Ozone-Depleting Substances: Alternatives

Surrounding the earth at a height of about 25 kilometers is the stratosphere, rich in ozone, which prevents the sun's harmful ultraviolet (UV-B) rays from reaching the earth. UV-B rays have an adverse effect on all living organisms, including marine life, crops, animals and birds, and humans. In humans, UV-B is known to affect the immune system; to cause skin cancer, eye damage, and cataracts; and to increase susceptibility to infectious diseases such as malaria.

In 1974, it was hypothesized that chlorinated compounds were able to persist in the atmosphere long enough to reach the stratosphere, where solar radiation would break up the molecules and release chlorine atoms that would destroy the ozone. Mounting evidence and the discovery of the Antarctic ozone hole in 1985 led to the global program to control chlorofluorocarbons (CFCs) and other ozone-destroying chemicals. In addition to Antarctica, ozone loss is now present over New Zealand, Australia, southern Argentina and Chile, North America, Europe, and Russia.

The ozone-depleting chemicals or substances (ODSs) of concern are CFCs, halons, methyl chloroform (1,1,1,-trichloroethane; MCF), carbon tetrachloride (CTC), hydrochlorofluorocarbons (HCFCs), and methyl bromide. The ozone depletion potential (ODP) for these chemicals is shown in Table 1. CFC-11 was assigned an ODP of 1.0; all other chemicals have an ODP relative to that of CFC-11. An ODP higher than 1.0 means that the chemical has a greater ability than CFC-11 to destroy the ozone layer; an ODP lower than 1.0 means that the chemical's ability to destroy the ozone layer is less than that of CFC-11.

In September 1987, the Montreal Protocol on Substances That Deplete the Ozone Layer (the Protocol) was signed by 25 nations and the European Community. The Protocol was the first international environmental agreement, and its signing by so many nations represented a major accomplishment, and a major shift in the approach to handling global environmental problems. The Protocol called for a freeze on the production of halons and a requirement to reduce the production of CFCs by 50% by 1999. However, new scientific evidence surfaced after the entry into force of the Protocol, indicating that ozone depletion was more serious than originally thought. Accordingly, in 1990 (London), 1992 (Copenhagen), and 1995 (Vienna), amendments were made to the Protocol to regulate the phase-out of the original chemicals and the control and phase-out of additional chemicals.

Table 1. Ozone Depletion Potential (ODP) of the Principal Ozone-Depleting Substances (ODSs)

ODS	*ODP*
CFC-11	1.0
CFC-12	1.0
CFC-113	0.8
CFC-114	1.0
CFC-115	0.6
CFC-111, -112, -13, -211, -212, -213, -214, -215, -216, -217	1.0
Halon 1211	3.0
Halon 1301	10.0
Halon 2402	6.0
Carbon tetrachloride (CTC)	1.1
Methyl chloroform (MCF); 1,1,1-trichloroethane	0.1
HCFC-22	0.05
HCFC-123	0.02
HCFC-124	0.02
HCFC-141b	0.15
HCFC-142b	0.06
HCFC-225ca	0.01
HCFC-225cb	0.04
Methyl bromide	0.7

The principal provisions of the Montreal Protocol as it now stands are as follows:

- Production of CFCs, halons, methyl chloroform, and CTC ceased at the end of 1995 in industrial countries and will cease by 2010 in developing countries. Developing countries are defined in the Protocol as those that use less than 0.3 kilograms (kg) of ODS per capita per year. They are often called Article 5 countries in reference to the defining article in the Montreal Protocol.
- HCFCs, originally developed as a less harmful class of CFC alternatives, will be phased out by 2020 in industrial countries, with some provisions for servicing equipment to 2030. Developing countries are to freeze consumption by 2016 (base year 2015) and phase out use by 2040.
- Consumption and production of methyl bromide will end in 2005 in industrial countries (subject to phase-out stages and exemptions) and in 2015 in developing countries.

It was early recognized that undue hardships might be experienced by industry in developing countries as they implemented replacement technologies. Therefore, a fund was established under the Montreal Protocol to pay for incremental costs such as technical expertise and new technologies, processes, and equipment associated with the phase-out. The Multilateral Fund of the Montreal Protocol is managed by an executive committee consisting of delegates from seven developing countries and seven industrial countries. The following international organizations have been made Implementing Agencies of the Multilateral Fund for the purpose of helping governments and industries in developing countries with their programs to eliminate ODSs. (The roles outlined here are not intended to be exhaustive.)

- The *World Bank* assists developing countries with investment projects, country programs, workshops, training, and institutional strengthening.
- The *United Nations Environment Programme (UNEP)* has a clearinghouse function that includes information exchange, country programs, training, and workshops.
- The *United Nations Development Programme (UNDP)* is responsible for feasibility and preinvestment studies, training and workshops, demonstration projects, investment project design, and country programs.
- The *United Nations Industrial Development Organization (UNIDO)* implements small and medium-scale projects, feasibility studies at the plant level, technical assistance and training, and country programs.

Uses of ODSs

In general, ODSs are most often used in the following applications:

- As propellants in aerosols (CFCs and HCFCs)
- In refrigeration, air conditioning, chillers, and other cooling equipment (CFCs and HCFCs)
- To extinguish fires (halons)
- In the manufacture of foams (CFCs and HCFCs)
- As solvents for cleaning printed circuit boards and precision parts and degreasing metal parts (CFCs, HCFCs, methyl chloroform, and CTC)
- In a variety of other areas, such as inks and coatings and medical applications (CFCs, HCFCs, methyl chloroform, and CTC)
- As a fumigant (methyl bromide).

Alternative Technologies, Processes, and Chemicals

The following discussion provides a brief overview of the alternatives to ODSs that have been developed in various sectors. It is not intended to be an exhaustive listing of all alternatives, but it does summarize some proven alternatives and give an indication of future development trends. The selection of any alternative should be made with due consideration of other issues that could affect the final choice.

Identification, development, and commercialization of alternatives to ODSs are going on constantly. For this reason it is important to seek information on the latest alternatives from the World Bank's Global Environment Coordination Division. Technological updates are provided by the World Bank's Ozone Operations Resource Group, which is made up of experts in halons, solvents, aerosols, refrigerants, mobile air conditioning, foam blowing, and chemical production. For any alternative, consideration needs to be given to, for example, its compatibility with existing equipment, its health and safety aspects, its direct global-warming potential, whether it increases or decreases energy consumption, and the costs that may be incurred in eventual conversion to a non-ODS technology if an interim HCFC alternative is chosen. New ways of doing business may also develop in the course of review and selection of alternatives. For example, many electronics companies have now converted their manufacturing plants to "no-clean" technology. The benefits include elimination of circuit board cleaning after soldering, savings in chemical costs and waste disposal costs, savings in maintenance and energy consumption, improved product quality, and advances toward new technologies such as fluxless soldering. The selection of any alternative should not be made in isolation from the factors listed above.

Flexible and Rigid Foams

Zero-ODP alternatives are the substitutes of choice in many foam-manufacturing applications. However, the use of HCFCs is sometimes necessary in order to meet some product specifications. The viability of liquid hydrofluorocarbon (HFC) isomers in this industry remains to be proved, and hydrocarbon alternatives need to be better qualified, as well. The issues in these evaluations are safety (toxicity and flammability), environmental impact (generation of volatile organic compounds and global warming), product performance (insulating properties, conformity to fire codes, and the like), cost and availability, and regulatory requirements.

The next sections summarize the alternatives for specific products of the foam manufacturing sector. Because of the complexity of the industry and the variety of products, the alternatives have been listed briefly as short-term and long-term options, without an elaboration of the merits of each. Additional information is available in the 1995 UNEP Technical Options Report for this sector.

Rigid polyurethane foams used in refrigerators and freezers. Alternatives include hydrocarbons (pentane) and HCFC-141b; long-term alternatives include HFCs (-134a, -245, -356, -365). Vacuum panels may be used in the future.

Rigid polyurethane for other appliances. Alternatives include HCFC-141b, HCFC-22, blends of -22 and HCFC-142b, pentane, and carbon dioxide / water blowing. In the long term, the alternatives include HFCs.

Rigid polyurethane used for boardstock and flexible-faced laminations. Alternatives include HCFC-141b and pentane; in the long term, the use of HFCs should be developed.

Sandwich panels of rigid polyurethane. HCFC-141b, HCFC-22, blends of HCFC-22 and -141b, pentane, and HFC-134a are now used as alternatives to CFCs in this application. In the long term, HFCs and carbon dioxide / water will be the replacement technologies.

Spray applications of rigid polyurethane. Alternatives currently in use for spray applications include carbon dioxide / water and HCFC-141b. Long-term alternatives will be HFCs.

Slabstock of rigid polyurethane. Alternatives include HCFC-141b; long-term alternatives include HFCs and carbon dioxide / water. Pentane may also be used.

Rigid polyurethane pipe construction. CFCs in this application are being replaced by carbon dioxide / water, HCFC-22, blends of HCFC-22 and -142b, HCFC-141b, and pentanes. Long-term alternatives will include HFCs and carbon dioxide / water. For district central heating pipes, pentane and carbon dioxide / water are the preferred technologies.

Polyurethane flexible slab. Many alternatives now exist for flexible slab construction, including extended range polyols, carbon dioxide / water, softening agents, methylene chloride, acetone, increased density, HCFC-141b, pentane, and other alternative technologies such as accelerated cooling and variable pressure. The long term will probably see the use of injected carbon dioxide and alternative technologies.

Molded flexible polyurethane. The standard now is carbon dioxide / water blowing.

Integral-skin polyurethane products. The current alternatives for these products include HCFC-22, hydrocarbons, carbon dioxide / water, HFC-134a, pentanes, and HCFC-141b. The long-term alternate is expected to be carbon dioxide / water.

Phenolic foams. Phenolic foams can now be made using HCFC-141b, hydrocarbons, injected carbon dioxide, or HFC-152a instead of CFCs. In the long term, HFCs may be the predominant alternative.

Extruded polystyrene sheet. Alternatives currently include HCFC-22, hydrocarbons, injected carbon dioxide, and HFC-152a. In the long term, these same alternatives (except for HCFC-22) will be used, along with possible use of atmospheric gases.

Extruded polystyrene boardstock. HCFC-22 and -142b and injected carbon dioxide are the current alternatives. Long-term alternatives will be HFCs and injected carbon dioxide.

Polyolefins. Polyolefins are now manufactured using alternatives such as hydrocarbons, HCFC-22 and -142b, injected carbon dioxide, and HFC-152a. Hydrocarbons and injected carbon dioxide will be long-term alternatives.

Refrigeration, Air Conditioning, and Heat Pumps

Refrigeration technology has also been rapidly evolving. Immediate replacements for many applications include hydrocarbons, HFCs, and HCFCs. Some of these will also be candidates for long-term replacement of the currently used CFCs. This section briefly describes the alternatives that are available for specific refrigeration, air conditioning, and heat pump applications.

Domestic refrigeration. Two refrigerant alternatives are predominant for the manufacture of new domestic refrigerators. HFC-134a has no ozone depletion potential and is nonflammable, but it has a high global-warming potential (GWP). HC-600a is flammable, has a zero ODP, and has a GWP approaching zero. Other alternatives for some applications include HFC-152a and binary and ternary blends of HCFCs and HFCs. Retrofitting alternatives may include HCFC / HFC blends, after CFCs are no longer available. However, the results obtained so far are still not satisfactory. Neither HC-600a nor HFC-134a is considered an alternative for retrofitting domestic refrigeration appliances, but preliminary data indicate that a combination of the two may be a retrofit, or “servicing,” candidate.

Commercial refrigeration. Alternatives to CFCs for new commercial refrigeration equipment include HCFCs (including HCFC mixtures) and HFCs and HFC mixtures. Retrofit of existing equipment is possible by using both HCFCs and HFCs, in conjunction with reduced charges and more efficient compressors. Hydrocarbons are, to a small extent, applied in hermetically sealed systems.

Cold storage and food processing. Although there has been a return to the use of ammonia for some cold storage facilities, there are safety issues, and some regulatory jurisdictions restrict its use. Other alternatives to CFCs in cold storage and large commercial food preservation facilities include HCFC-22 and HFC blends. Hydrocarbons and HCFC-22 will continue to be the favored alternatives until equipment using other alternatives is developed; ammonia will be used in selected applications.

Industrial refrigeration. New industrial refrigeration systems that are used by the chemical, petrochemical, pharmaceutical, oil and gas, and metallurgical industries, as well for industrial ice making and for sports and leisure facilities, can use ammonia and hydrocarbons as the refrigerant. Although the product base concerned is small, existing CFC equipment can be retrofitted to use HCFC-22, HFCs and HFC blends, and hydrocarbons.

Air conditioning and heat pumps (air-cooled systems). Equipment manufactured in this category generally uses HCFC-22 as the refrigerant. Alternatives under investigation include HFCs and HCs (propane). The most promising of these are the nonflammable, nontoxic HFC compounds, although there is more interest in propane in various regions. HCFs have been criticized for their global warming potential, but their total equivalent warming impact (TEWI), a measure that combines GWP and energy efficiency. is equal to or lower than that of the other alternatives.

Air conditioning (water chillers). HCFC-22 has been used in small chillers, and CFC-11 and -12 have been used in large chillers that employ centrifugal compressors. HFC blends are now beginning to be introduced to replace HCFC-22 in small chillers; HCFC-123 and HFC-134a are the preferred replacements for large units. Chillers that have used CFC-114 can be converted to use HCFC-124 or can be replaced by HFC-134a units.

Transport refrigeration. HCFC-22 and CFC-502 have been the refrigerants of choice for transport refrigeration units, although some applications are using ammonia as the refrigerant. The alternatives include various HFC blends.

Automotive air conditioning. The manufacturers of new automobiles have chosen HFC-134a as the fluid for air conditioning units, and retrofit kits are now available to allow older automobiles to convert to this alternative.

Heat pumps (heating-only and heat recovery). New heating-only heat pumps use HCFC-22, and this is expected to continue. HFC-134a is an alternative for retrofitting existing heat pumps, and investigation into the use of ammonia for large-capacity heat pumps is continuing. Other alternatives being explored include propane, other hydrocarbons, and hydrocarbon blends.

Solvents, Coatings, Inks, and Adhesives

There now exist alternatives or sufficient quantities of controlled substances for almost all applications of ozone-depleting solvents. Exceptions have been noted for certain laboratory and analytical uses and for manufacture of space shuttle rocket motors. HCFCs have not been adopted on a large scale as alternatives to CFC solvents. In the near term, however, they may be needed as transitional substances in some limited and unique applications. The UNEP Solvents Technical Options Committee does not recommend HCFC-141b as a replacement for methyl chloroform (1,1,1-trichloroethane) because its ODP is three times higher. Alternatives for specific uses of ozone-depleting solvents are described in this section.

Electronics cleaning. Experience has confirmed that for most uses in the electronics industry, ozone-depleting solvents can be replaced easily and, often, economically. A wide choice of alternatives exists. If technical specifications do not require postsolder cleaning, no-clean is the preferred technology. If cleaning is required, the use of water-soluble chemistry has generally proved to be reliable. Water-soluble chemistry is not, however, suitable for all applications.

Precision cleaning. Precision cleaning applications are defined as requiring a high level of cleanliness in order to maintain low-clearance or high-reliability components in working order. To meet exacting specifications, the alternatives that have been developed include solvent and nonsolvent applications. Solvent options include alcohols, aliphatic hydrocarbons, HCFCs and their blends, and aqueous and semiaqueous cleaners. Nonsolvent options include supercritical fluid cleaning (SCF), ultraviolet (UV)/ozone cleaning, pressurized gases, and plasma cleaning.

Metal cleaning. Oils and greases, particulate matter, and inorganic particles are removed from metal parts prior to subsequent processing steps such as further machining, electroplating, painting. Alternatives to ozone-depleting solvents that have been developed include solvent blends, aqueous cleaners, emulsion cleaners, mechanical cleaning, thermal vacuum deoiling, and no-clean alternatives.

Dry cleaning. Several solvents exist to replace the ozone-depleting solvents that have traditionally been used by the dry cleaning industry. Perchloroethylene has been used for over 30 years. Petroleum solvents, while flammable, can be safely used when appropriate safety precautions are taken. They include white spirit, Stoddard solvent, hydrocarbon solvents, isoparaffins, and n-paraffin. A number of HCFCs can also be used but should be considered only as transitional alternatives.

Adhesives. Methyl chloroform has been used extensively by the adhesives manufacturing industry because of its characteristics—it is nonflammable and quick drying, and it does not contribute to local air pollution—and its performance. One alternative for some applications is water-based adhesives. Other alternatives include hot melt adhesives; radiation-cured adhesives; high-solids adhesives; one-part epoxies, urethanes, and natural resins in powder form; moisture-cured adhesives; and reactive liquids.

Coatings and inks. Improvements have been made to water-based coatings, and these can be a substitute for ODS-based applications. Water-based coatings have been used in the following industries and manufacturing sectors: furniture, automotive electronics, aluminum siding, hardboard, metal containers, appliances, structural steel, and heavy equipment. Water-based inks are used successfully for flexographic and rotogravure laminates. High-solids coatings are now used for appliances, metal furniture, and a variety of construction equipment. Powder coatings are used for underground pipes, appliances, and automobiles. Ultraviolet light/electron beam (UV/EB) cured coatings and inks have been in limited use over the past 20 years, but their use is increasing. They are now used in flexographic inks and coatings, wood furniture and cabinets, and automotive applications.

Aerosol solvent products. Methyl chloroform is most often the solvent in aerosol applications, but some CFC-113 has also been used. Most of these applications can now be reformulated to avoid the use of ozone-depleting chemicals. With the exception of water, methylene chloride, and some HCFCs and non-ozone-depleting chlorinated solvents such as trichloroethylene and perchloroethylene, all of the alternatives to aerosol-applied solvents are more flammable than the solvents they replace. Alternative means of delivering the solvent can be considered.

Other solvent uses of CFC-113, methyl chloroform, and carbon tetrachloride. Specialized applications of ozone-depleting solvents include drying of components, film cleaning, fabric protection, manufacture of solid-fuel rockets, laboratory testing and analysis, process solvents, and semiconductor manufacture. Some of these applications have been granted an exemption under the Montreal Protocol, but it is the consensus of the experts on the UNEP Solvents Technical Options Committee that alternatives will be developed for all these specialized uses.

Halons

Halon hand-held extinguishers (containing 1211). These can be replaced, in most applications, by multipurpose dry chemical extinguishers.

Halon 1301 total flood systems. New and existing alternatives are available for most halon 1301 total flood systems. These alternatives include zero-ODP halocarbons, inert gas mixtures, and new water-based technologies (e.g., water mist). The use of HCFCs and hydrobromofluorocarbons (HBFCs) as alternatives is not encouraged, and perfluorocarbons (PFCs) should not be used indiscriminately.

Nonmedical Inhalants, Aerosols, Sterilants, and Carbon Tetrachloride Not Used as a Solvent

Nonmedical aerosol products. A variety of alternatives to CFCs are used in nonmedical aerosol applications. Alternatives include hydrocarbons (HCs); dimethyl ether (DME); compressed gases such as carbon dioxide, nitrogen, and air; HCFC-142b and -22; HFC-134a -152a, and -227ea; and nonaerosol delivery means such as pump sprays, solid sticks, roll-ons, brushes, and the like. Because hydrocarbons, DME, and HFC-152a are flammable, there may be products in which they cannot be used. In a manufacturing plant where they are used for aerosol products, appropriate safety precautions will be required.

Inhalant drug products. Some medical aerosol products such as nasal preparations, local anesthetics, and antibiotics can be reformulated through the use of alternative propellants, mechanical pumps, and so on. However, finding suitable alternatives to the CFCs in metered dose inhalers (MDIs) used by asthma sufferers has been a challenge. Alternatives that have been developed and proven to date include dry powder inhalers and HFC-134a and -227.

Sterilants. A gas mixture of 88% CFC-12 and 12% ethylene oxide (EO) has been used by the medical community to sterilize equipment and parts. Replacement alternatives include steam sterilization; 100% EO; blends of carbon dioxide (10%) and EO (90%); formaldehyde; HCFC-124 (91.4%) and EO (8.6%); and other means such as gas plasma, chlorine dioxide, ozone, and radiation. Ethylene oxide is toxic, mutagenic, flammable, and explosive and is a suspected carcinogen. Its use must therefore be carefully controlled.

Carbon tetrachloride (nonsolvent uses). Carbon tetrachloride (CTC) has been used as a feedstock for the production of CFC-11 and –12. This application will cease with the closing of CFC production operations. CTC is also used as a feedstock and processing agent for some pharmaceuticals and agricultural chemicals and in the production of chlorinated rubber. The establishment of an alternative for each application will be found only through product-specific research.

Methyl Bromide

Methyl bromide is used primarily as a fumigant. Only 3.2% of the global sale of more than 75,000 tons in 1992 was for nonfumigant purposes, as a feedstock for chemical synthesis. The greatest part was used to treat soil, to fumigate durables and perishables, and to fumigate structures and transport equipment. From a conservation perspective, technology exists to control the release of methyl bromide when treating soil and crops. Molecular sieves are shown to capture the methyl bromide that otherwise would have been lost to the atmosphere after batch fumigation and to regenerate the methyl bromide for use in subsequent batches. Alternatives to methyl bromide in each application area described below.

Soil. Chemical alternatives include 1,3-dichloropropene, dazomet, chloropicrin, metam sodium, and selective contact insecticides and herbicides. Nonchemical alternatives include crop rotation, organic amendments, steam, solar heating, biological control agents, cultural practices, and plant breeding.

Commodities. Chemical alternatives for crop fumigation include phosphine and carbonyl sulfide, as well as insecticides and rodenticides. Nonchemical alternatives include irradiation, controlled atmospheres utilizing nitrogen and carbon dioxide, and heat and cold.

Structural. Chemical alternatives include sulfuryl fluoride and phosphine, as well as contact insecticides and rodenticides. Nonchemical alternatives are the same as for commodity fumigation.

Progress in Eliminating Ozone-Depleting Substances

Significant progress has been made in eliminating ozone-depleting substances since the entry into force of the Montreal Protocol in late 1987. For example, in the aerosol industry, the use of ODSs has been reduced from 300,000 metric tons (t) globally in 1986 to 180,000 t in 1989 to, it is estimated, less than 80,000 t in 1992. In the refrigeration sector, use of CFC refrigerants in industrial countries dropped from 862,000 t in 1986 to 302,000 t in 1993. Globally, CFC refrigerant use decreased from 1,133,000 t in 1986 to 643,000 t in 1992. To help in managing the phase-out of ODS refrigerants, a service industry has been established in most countries that captures and purifies ODSs during the servicing of equipment. The removed ODSs are then used to service the ongoing needs of ODS-containing refrigeration and cooling equipment until it has reached the end of its useful life. In the fire protection sector, the focus has been on establishing halon banks to recondition and store halon that has been removed from service and to make it available for maintaining other installations that require continued use of halon until suitable replacements are developed. The foam plastics industry has progressed from a global CFC use of 267,000 t in 1986 to 133,000 t in 1993—a reduction of 50%, in spite of a 45% increase in the size of the industry during the same period. The phase-out of ozone-depleting solvents is well advanced in industrial countries, and users are drawing on stockpiled solvents. In developing countries, CFC-113 use has been largely halted, and production facilities are shutting down. The use of methyl chloroform is no longer increasing in these countries. Countries such as Malaysia, Thailand, and Turkey have dramatically reduced solvent use.

It is important to note that the commercial supply chain has had a role to play in the speed of phase-out of ODSs. In many instances, customers have asked their suppliers to implement a phase-out program. These requests may originate because of labeling and tax legislation such as that implemented by the United States or because the customer has an environmental policy in place that commits it to encourage its suppliers to improve their environmental performance. Manufacturers also understand that the dwindling supply of ODSs causes price increases that will eventually make those products more expensive and less competitive.