Article 5 countries face few serious barriers to the phase out process. A major effort remains for small and medium size enterprises which, when taken collectively, consume the greatest volume of ozone-depleting solvents.

Efficient dissemination of technical and commercial information will be another challenge to a successful phase out of ozone-depleting solvents. Much inefficiency has arisen in past efforts because of poor distribution of information. For example, although the Internet contains much useful and impartial information, it also publishes the ideas of vested interests and extremist views. Article 5 countries will need enough technical expertise to evaluate the information supplied and, if there are any contradictions, to obtain impartial advice from reliable third parties.

As planned, the transitional HCFC solvents will remain in use longer. Production levels will not be frozen until 2016 and may continue until 2040. Once again, phase out of these solvents is technically feasible now. However, many of the alternative substitutes are much more expensive. The sooner this cost disparity is bridged, the sooner phase out will be possible.

### **Illicit trade**

Non-Article 5 countries have been fighting illicit trade since shortly after the 1996 phase out. The problem is very difficult to control for a number of reasons. There is hope that, as the number of countries producing ozone-depleting solvents drops, the sources of illicit trade will also decline. However, countries that most recently “phase out” use of ozone-depleting solvents will have to guard against becoming the next high-demand customer for illegal imports. Identification of remaining users will be invaluable to the effort to control illicit trade.

## Resources

### Secretariats and Implementing Agencies

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## Contact points

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### Friends of the Earth (FOE)

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## Equipment

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 the Thomas Register at <http://www.thomasregister.com/>

### 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  
 Waste water treatment equipment

### General metal cleaning

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

### ozone-depleting solvent products and manufacturer names

It can be difficult to identify products containing ozone-depleting solvents. As opposed to refrigerated gases, halons, aerosol propellants, some foam blowing agents and other ozone-depleting substances, the ozone-depleting solvents are shipped and labelled in identical ways to hundreds of those that are not ozone depleting. Users, agents, ozone officers, customs officers and others are directed to a STOC recommended web site that will help to identify ozone-depleting solvent products that fall under the regulations of the Montreal Protocol: <http://www.protonique.com/unepstoc/stocfile/stocrr.htm>

## **Further reading**

The following six UNEP Technical Options Committees reports can be found at:

<http://www.teap.org/>

1998 Assessment Report of the Aerosols, Sterilants, Miscellaneous Uses and Carbon Tetrachloride Technical Options Committee

1998 Assessment Report of the Flexible and Rigid Foams Technical Options Committee

1998 Assessment Report of the Halons Technical Options Committee

1998 Assessment Report of the Methyl Bromide Technical Options Committee

1998 Assessment Report of the Refrigeration, Air Conditioning and Heat Pumps Technical Options Committee

1998 Assessment Report of the Solvent, Coatings and Adhesives Technical Options Committee

## Glossary

adsorption	surface phenomenon in which substances form physiochemical bonds with other materials.
alcohol	hydrocarbon derivatives with at least one hydrogen atom replaced by -OH.
aqueous cleaning	cleaning with water to which suitable detergents, saponifiers, or other additives may be added.
Article 5 country	a Member State or Party to the Montreal Protocol, defined as a developing nation according to criteria in Article 5, paragraph 1, of the Protocol and which enjoys certain privileges in the phase out timetable.
azeotrope	chemical mixture where vapour and liquid composition are identical.
biodegradable	products easily broken down by living organisms.
brominated solvents	unregulated ozone-depleting solvents, represented at the time of writing, mainly by bromochloromethane and n-propyl bromide.
CFC	chlorofluorocarbon.
CTC	carbon tetrachloride.
carbon tetrachloride	chlorocarbon solvent with an ODP of approximately 1.1. Also considered toxic and a human carcinogen.
carcinogen	causing cancer in animals and humans.
bromochloromethane	see brominated solvents.
closed-top vapour degreaser	a vapour degreaser designed so that the solvent and its vapour are separated from the external atmosphere. Also known as low-emission, airtight or zero-emission vapour degreaser.
combustible	property of a product whose flash point is fixed at over 50°C (arbitrary limit).
detergent	product designed to render soils soluble in water, usually made from synthetic surfactants.
distillation	means for purifying solvents by boiling into a vapour and collecting the vapour condensate.
dry cleaning	common term for cleaning textiles in organic solvents, as opposed to water.
emulsion	suspension of very fine droplets of one liquid in another, where the two liquids are normally immiscible.
ester	fruity smelling acid derivative obtained by exchanging replaceable hydrogen for alkyl radicals; used as solvents or artificial fruit essences.
flux	chemical employed in soldering to facilitate solder joint production, often rosin-based.
flammable	property of a product whose flash point is fixed at under 50°C (arbitrary limit).
flash point	temperature at which a substance ignites on contact with a flame.
GWP	global warming potential (potential of a substance to contribute to the greenhouse effect).
glycol	loose term for a diol or a dihydric alcohol, i.e. one containing two -OH groups per molecule.
HCFC	hydrochlorofluorocarbon.
HFC	hydrofluorocarbon.
HFE	hydrofluoroether.
halocarbon	organic substance where at least one hydrogen atom has been replaced by a halogen atom (fluorine, chlorine, bromine, iodine, or astatine).

hydrocarbon	organic substance made of hydrogen and carbon.
hydrocarbon/ surfactant blend	less volatile hydrocarbon solvents. mixed with surfactants that can be used in two-phase cleaning, with water (semi-aqueous cleaning).
ion	electrically charged particle.
Kauri-Butanol index	used to provide an indication of a solvent's soil solubilization ability.
ketone	very reactive compound containing a carbonyl group, that may be formed by oxidation of secondary alcohols.
low-solids flux	flux containing little solid matter, eliminating the need for cleaning.
naphtha	hydrocarbon mixture, usually a cut between gasoline and kerosene.
neutralizer	substance added to balance the acid/alkaline content of water.
'No-clean' flux	soldering flux whose residues are designed to be safe for certain applications, without requiring a cleaning operation.
non-ionic	uncharged.
n-propyl bromide	see brominated solvents.
ODP	ozone-depletion potential.
organic	compound containing carbon and hydrogen.
ozone	gas formed from three oxygen atoms.
PCB	printed circuit board.
perchloroethylene	chlorocarbon solvent used extensively in industrial degreasing and dry cleaning.
polar	molecule in which electric charges are unbalanced.
precision cleaning	cleaning of high-precision mechanical parts, optical parts and electronic sensors, as opposed to general metal cleaning.
rosin	solid rosin made from pine-tree resin.
saponifier	chemical that reacts with organic fatty acids (such as rosin), oils and greases to form water-soluble alkaline soaps, mineral- or organic-based.
semi-aqueous solvents	another name for hydrocarbon/surfactant (HCS) solvents.
solvent	liquid in which another substance (the solute) is dissolved to form a solution.
SMT	surface mount technology of printed circuit boards.
surfactant	chemical that reduces water surface tension to enable cleaning.
terpene	any homocyclic hydrocarbon with a formula C <sub>10</sub> H <sub>16</sub> .
vapour phase cleaning	cleaning process where final rinse is achieved by condensing solvent vapour on parts being cleaned.
ultrasonic cleaning	immersion cleaning to maximize cleaning efficiency using high frequency sound waves to create cavitation implosions close to parts.
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.
wave soldering	mass soldering electronics assemblies after fluxing by passing them through a wave of molten solder.
water-soluble flux	flux where post-solder residue can be removed by water – usually very active – also known as organic acid fluxes.
zero emissions	
vapour degreaser	see closed-top vapour degreaser.

## About the UNEP DTIE OzonAction Programme

Nations around the world are taking concrete actions to reduce and eliminate production and consumption of CFCs, halons, carbon tetrachloride, methyl chloroform, methyl bromide and HCFCs. When released into the atmosphere these substances damage the stratospheric ozone layer – a shield that protects life on Earth from the dangerous effects of solar ultraviolet radiation. Nearly every country in the world has committed itself under the Montreal Protocol to phase out the use and production of ODS. Recognizing that developing countries require special technical and financial assistance in order to meet their commitments under the Montreal Protocol, the Parties established the Multilateral Fund and requested UNEP, along with UNDP, UNIDO and the World Bank, to provide the necessary support. In addition, UNEP supports ozone protection activities in Countries with Economies in Transition (CEITs) as an implementing agency of the Global Environment Facility (GEF).

Since 1991, the UNEP DTIE OzonAction Programme has strengthened the capacity of governments (particularly National Ozone Units or “NOUs”) and industry in developing countries to make informed decisions about technology choices and to develop the policies required to implement the Montreal Protocol. By delivering the following services to developing countries, tailored to their individual needs, the OzonAction Programme has helped promote cost-effective phase out activities at the national and regional levels:

### Information Exchange

Provides information tools and services to encourage and enable decision makers to make informed decisions on policies and investments required to phase out ODS. Since 1991, the Programme has developed and disseminated to NOUs over 100 individual publications, videos, and databases that include public awareness materials, a quarterly newsletter, a web site, sector-specific technical publications for identifying and selecting alternative technologies and guidelines to help governments establish policies and regulations.

### Training

Builds the capacity of policy makers, customs officials and local industry to implement national ODS phase out activities. The Programme promotes the involvement of local experts from industry and academia in training workshops and brings together local stakeholders with experts from the global ozone protection community. UNEP conducts training at the regional level and also supports national training activities (including providing training manuals and other materials).

### Networking

Provides a regular forum for officers in NOUs to meet to exchange experiences, develop skills, and share knowledge and ideas with counterparts from both developing and developed countries. Networking helps ensure that NOUs have the information, skills and contacts required for managing national ODS phase out activities successfully. UNEP currently operates 8 regional/sub-regional Networks involving 109 developing and 8 developed countries, which have resulted in member countries taking early steps to implement the Montreal Protocol.

### **Refrigerant Management Plans (RMPs)**

Provide countries with an integrated, cost-effective strategy for ODS phase out in the refrigeration and air conditioning sectors. RMPs have to assist developing countries (especially those that consume low volumes of ODS) to overcome the numerous obstacles to phase out ODS in the critical refrigeration sector. UNEP DTIE is currently providing specific expertise, information and guidance to support the development of RMPs in 60 countries.

### **Country Programmes and Institutional Strengthening**

Support the development and implementation of national ODS phase out strategies especially for low-volume ODS-consuming countries. The Programme is currently assisting 90 countries to develop their Country Programmes and 76 countries to implement their Institutional-Strengthening projects.

For more information about these services please contact:

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## About the UNEP Division of Technology, Industry and Economics

The mission of the UNEP Division of Technology, Industry and Economics is to help decision-makers in government, local authorities, and industry develop and adopt policies and practices that:

- are cleaner and safer;
- make efficient use of natural resources;
- ensure adequate management of chemicals;
- incorporate environmental costs;
- reduce pollution and risks for humans and the environment.

The UNEP Division of Technology, Industry and Economics (UNEP DTIE), with its head office in Paris, is composed of one centre and four units:

- The International Environmental Technology Centre (Osaka), which promotes the adoption and use of environmentally sound technologies with a focus on the environmental management of cities and freshwater basins, in developing countries and countries in transition.
- Production and Consumption (Paris), which fosters the development of cleaner and safer production and consumption patterns that lead to increased efficiency in the use of natural resources and reductions in pollution.
- Chemicals (Geneva), which promotes sustainable development by catalysing global actions and building national capacities for the sound management of chemicals and the improvement of chemical safety world-wide, with a priority on Persistent Organic Pollutants (POPs) and Prior Informed Consent (PIC, jointly with FAO).
- Energy and OzonAction (Paris), which supports the phase out of ozone depleting substances in developing countries and countries with economies in transition, and promotes good management practices and use of energy, with a focus on atmospheric impacts. The UNEP/RISØ Collaborating Centre on Energy and Environment supports the work of the Unit.
- Economics and Trade (Geneva), which promotes the use and application of assessment and incentive tools for environmental policy and helps improve the understanding of linkages between trade and environment and the role of financial institutions in promoting sustainable development.

UNEP DTIE activities focus on raising awareness, improving the transfer of information, building capacity, fostering technology cooperation, partnerships and transfer, improving understanding of environmental impacts of trade issues, promoting integration of environmental considerations into economic policies, and catalysing global chemical safety.

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