

**MONTREAL PROTOCOL
ON SUBSTANCES THAT DEplete
THE OZONE LAYER**



Technology and Economic Assessment Panel

- Part I:** Report of the Aerosols, Sterilants, Miscellaneous Uses and Carbon Tetrachloride TOC
- Update on Developments
- Issues Surrounding a Transition to Non-CFC Treatments
- Evaluation of Status of Use of ODS and Alternatives
- Part II:** Report of the Process Agents Task Force
- Part III:** Assessment of the Use of Flammable Refrigerants
- Part IV:** Assessment of the Economic Viability of Methyl Bromide Alternatives

**April 1997 Report
Volume II**

**UNEP
APRIL 1997 REPORT OF THE
TECHNOLOGY AND ECONOMIC
ASSESSMENT PANEL**

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- PART II: REPORT OF THE PROCESS AGENTS TASK FORCE**
- PART III: ASSESSMENT OF THE USE OF FLAMMABLE REFRIGERANTS**
- PART IV: ASSESSMENT OF THE ECONOMIC VIABILITY OF METHYL BROMIDE
ALTERNATIVES**

April 1997 Report, Volume II

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VOLUME II

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**UNEP APRIL 1997 REPORT OF THE
TECHNOLOGY AND ECONOMIC ASSESSMENT PANEL
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INTRODUCTION

The Seventh Meeting of the Parties (Vienna, December 1995) and the Eighth Meeting of the Parties (Costa Rica, November 1996) took a number of decisions which request actions by the UNEP Technology and Economic Assessment Panel (TEAP) and which request reporting in 1997. Responses of the TEAP to several of the 1995 requests can be found in its March and June 1996 reports; some are presented in this report.

In Volume I of the April 1997 TEAP report many responses from TEAP to Decisions taken by the Parties were given. This Volume II presents a number of reports as responses to a number of Decisions:

a. Decisions taken at the Eighth Meeting:

Decision VIII/10 *“Promotion of industry’s participation on a smooth and efficient transition away from CFC-based MDIs”*

Decision VIII/11 *“Measures to facilitate a transition, etc.”*

Decision VIII/12 *“Information gathering on a transition, etc.”*

As a follow-up to the study given in the TEAP June 1996 report (Part III, Sections 1/2), a more elaborate study on these “transition-issues” is given in Part I of this Volume II report by the TOC Aerosols, Sterilants, Miscellaneous Uses and CTC. An Executive Summary of this report has also been given in Volume I, Part III of this April 1997 report.

b. Decisions taken at the Seventh Meeting:

Decision VII/8 *“Review of methyl bromide controls”*

In this Decision the TEAP was requested to prepare a report to the Ninth Meeting of the Parties to enable them to consider further adjustments to the control measures on methyl bromide. This report is contained in Volume I of the TEAP 1997 report, Part II.

A Methyl Bromide Task Force has also prepared a report on the economic feasibility of alternatives to methyl bromide. This assessment report is given as part IV of this April 1997 report, Volume II; it also contains the **final executive summary** after full review.

(NOTE: the Executive Summary of this report as presented in Volume I, Part III, is slightly different from the one presented here in Volume II. The reason for this fact is that a draft Executive Summary was put into Volume I as a placeholder; it was due to the stringent framework within which time a complete review could not be done).

Decision VII/10 *“Continued use of controlled substances as chemical process agents after 1996”*

In 1995, Parties decided to further consider this issue and to take decisions in 1997, following recommendations by the TEAP.

The report by the Process Agent Task Force (PATF) under the TEAP is given as part II in this 1997 report, Volume II (the Executive Summary has also been presented in part III of Volume I).

Decision VII/11

“Laboratory and analytical uses”

In this Decision the Parties expressed their appreciation for the work done by the TEAP and its Laboratory and Analytical Uses Working Group. They also requested to evaluate the current status of use of controlled substances and alternatives and report progress on the availability of alternatives to the Ninth Meeting. Since the above mentioned Working Group had been dissolved after completion of its 1995 task, a response to the Decision has been given by the by the TOC Aerosols, Sterilants, Miscellaneous Uses and CTC in part I of this Volume II.

Decision VII/34

“Progress and development in the control of substances”

In Decision VII/34 (c) the TEAP was requested to report on progress and developments in the control of substances each year. Progress reports of the different TOCs can be found in Volume I, Part III, Section 1.0 of this report. The progress reported by the TOC Aerosols, Sterilants, Miscellaneous Uses and CTC has once more been given in part I of this Volume II report.

A -progress- report on the use of flammable refrigerants is presented by the TOC Refrigeration, AC and Heat Pumps in part III of this Volume II report (the Executive Summary has also been given in Part III of Volume I).

Some of the contributions contained in this April 1997 report, Volume I and II, have also been transferred to the TEAP Internet Site (<http://www.teap.org>).

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REPORT OF THE TOC AEROSOLS, STERILANTS, MISCELLANEOUS USES AND CTC

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EXECUTIVE SUMMARY

Aerosol Products

For aerosol products, other than MDIs, there are no technical barriers to global transition. The major issue remaining for Parties to address is the use of CFCs in Article 5(1) countries and CEIT. The TOC believes that 1996 CFC consumption in the aerosol sector was less than 24,000 metric tonnes in Article 5(1) countries and CEIT excluding MDI use and some pharmaceutical products.

The phaseout of the remaining CFCs in the aerosol sector is dependent upon the availability of hydrocarbon propellants (HAPs). Risks associated with poorly planned or executed conversions to hydrocarbons makes it obligatory for governments to develop suitable monitoring procedures to ensure safe practices including proper design, management and use of prescribed filling equipment, hydrocarbon storage and handling facilities.

Negotiations between the World Bank/GEF and the Russian Government resulted in the approval of seven projects to phaseout CFC use in the aerosol sector. Since GEF funding of these projects has not become available, it is not expected that significant reductions of CFC consumption will occur before 1999. Acceleration of the implementation of these approved projects is particularly important to achieve reductions.

Use of HCFCs in aerosols is prohibited in many European countries and severely restricted in the USA. In Article 5(1) countries HCFCs will be limited in their use by cost considerations.

Metered Dose Inhalers

CFC-containing metered dose inhalers (MDIs) are inexpensive, reliable and effective therapy for respiratory diseases such as asthma and chronic obstructive pulmonary disease (COPD). Currently, some 500 million MDIs are used annually world-wide, using approximately 10,000 tonnes of CFC.

The TOC has reviewed the issue of the essentiality of MDIs for asthma and COPD, and concluded that they remain essential for patient health until an adequate range of technically and economically feasible alternatives are available.

The schedule for the safe introduction of new propellants and reformulated products suggested in the 1994 report and updated in the 1996 report of the Aerosols TOC remains on target. It remains possible that the major part of transition in most Non-Article 5(1) countries may have occurred by the year 2000 and minimal need for CFCs for MDIs is envisaged by the year 2005. However, at this point in time there are still many variables and an exact time scale is not possible to predict with certainty.

Dry Powder Inhalers (DPIs) are continuing to be introduced by a number of companies into many countries. There is good evidence that the previously noted trend of increased DPI usage continues but since overall inhaled therapy has increased further, they have not reduced the sales of MDIs.

In March 1995 the first approval for a CFC-free MDI was granted to 3M's Airomir™, a salbutamol product reformulated with HFA-134a propellant. By March 1997, over thirty five countries had approved Airomir™ (Proventil™-HFA in the USA) for use. Additional companies have submitted applications to market CFC-free inhalers in a number of countries. Approvals are

anticipated in the coming year. It is anticipated that at least two salbutamol CFC-free MDIs will be available in a number of countries by the end of 1998. Since salbutamol MDIs are estimated to comprise half the total global use of MDIs the potential exists for a significant reduction in consumption of CFCs in 1999.

However two years after the introduction of Airomir™ in the United Kingdom it had only reached 1.5% market share. Factors influencing uptake of this non-CFC product include: lack of incremental benefit to patients, apathy of physicians to environmental benefits and higher cost than generic CFC salbutamol products although costs are similar to branded CFC MDIs. It is important to note that the lack of motivation to physician prescribing and economic considerations makes it unlikely that marketing and education programmes alone will produce a significant switch away from CFC products in the absence of clearly defined and implemented national transition policies. However, to facilitate patient and physician utilisation of the reformulated products, education and training are required.

Most intellectual property protection concerning MDIs with CFCs has expired, and this technology has been widely copied without compensation. In contrast, there is very extensive world-wide intellectual property protection in place concerning the new HFC MDIs, and this may restrict the number of MDI manufacturers unless licensing agreements are reached.

For Article 5(1) countries where multinational companies are already operating, adoption of CFC-free technologies should take place as soon as possible. Parties may wish to add this commitment to the Code of Conduct approved at the Eighth Meeting of the Parties to encourage phaseout of CFCs.

Adequate supplies of CFCs to meet patient demand until non-CFC alternatives are available have to be provided. These are currently being met in Non-Article 5(1) countries through Essential Use allocations and existing stockpiles. However, as non-CFC alternatives become available and rationalisation across CFC suppliers and CFC MDI manufacturers occurs, there will be a need to carefully manage supplies. Parties may wish to monitor existing stockpiles to ensure a smooth transition.

At their Eighth Meeting, Parties granted a single request to transfer an essential use authorisation on a one-time basis. This Decision ensured an uninterrupted supply of CFCs to a Party where the CFC MDI manufacturer had chosen to rationalise production outside that Party. The TOC believes this one-time transfer could serve as a model for similar situations provided:

- both Parties agree to the transfer;
- total production volume does not increase; and
- the intended use does not change.

The Parties may wish to consider the advantages of a decision allowing for flexibility in transfer without previous approval by the Parties, but with subsequent approval at a Meeting of the Parties provided these conditions are met.

With the phaseout of other CFC uses, an imbalance between the capacity of the plants that still produce CFCs and the demand they have to meet could occur. To operate a CFC unit efficiently it is necessary to run it above a minimum capacity, therefore, the CFC producer will be forced to run it intermittently in what is called a “campaign”. Given the current schedule for final phaseout of CFC MDIs this campaign production probably will not be needed, except possibly at the end of the CFC MDI transition to provide for a final stockpile of pharmaceutical grade CFCs to meet special patient needs.

Prior to 1996 a number of drug manufacturers established strategic stockpiles of CFCs (estimated at 3-12 months of use in production) as contingency against uncertainties in the Essential Use process, and unforeseen disruption in Essential Use supplies (catastrophic plant failures, contamination of supplies, shifts in market share etc.). Reporting under the Accounting Framework will enable Parties to assess the size of existing stockpiles and determine whether these stockpiles represent a reasonable amount for contingencies. Whilst the Committee believes stockpiles of reasonable size are sensible and represent a safeguard of public health needs, excessive stockpiles could be utilised to prolong CFC MDI manufacture against the spirit of the Montreal Protocol, and act as an impediment to the transition to CFC-free alternatives.

The TOC believes that it is still too early to craft a global framework for CFC MDI phaseout because it is not currently possible to make accurate predictions on the introduction of non CFC alternatives. The TOC recognises that no single strategy will be applicable to all countries. The process of transition to non-CFC alternatives is best handled at the national level, involving dialogue between health authorities, environmental agencies and other interested groups.

The TOC congratulates the USA and Australia for the development of a proposed strategy for phaseout at the national level. The TOC recognises that other Parties may feel that different strategies better fit their needs. Preliminary examples of possible national strategies that Parties may wish to consider when they study their particular situation have been presented (these are examples and are in no way fully inclusive). Parties are encouraged to submit details of national policies for consideration by the TOC to facilitate policy sharing and to gain a better understanding of issues in different Parties involved with transition.

Under the Montreal Protocol, there is no restriction on movement of finished goods, i.e. manufactured MDIs. The Parties should note that if individual countries adopt export bans for CFC MDIs they could disrupt access to treatment options in importing countries. Conversely, once transition has taken place in a Party, there is potential for continued imports of CFC containing products from another Party. However, in a number of countries this will be controlled through existing regulations on the import of therapeutic goods and product license approvals.

The Aerosols, Sterilants, Miscellaneous Uses and CTC Technical Options Committee reviewed nominations for essential use production exemptions from 5 Parties and the European Community. For MDIs there was an almost universal reduction in CFC volumes requested for essential use exemption. The TOC approved only those nominations for asthma and COPD treatment.

An emergency request was made by the United States for 1997 under Decision VIII/9(10) for the transfer of 3 tonnes of CFCs approved for MDI use in a sterile aerosol talc. The United States also made an essential use nomination for CFC manufacture for sterile aerosol talc for 1998 and 1999. This product is used for the treatment of pleural effusion and it is not an inhalation product. The majority of TOC physicians favoured the limited availability of talc formulated as a CFC containing aerosol but a minority considered a dry powder insufflation method which has been in use for many years as a possible adequate alternative. The TOC found it difficult to make a firm recommendation on either the emergency request or the nomination. The request and nomination were inadequate as they do not provide sufficient information to allow a decision on essentiality. Therefore, the TOC were unable to recommend this nomination. However, the Secretariat may wish to grant the emergency request for 1997 and Parties may wish to consider a one year exemption for 1998. Further data is needed at the beginning of 1998 to justify essentiality for 1999.

Sterilisation

By the beginning of 1997, in Non-Article 5(1) countries CFC-12 use for "12/88" sterilant gas had virtually disappeared, as final inventories were depleted. There remain no technical barriers to the phase out of CFCs in sterilisation.

Global consumption of CFC-12 in this sector has decreased from 20,000 metric tonnes in 1991 to less than an expected 500 metric tonnes in 1997. It is anticipated that virtually all CFC-12 use in this sector will be discontinued by 1999.

HCFCs are important as transitional products in both Non-Article 5(1) and Article 5(1) countries for hospital sterilisation. The only barrier to the final conversion from CFCs to HCFCs remains cost. Where CFCs remain relatively inexpensive and there is no regulation to require conversion, there is no incentive for the final conversion from CFCs to HCFCs.

Global consumption of HCFCs in 1996 for sterilisation was 2,900 metric tonnes and estimated global consumption of HCFCs for 1997 is 3,100 metric tonnes. The projected global usage for HCFCs is expected to peak at no greater than 3,400 metric tonnes and then decline after the year 2000 as HFC replacements and new technologies replace HCFCs.

Miscellaneous Uses

Ozone-depleting substances have been used in a variety of miscellaneous uses including tobacco expansion, and laboratory and analytical uses amongst others. This report evaluates the current status of use of controlled substances and alternatives and reports progress on the availability of alternatives for laboratory and analytical uses. For other miscellaneous uses there have been no further developments as to alternatives. Further information will be provided in the 1998 report of the Aerosols, Sterilants, Miscellaneous Uses and CTC Technical Options Committee.

Parties may wish to consider the issue of the laboratory and analytical use exemption at their 9th Meeting in 1997. The global exemption expires at the end of 1997. Little progress has been made toward eliminating this use.

The TOC recommends that the Parties grant a further two year global exemption for the use of controlled substances for laboratory and analytical uses. Furthermore, it is recommended that Parties are encouraged to adopt within their National Ozone Programmes measures designed to reduce these uses.

The TOC also reiterates the importance of:

- organising National Consultative Committees to review and identify alternatives to laboratory and analytical uses and encouraging the sharing of information concerning alternatives and their wider use;
- encouraging national standards organisations to identify and review those standards which mandate the use of ODS in order to move to ODS-free alternatives;
- developing an international labelling scheme; and
- reporting data annually under a global essential use exemption framework which allows Parties to monitor the success of reduction strategies, and investigating and reporting published instructions, standards, specifications and regulations requiring the use of ODS.

Carbon Tetrachloride

CTC is an easily manufactured chemical which is widely available. To better understand the role of this chemical it is important to keep in mind that CTC can be:

- Used as a feedstock for other chemicals. The 1997 Report of the Process Agents Task Force (PATF) recommends that Parties consider feedstock to be defined as:

“A controlled substance that undergoes transformation in a process in which it is converted from its original composition except for insignificant trace emissions as allowed by Decision IV/12.”

- Used as a process agent. The 1997 Report of the PATF recommends that Parties consider process agent to be defined as:

“A controlled substance, that because of its unique chemical and/or physical properties, facilitates an intended chemical reaction and/or inhibits an unintended chemical reaction.

Controlled substances are typically used in chemical processes as process agents for at least two of the following unique chemical and/or physical properties:

- 1.) *Chemically inert during a chemical reaction*
- 2.) *Physical properties, e.g.*
 - *boiling point*
 - *vapour pressure*
 - *specific solvency*
- 3.) *To act as a chain transfer agent*
- 4.) *To control the desired physical properties of a process, e.g.,*
 - *molecular weight*
 - *viscosity*
- 5.) *To increase plant yield*

- 6.) *Non-flammable/non-explosive*
- 7.) *To minimise undesirable by-product formation*

Note 1: *Refrigeration, solvent cleaning, sterilisation, aerosol propellants and fire-fighting are not process agents according to this definition.*

Note 2: *Parties need not consider use of ODS for foam blowing, tobacco puffing, caffeine extraction, or fumigation because these uses are already covered in other Decisions and/or by Technical Options Committee Reports.”*

- Used as a solvent. This includes simple solvent extraction such as caffeine extraction and palm oil extraction, and cleaning applications such as metal degreasing and textile spotting. These uses should be discontinued to protect the ozone layer as well as to safeguard the health and safety of people using CTC where safer alternatives exist.
- Used in miscellaneous applications such as fire extinguishers, as grain insecticide fumigants, and as an antihelminthic agent (especially for the treatment of liver fluke in sheep).
- Used as a laboratory chemical.
- Produced inadvertently in some important industrial processes.

The distinction between these uses is not always clear cut and therefore makes it difficult to provide global data on both CTC production and consumption. Further information is required in some areas and where available will be presented in the next Report of the Aerosols, Sterilants, Miscellaneous Uses and Carbon Tetrachloride Technical Options Committee.

The main use of CTC is that of feedstock for the production of CFC-11 and CFC-12. Using 1995 data provided by the UNEP Ozone Secretariat, it is possible to extrapolate feedstock volumes of CTC from the figures that Parties reported for CFC production. Non-Article 5(1) countries declared that approximately 131,000 tonnes of CFC were produced in 1995 and Article 5(1) countries reported 107,000 tonnes of CFC production for the same year. From these figures, the TOC estimates a total CTC requirement as feedstock for CFC production of 285,000 tonnes in 1995. It can be estimated that 95 to 97% of CTC production is used in this manner. Given 1995 was the last year that Non-Article 5(1) countries were allowed normal manufacture of CFCs, the TOC believes that a substantial reduction could be expected for 1996 in Non-Article 5(1) countries.

The other major recognised use is as process agents. In its 1997 report, the Process Agent Task Force has estimated that production of carbon tetrachloride for process agent use is approximately 10,000 tonnes in Non-Article 5 and Article 5(1) countries for 1995.

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1 1997 UPDATE OF TECHNICAL AND ECONOMIC DEVELOPMENTS

At the Seventh Meeting of the Parties to the Montreal Protocol in Vienna in December 1995, the Parties requested the TEAP and its Technical Options Committees under Decision VII/34 5b(ii-iv) and 5d) to keep the Parties to the Montreal Protocol informed of any important new technical and economic developments on a year- to- year basis.

The following sections summarise the findings of the Aerosols, Sterilants, Miscellaneous Uses and CTC Technical Options Committee in March 1997.

1.1 Aerosol Products

World-wide Use of CFCs in Aerosol Products

For aerosol products, other than MDIs, there are no technical barriers to global transition to alternatives. The major issue remaining for Parties to address is the use of CFCs in Article 5(1) countries and CEIT. Some significant reductions have been achieved in recent years, and some additional reductions can be expected in the near future. The TOC believes that 1996 CFC consumption in the aerosol sector was less than 24,000 metric tonnes in Article 5(1) countries and CEIT countries excluding MDI use and some pharmaceutical products.

Comprehensive CFC consumption data for aerosol products is difficult to obtain. However the best estimate of regional break down of quantities for 1996 is as follows:

1996 CFC Consumption in non-MDI Aerosols (metric tonnes)

Russian Federation	8,600
China	7,700
Indonesia	1,500
Ukraine	1,200
Other CEIT	1,000
ASEAN and Indian Subcontinent Countries	1,700
Middle East, Africa	800
Latin America	600
Total	23,100

Since the 1996 Report, significant reductions have occurred due to the completion of two of the three large projects approved in China (Shanghai and Tianjin - the project at Guangdong is not yet completed). A large reduction in aerosol fillings in the Russian Federation was due to a new high excise tax on ethanol which is used as a solvent in aerosol products. This tax resulted in a dramatic reduction in the number of cosmetic aerosols filled, and a corresponding reduction of CFC propellant use of approximately 4,000 metric tonnes. This reduction, however, is likely to

be temporary. Additional reductions are due to ongoing phaseout projects in several countries, such as Bangladesh, Jordan, Malaysia, Sri Lanka, Thailand, Uruguay, Vietnam.

Final Phaseout

In the near-term additional phaseout of CFC consumption will result mainly from the implementation of already approved projects (especially the large China and Russian Federation projects).

The phaseout of the remaining CFCs in the aerosol sector is dependent upon the availability of hydrocarbon propellants (HAPs). Where HAP supplies were available at reasonable cost transition out of CFCs has already taken place. It is worth mentioning that HAP, being liquefied gases, cannot be transported long distances without a heavy penalty on price due to their high flammability.

Construction of suitable HAP plants under the MLF are contingent on a corresponding volume reduction in CFC production. Usually the HAP supplier is neither a CFC manufacturer nor an aerosol producer. Furthermore, there is no link between aerosol product manufacturers and CFC producers. Neither the HAP manufacturer nor the aerosol manufacturer is in a position to guarantee the reductions in CFC production that the MLF is requesting to fund HAP projects. Consequently although there are no technical barriers to transition, it is difficult to predict when final phase out in the aerosol sector will occur.

Article 5(1) and CEIT Countries

Some reduction in CFC usage has already occurred in Article 5(1) and CEIT countries. The phaseout of CFCs for aerosols in these countries is related to:

- inadequate supply of hydrocarbon propellants
- financial costs of retrofitting to handle flammable propellants
- need for technical assistance

Where the cost of CFCs is in the same range of hydrocarbon propellants there is little incentive to change. This is the case in India, ASEAN countries, and some other countries where aerosol grade HAP propellants are not available.

Hydrocarbons are the principal substitutes for CFCs used in aerosols. A HAPs plant may be a simple facility that consists of storage tanks for crude propane and butane, storage tanks for purified propane and butane, and several towers with molecular sieves; or it may be a much more complicated facility that uses the petrochemical process of hydrogenation to saturate undesired olefin molecules. The type of process required depends entirely upon the quality of feedstock available. Transport and safety equipment is also needed.

Non-availability of suitable quality hydrocarbon in many cases continues to thwart efforts to replace CFCs. Risks associated with haphazard conversions to hydrocarbons makes it obligatory for governments to develop suitable monitoring procedures to ensure safe practices including proper design, management and use of prescribed filling equipment, hydrocarbon storage and handling facilities. Indeed when considering the conversion of CFCs to hydrocarbons, the problems facing small aerosol fillers operating in congested areas in Article 5(1) countries need to be resolved.

In the Russian Federation the preferred substitute is also HAPs. In 1996 CFC use was reduced to 8,600 metric tonnes due to several factors that included a new high excise tax on the use of ethanol, continued depressed economic conditions, and some reformulation efforts to use blends of HAPs and CFCs. It is expected that in 1997 CFC use will increase above 1996 levels. Negotiations between the World Bank/GEF and the Russian Government resulted in the approval of seven projects to phaseout CFC use in the aerosol sector. Of these, six require the use of HAPs and one uses pump sprays. Since GEF funding of these projects has not become available, it is not expected that significant reductions of CFC consumption will occur before 1999. Therefore acceleration of the implementation of these approved projects becomes particularly important.

Sources of suitable HAPs must be available in Article 5(1) countries and CEIT to achieve significant conversion from CFCs and to prevent a growth in HCFC use. Financial and technical assistance must also be provided to aerosol fillers to convert to hydrocarbons. If these conditions were met, a very substantial decrease in CFC use could be achieved by the year 2000. The TOC is concerned that these conditions are not currently being met. The potential exists for continued consumption and emission in excess of 10,000 metric tonnes of CFCs in aerosol products, other than MDIs, in future years, if sources of suitable HAPs are not available to remaining users.

Estimated Future Use of HCFCs

Use of HCFCs in aerosols is prohibited in many European countries and severely restricted in the USA. In the USA only HCFC-141b is allowed as a solvent where there are no technically feasible alternatives due to health or safety considerations.

There are two possible factors that could affect the utilisation of HCFCs in aerosols. First, if electronic cleaners convert from CFC-113 to HCFC-141b it is estimated that the consumption of HCFC-141b could be between 2,000-4,000 metric tonnes per year. Formulators should be aware that HCFC-141b is a more aggressive solvent than CFC-113 and can damage some materials.

Some Russian Federation enterprises have indicated that they may use blends of HCFC-21 and HCFC-22 to reformulate products that should not be flammable. However, this use is currently not anticipated to be very large.

In Article 5(1) countries HCFCs will be limited in their use by cost considerations.

1.2 Metered Dose Inhalers

CFC-containing metered dose inhalers (MDIs) are inexpensive, reliable and effective therapy for respiratory diseases such as asthma and chronic obstructive pulmonary disease (COPD). MDIs generally use CFC-12 as a propellant and most use CFC-11 and CFC-114 either alone or in a mixture to suspend or dissolve medication.

Within the category of aerosol products, MDIs for asthma and COPD are recognised as the most difficult to substitute and have been granted essential use exemptions for the production of the CFCs required for their manufacture in Non-Article 5(1) countries.

The prevalence of asthma and chronic obstructive pulmonary disease (COPD) is increasing world-wide. There are at least 300 million people with asthma world-wide and there may be comparable numbers with COPD. Evidence now confirms that asthma prevalence is increasing as urbanisation of developing countries continues. Currently, some 500 million MDIs are used annually world-wide, using approximately 10,000 tonnes of CFC.

There is international consensus that primary treatment of these diseases should be by the inhaled route. This permits treatment to be delivered quickly and efficiently to the airways, with minimal risk of adverse reactions. Therapy necessitates regular treatment, often with more than one drug.

As a consequence of the above factors, there remains a requirement for inhaled medications such as the CFC-containing MDI.

Status of Introduction of Alternatives

Dry Powder Inhalers (DPIs) are continuing to be introduced by a number of companies into many countries. There is good evidence that the previously noted trend of increased DPI usage continues but since overall inhaled therapy has increased further, they have not reduced the sales of MDIs. Penetration of DPIs into a market depends on health professional and patient acceptance and on cost. There still remains several DPIs which are not available in some countries e.g. USA and Japan.

The figures below illustrate respectively:

- by drug category, the percentage of the MDI and DPI market shared by each device in approximately 54 Party states world-wide;
- the usage of MDIs and DPIs in treatment months from October 1995 through September 1996 in 19 Party states where inhaled therapies are most widely prescribed.

These figures have been provided by the International Pharmaceutical Aerosol Consortium (IPAC).

New Therapy (oral) Two novel oral compound (leukotriene modifiers) for the treatment of asthma have been approved by the regulatory authorities in some countries. These may be of value to a small number of those with asthma, but is highly unlikely that these will be a substitute for the current effective inhaled preventative therapy. For the reasons outlined in the 1994 Technical Options Committee Report, overall use of inhaled medication is increasing because of increased disease prevalence. World Health Organisation/US National Heart, Lung and Blood Institute (WHO/NHLBI) Guidelines in asthma management also encourage the inhaled route as the preferred method of administering medicine. The mainstay of therapy for asthma/COPD is likely to remain therapy administered by the inhaled route.

Alternative technologies, e.g. portable handheld nebulisers, are also being evaluated.

MDIs Reformulated Without CFCs

MDIs remain the dominant inhaled delivery system in most countries and for all categories of drugs. HFC-134a and HFC-227 have been approved as propellants in MDIs.

In March 1995 the first approval for a CFC-free MDI was granted to 3M's Airomir™, a salbutamol product reformulated with HFA-134a propellant. By March 1997, over thirty five countries had approved Airomir™ (Proventil™-HFA in the USA) for use, and approval was being sought in a number of additional countries.

Additional companies have submitted applications to market CFC-free inhalers in a number of countries. Approvals are anticipated in the coming year.

It is anticipated that at least two salbutamol CFC-free MDIs will be available in a number of countries by the end of 1998. Since salbutamol MDIs are estimated to comprise half the total global use of MDIs the potential exists for a significant reduction in consumption of CFCs in 1999. This is dependent on regulatory approval, reimbursement approval, patient/physician uptake, and subsequent early phaseout of CFC inhalers.

Reformulation efforts for the remaining inhaled medications is well advanced with HFC-134a and HFC-227.

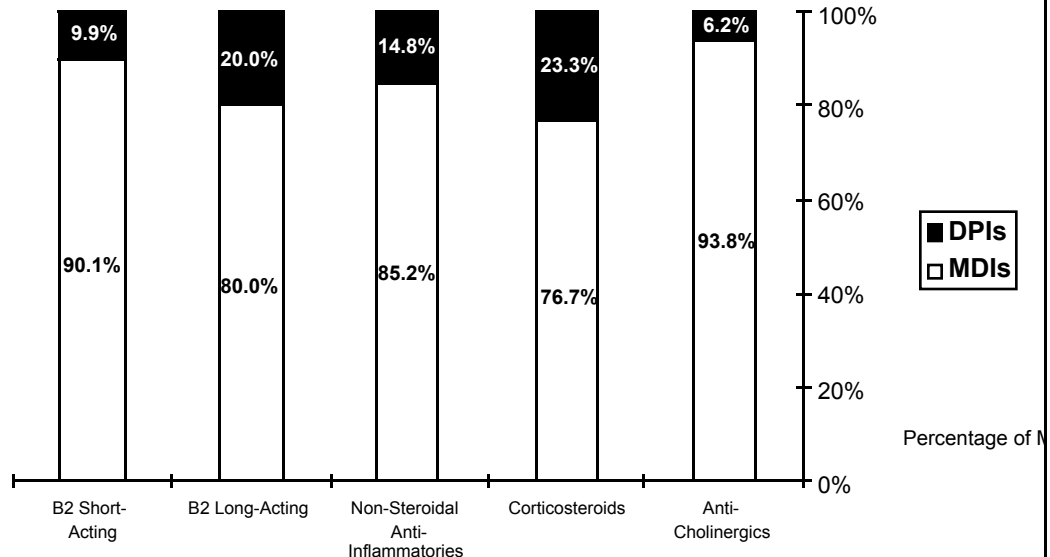
The figures below illustrate projected timetables for the first launch of HFC MDI products in the European Union (in any one member state) and for the launch of HFC MDI products in the United States from 1996 to 2005, showing a best possible scenario and a scenario with some reasonable delay (figures provided by IPAC from data collected through industry surveys undertaken during 1996). The different scenarios reflect the uncertainties of the issues described above but in either case a substantial number of reformulated CFC-free MDIs will be available in the next 5 years (note, in the figure, an "HFC MDI product" represents a single dosage of a single brand).

Education and Training

To facilitate patient and physician utilisation of the reformulated products, education and training are required. Options currently employed and planned include:

- Professional Associations - through medical journals, reports, newsletters and conferences. The TOC welcomes national initiatives such as the professional/pharmaceutical collaboration embodied in the National Asthma Education and Prevention Programme in the USA.

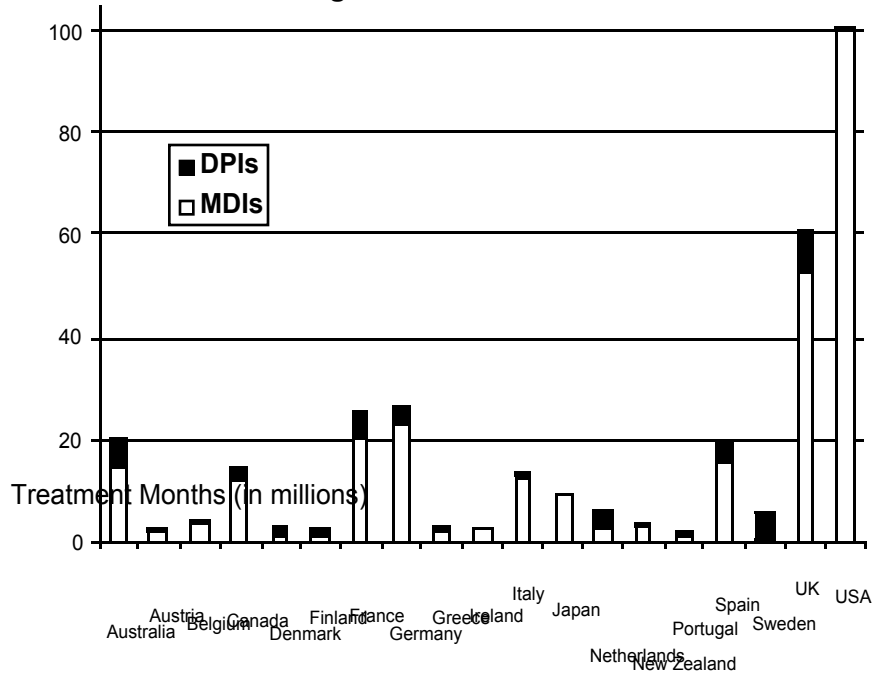
MDIs vs. DPIs by Drug Category In Approximately 54 Countries*



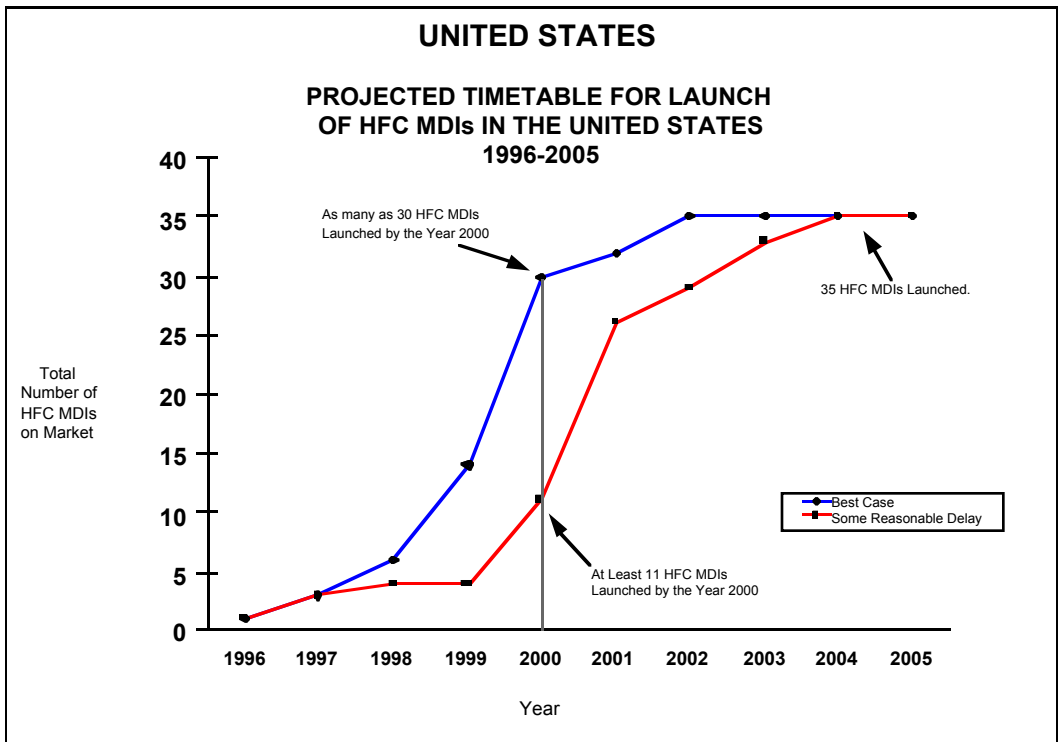
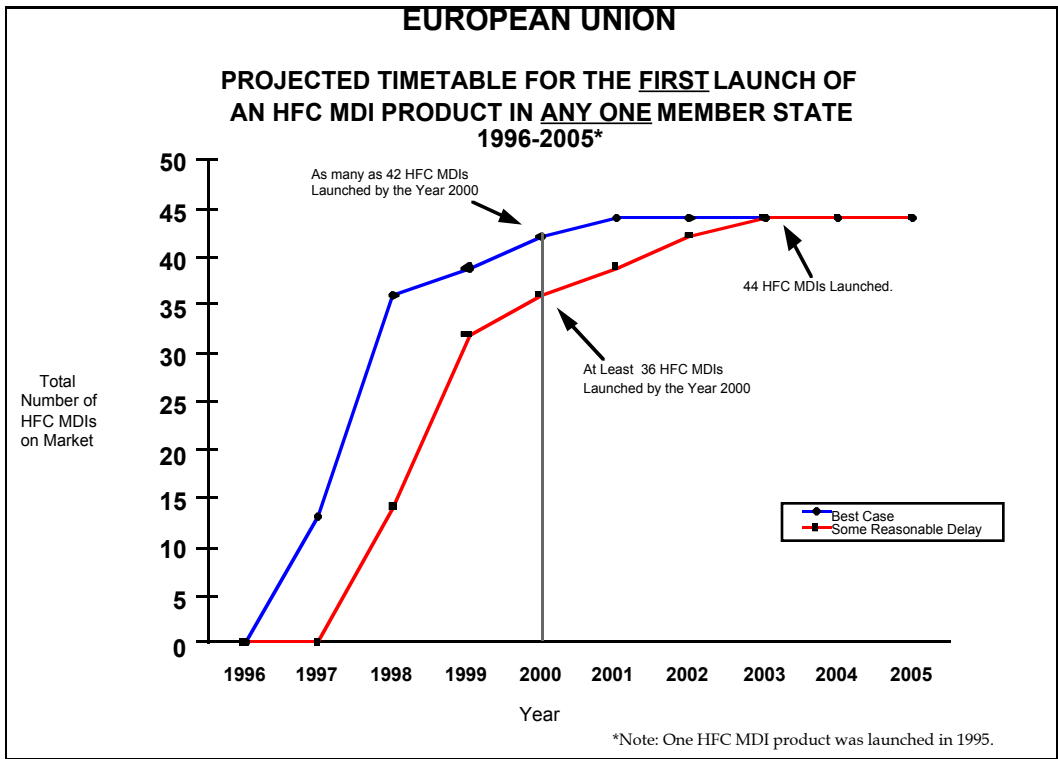
* Calculated on the basis of pack units. Please note that the number of doses in pack units may vary.

Based on IMS Market Sales Data For the Twelve Month Period Ending September 1996

MDIs vs. DPIs Usage in Treatment Months



Based on IMS Market Sales Data For the Twelve Month Period Ending September 1996



- Treatment guidelines issued by the country's medical authority which document the advantages and drawbacks of different forms of therapy and recommend specific forms of care for specific patient groups. All countries with guidelines continually review and revise their nations guidelines and many now include reference to the CFC/MDI issue. During 1995 the US National Heart Lung and Blood Institute (NHLBI) and WHO introduced a Global Initiative on Asthma (GINA). This is educationally active within Non-Article 5(1) and Article 5(1) countries and is likely to be one appropriate body through which to increase international awareness of this subject.
- Medical Symposia where international leaders in the respiratory care field gather. Here physicians, medical researchers and pharmaceutical development experts can present, discuss and evaluate the advances and latest development of alternative treatment. During 1996 many more symposia were held where alternatives and current research efforts were discussed and examples include the European Respiratory Society, the American Thoracic Society and the American Academy of Allergy and Immunology. In the US the National Asthma Education Programme is in discussion with the American Lung Association regarding increasing awareness of the CFC/MDI issue, and other initiatives are taking place elsewhere.
- Promotional Material and Media Coverage Advertising and promotional material placed in medical journals and circulated to physicians by pharmaceutical companies. Also articles in popular media promote awareness in the public of new products. There is a need for further publicity by means of television and newspapers.
- Pharmaceutical Industry Education of the medical profession, support of medical symposia, reprint of pertinent articles and reports and information sheets to patients are strategies to help to inform both professionals and the public of developments and alternatives. The International Pharmaceutical Aerosol Consortium (IPAC) developed a brochure for health professionals entitled "Moving Towards CFC-free Metered Dose Inhalers".
- Medical Literature Articles appearing in the medical journals inform professionals of developments, and several were published during 1994-1996, many written by members of the TOC.
- Support Groups which provide information, seminars and programmes aimed at both the general community and through schools, sporting groups etc., e.g. National Asthma Campaign (Australia), Asthma Society of Canada. The United Kingdom National Asthma Campaign has produced a fact sheet to help prepare patients for changeover of their inhalers.

The amount of educational activity being undertaken varies from country to country and should involve increasing awareness of DPIs as well as the reformulated MDI products. As more alternatives become available it is essential that a more active patient strategy is developed. This will involve concerted effort by the industry, and by health professional associations and national health authorities working together with patient support associations (e.g. National Asthma Campaigns and Asthma Foundations). For countries without patient support associations it is possible that the NHLBI/WHO Global Initiative (GINA) may be able to have available suitable literature for copying in the same way as they do with their current patient booklet, or add transition information to the GINA page on the Internet (<http://www.ginasthma.com>).

Professional bodies and patient associations are most likely to address this issue if governments take a lead in highlighting the importance of the subject. These educational activities are likely to cost money and responsibility and adequate funding need to be identified if a successful transition is to occur.

Increasing numbers of medical symposia are scheduled for 1997/8, culminating in a World Asthma Meeting in December 1998. This is supported by the major world respiratory organisations (European Respiratory Society, European Society for Asthma, Allergy and Immunology, American Thoracic Society, Asia-Pacific Society of Respiriology, American Academy for Asthma, Allergy and Immunology, International Union Against Tuberculosis and Infectious Disease WHO/GINA). This meeting will highlight issues surrounding the safe transition to non-CFC treatments. The TOC encourages UNEP to actively support the 1998 World Asthma Meeting.

Asthma and COPD Treatment in Article 5(1) and CEIT Markets

Prevalence of asthma fluctuates from country to country, but the condition is diagnosed world-wide. The guidelines for its treatment and management by oral inhalation are accepted by the medical community. However, cost considerations may have restricted the use of inhaled therapy. As economies expand it is expected that MDI consumption in Article 5(1) and CEIT markets will continue to grow.

Article 5(1) countries and CEIT satisfy their MDI technology needs in the following manners:

Imports as Sole Source:

Countries such as Ecuador, Tunisia and Guatemala import all MDIs. No technology transfer is necessary.

Multinational Local Production:

Countries such as China and India (Glaxo Wellcome, Astra), Indonesia (Schering Plough) Brazil (Glaxo Wellcome, Boehringer de Angelli, and others), and Mexico (Glaxo Wellcome). depend in part upon multinational companies that locally manufacture MDIs. Each company has its own technology. However, many of these countries also rely on imports to supply domestic needs for the full MDI product range.

Independent Local Production:

Companies such as Lek (Slovenia), Exacerbazi (Turkey), Micropharm (Ukraine), CIPLA (India) and SINE (China) are independent companies which have adopted CFC-based technology.

Technology Transfer to the Article 5(1) and CEIT Countries

Most intellectual property protection concerning MDIs with CFCs has expired, and this technology has been widely copied without compensation. In contrast, there is very extensive world-wide intellectual property protection in place concerning the new HFC MDIs, and it may be necessary to acquire and compensate innovators for the use of these technologies unless local producers can develop novel manufacturing technologies and formulations.

In those countries where multinational companies are already operating, adoption of CFC-free technologies should take place as soon as possible. Parties may wish to add this commitment to the Code of Conduct approved at the Eighth Meeting of the Parties to encourage phaseout of CFCs.

Independent local producers may be able to obtain the necessary technology under licensing agreements. Financial assistance to obtain this technology will be necessary. Furthermore the availability and incremental cost of the non CFC propellants and other unique components of CFC-free MDIs are to be considered.

1.3 Sterilisation

By the beginning of 1997, CFC-12 use in Non-Article 5(1) countries for 12/88 sterilant gas had virtually disappeared, as final inventories were depleted. There remain no technical barriers to the phase out of CFCs in sterilisation.

Global consumption of CFC-12 in this sector has decreased from 20,000 metric tonnes in 1991 to less than an expected 500 metric tonnes in 1997. It is anticipated that virtually all CFC-12 use in this sector will be discontinued by 1999.

HCFCs are important as transitional products in both Non-Article 5(1) and Article 5(1) countries for hospital sterilisation. The only barrier to the final conversion from CFCs to HCFCs remains cost. Where CFCs remain relatively inexpensive and there is no regulation to require conversion, there is no incentive for the final conversion from CFCs to HCFCs.

Global consumption of HCFCs in 1996 for sterilisation was 2,900 metric tonnes and estimated global consumption of HCFCs for 1997 is 3,100 metric tonnes. The projected global usage for HCFCs is expected to peak at no greater than 3,400 metric tonnes and then decline after the year 2000 as HFC replacements and new technologies replace HCFCs.

1.4 Miscellaneous Uses (including Laboratory and Analytical Uses)

Ozone-depleting substances have been used in a variety of miscellaneous uses including tobacco expansion and laboratory and analytical uses amongst others. This report evaluates the current status of use of controlled substances and alternatives and reports progress on the availability of alternatives for laboratory and analytical uses. For other miscellaneous uses there have been no further developments as to alternatives. Further information will be provided in the 1998 report of the Aerosols, Sterilants, Miscellaneous Uses and CTC Technical Options Committee.

1.5 Carbon Tetrachloride

Carbon tetrachloride (CTC) is a heavy, colourless liquid at normal temperatures and pressures (boiling point 77°C). It is non-flammable, miscible with most organic liquids and is a powerful solvent. CTC is the most toxic of the chloromethanes (10 ppm by volume in air threshold limit as a maximum safe concentration for daily 8hr exposure). It is harmful if swallowed, inhaled or absorbed through the skin and its vapour decomposes on contact with flame or very hot surfaces to give off phosgene and other toxic products. CTC vapour or mist is irritating to the skin, eyes, mucous membranes and upper respiratory tract. Exposure can cause stomach pains, vomiting, diarrhoea, nausea, dizziness and headaches, and damage to the eyes, liver and kidneys.

CTC is an easily manufactured chemical which is widely available. Because of its relevance to the ozone layer, CTC has been extensively reviewed in the Report of the Aerosols, Sterilants, Miscellaneous Uses and Carbon Tetrachloride Technical Options Committee 1994. Specific applications of CTC have been investigated by the Process Agents Working Group in 1995 and are further elaborated upon by the Process Agents Task Force (PATF) in 1997; review can also be found in the Report of the Laboratory and Analytical Uses Working Group. Inadvertent Emissions and Process Losses were discussed in the 1994 Report of the Technical and Economic Assessment Panel (TEAP).

This large number of studies reflects the multiple nature of CTC uses. To better understand the role of this chemical it is important to keep in mind that CTC can be:

- Used as a feedstock for other chemicals. In the 1997 Report of the Process Agents Task Force (PATF), feedstock is defined as:

“A controlled substance that undergoes transformation in a process in which it is converted from its original composition except for insignificant trace emissions as allowed by Decision IV/12.”

- Used as a process agent. The 1997 Report of the PATF recommends that Parties consider process agent to be defined as:

“A controlled substance that because of its unique chemical and/or physical properties, facilitates an intended chemical reaction and/or inhibits an unintended chemical reaction.

Controlled substances are typically used in chemical processes as process agents for at least two of the following unique chemical and/or physical properties:

- 1.) *Chemically inert during a chemical reaction*
- 2.) *Physical properties, e.g.*
 - *boiling point*
 - *vapour pressure*
 - *specific solvency*
- 3.) *To act as a chain transfer agent*
- 4.) *To control the desired physical properties of a process, e.g.,*
 - *molecular weight*
 - *viscosity*
- 5.) *To increase plant yield*
- 6.) *Non-flammable/non-explosive*
- 7.) *To minimise undesirable by-product formation*

Note 1: Refrigeration, solvent cleaning, sterilisation, aerosol propellants and fire-fighting are not process agents according to this definition.

Note 2: Parties need not consider use of ODS for foam blowing, tobacco puffing, caffeine extraction, or fumigation because these uses are already covered in other Decisions and/or by Technical Options Committee Reports.”

- Used as a solvent. This includes simple solvent extraction such as caffeine extraction and palm oil extraction, and cleaning applications such as metal degreasing and textile spotting. These uses should be discontinued to protect the ozone layer as well as to safeguard the health and safety of people using CTC where safer alternatives exist.
- Used in miscellaneous applications such as fire extinguishers, as grain insecticide fumigants, and as an antihelminthic agent (especially for the treatment of liver fluke in sheep).
- Used as a laboratory chemical.
- Produced inadvertently in some important industrial processes.

The distinction between these uses is not always clear cut and therefore makes it difficult to provide global data on both CTC production and consumption. Further information is required in some areas and where available will be presented in the next Report of the Aerosols, Sterilants, Miscellaneous Uses and Carbon Tetrachloride Technical Options Committee.

The remainder of this progress report will cover feedstock, solvent, miscellaneous and laboratory uses. The role of CTC as a process agent has already been studied extensively in the 1997 PATF Report.

Recent atmospheric measurements have demonstrated that the atmospheric levels of carbon tetrachloride are falling (Simmonds *et al.*, *Atmospheric Environment*, 30 (23), pp 4041-4063, 1996). There are a number of possible reasons for this reduction:

- Reduction in the use of CTC as a feedstock to produce CFC-11 and CFC-12 in Non-Article 5(1) countries and CEITs resulting in a reduction in emissions during the manufacturing processes.
- Improvements in containment technologies in process agent applications in Article 2 countries.
- Reductions in the use of CTC in process agent and other applications in CEITs.

These reductions could be partially offset by increased use and emissions of CTC in some Article 5(1) countries. However, the TOC believes that the degree of CTC emissions varies significantly from country to country depending on the type of process, use and emission control techniques.

CTC Production and Consumption

CTC is normally produced by the high temperature chlorination of propylene or methanes, known as chlorinolysis. Other starting materials have been used. Most production facilities to manufacture CTC alone have closed in Non-Article 5(1) countries. Some facilities can produce CTC and perchlorethylene as joint products - these latter facilities can usually be tuned to produce either 100% perchlorethylene or 100% CTC by recycling within the plant.

The global production data for CTC are hard to obtain and difficult to interpret due to the dual nature of CTC as a feedstock and as a final product. It is possible to estimate the total CTC production for CFC production by using the following formula:

$$\text{CFC-11 produced} \times 1.14^* = \text{CTC consumed}$$

$$\text{CFC-12 produced} \times 1.30^* = \text{CTC consumed}$$

(*) These figures are average values and for guidance only

By using data provided by the Alternative Fluorocarbon Environmental Acceptability Study (AFEAS) Production, Sales and Atmospheric Release of Fluorocarbons through 1995, Alternative Fluorocarbons Environmental Acceptability Study 1997, it is possible to make the following estimates (in tonnes).

Production of CTC as feedstock for CFC manufacture (metric tonnes)

Year	CTC	CFC-11	CTC	CFC-12	Total CTC
1993	167,729	147,131	279,063	214,664	446,792
1994	68,665	60,232	173,680	133,600	242,345
1995	37,259	32,683	107,669	82,822	144,928

The AFEAS data includes production in all Non-Article 5(1) countries, plus their subsidiaries in Article 5(1) countries, and exclude CEIT countries. Traditionally, AFEAS data have not included countries such as the CEIT countries, India and China. However, unofficial data for the Russian Federation indicates that in 1995 31,082 tonnes of CTC were manufactured and 28,596 were used as feedstock, the remainder being exported. Figures for 1996 indicate a 40% reduction in CTC manufacture for the Russian Federation from 1995. The only other country of the former USSR which produced CTC in the last 2 years was the Ukraine which manufactured about 9,000 metric tonnes. In 1995, China used as feedstock 52,400 tonnes of CTC of which 30,500 tonnes were produced domestically. Other non-feedstock uses in China amounted to 459 metric tonnes. For India, it is estimated that an additional 25,000 tonnes of CTC were used for CFC manufacture in 1995. From this data it can be estimated that approximately 240,000 metric tonnes of CTC were produced for the manufacture of CFCs in 1995.

Using 1995 data provided by the UNEP Ozone Secretariat, it is possible to extrapolate feedstock volumes of CTC from the figures that Parties reported for CFC production. Non-Article 5(1) countries declared that approximately 131,000 tonnes of CFC were produced in 1995 and Article 5(1) countries reported 107,000 tonnes of CFC production for the same year. From these figures, the TOC estimates a total CTC requirement for CFC production of 285,000 tonnes in 1995. This latter figure is approximately 20% higher than the figure calculated from the AFEAS and other data presented above and probably reflects the absence of data for some countries that do not report to AFEAS. Given 1995 was the last year that Non-Article 5(1) countries were allowed normal manufacture of CFCs, the TOC believes that a substantial reduction could be expected for 1996 in Non-Article 5(1) countries.

The main use of CTC is that of feedstock for the production of CFC-11 and CFC-12. It can be estimated that about 95% of CTC production is used in this manner. The other major recognised use is as process agents. In its 1997 report, the Process Agent Task Force has estimated that production of carbon tetrachloride for process agent use is approximately 10,000 tonnes in Non-Article 5 and Article 5(1) countries for 1995.

Other uses of CTC, such as metal and textile cleaning and fumigants have been described in previous reports of the Aerosols, Sterilants, Miscellaneous Uses and Carbon Tetrachloride Technical Options Committee (1991, 1994). Alternatives already exist for the majority of these uses, and are widely available as discussed in the 1994 UNEP Solvents, Coatings and Adhesives Technical Options Report. The TOC will investigate these other uses of CTC in more detail for its 1998 report.

2 PROGRESS REPORT ON ISSUES SURROUNDING A TRANSITION TO NON-CFC TREATMENTS FOR ASTHMA AND COPD AND NATIONAL TRANSITION STRATEGIES

2.1 Predicted Global Schedule

The schedule for the safe introduction of new propellants and reformulated products suggested in the 1994 report and updated in the 1996 report of the Aerosols TOC remains on target.

One reformulated salbutamol product has been on the market for 2 years and is now available in more than 35 countries. Some further reformulated products containing the most commonly used drug entities have been submitted for approval by regulatory authorities in some countries. It remains possible that the major part of transition in most developed nations may have occurred by the year 2000 and minimal need for CFCs for MDIs is envisaged by the year 2005.

However, at this point in time there are still many variables and an exact time scale is not possible to predict with certainty.

2.2 TOC Consultation Process

The TOC is consulting widely with representatives of the asthma/COPD community and has contact with the following organisations:

- Global Initiative on Asthma (NHLBI/WHO Initiative)
- American Thoracic Society/American Lung Association
- European Respiratory Society
- American Academy of Allergy, Asthma and Immunology
- National Asthma Education and Prevention Programme (USA)
- National Asthma Campaign (UK)
- National Asthma Campaign (Australia)
- many health and environment regulatory authorities and patient support groups
- IPAC, MDI manufacturers and bulk CFC manufacturers
- Friends of the Earth.

The TOC will continue consultation with these and other groups as the process evolves.

2.3 How a Global Framework and National Strategies Might be Complementary

The TOC believes that it is still too early to craft a global framework and it is not currently possible to make accurate predictions on the introduction of non-CFC alternatives. For example IPAC has predicted that as few as 11 and as many as 30 HFC MDI entities will be reformulated and launched by the year 2000 in the USA. In Europe the corresponding figures range from 36 to 42. This estimate may differ between countries.

The TOC recognises that no single strategy will be applicable to all countries. The process of transition to non-CFC alternatives is complex involving the need for dialogue between health authorities, environmental agencies and other interested groups.

A number of factors need to be evaluated in detail and individual parties may wish to consider the following preliminary points when developing national strategies for CFC phaseout.

- Sufficient technically and economically feasible alternatives are available to assure an uninterrupted supply of medications in that country.
- One or more separate formulations of the same therapeutic substances need to be available.
- Sufficient post marketing surveillance of the reformulated products.
- Sufficient choice to assure that patient sub groups are served by alternatives.
- Sufficient time and resources are available for health professional and patient education.
- The legal and economic framework in that country
- The level of company commitment to reformulation (consistent with Decision VIII/10)

The TOC congratulates the USA for the development of a proposed strategy and Australia for its interim report of a proposed strategy for phaseout at the national level (copies of which are included in Appendix 1). The TOC recognises that other Parties may feel that different strategies better fit their needs. The TOC has given preliminary examples of possible national strategies that Parties may wish to consider when they study their particular situation. It should be stressed that these are examples and are in no way fully exclusive.

Parties are encouraged to submit details of national policies for consideration by the TOC to facilitate policy sharing and to gain a better understanding of issues in different Parties involved with transition.

2.4 Implications of Different Policy Options for the Transition

The TOC has considered a variety of approaches that an individual Article 2 country might take to facilitate the transition from CFC MDIs (see below). The TOC considered these approaches and some of the possible advantages and disadvantages. These approaches are not meant to be comprehensive nor prescriptive. The TOC has simply tried to reflect some of the considerations that a national authority might make in crafting its own national transition strategy in the light of its own national circumstances. It has to be kept in mind that license withdrawal may necessitate local change to drug approval legislation.

In order to explain some of these strategies it needs to be understood that there are several types of drugs used in the treatment of asthma and COPD. These types of drugs can be grouped into categories as shown below. The number of drugs in each category will vary from country to country depending on domestic availability of products. Drug categories are as follows:

- A. Short acting beta agonist bronchodilators
eg. salbutamol (albuterol in USA) terbutaline, fenoterol
- B. Inhaled Steroids
eg. beclomethasone, budesonide, flunisolide, fluticasone, triamcinolone
- C. Non Steroidal anti-inflammatories
eg. cromoglycate, nedocromil
- D. Anticholinergic bronchodilators
eg. ipratropium bromide/combinations
- E. Long acting beta agonists bronchodilators
eg. salmeterol, eformoterol
- F. Other combinations

It is important to realise that on a global basis categories A and B combined account for approximately 75% of CFC MDIs

Policy Options

The four approaches listed below are not mutually exclusive and could be combined.

1) By Individual Product Brand (Brand by Brand)

When a company produces a new reformulated product which replaces its existing product, it would be required to introduce the new product and phase out the old over a time scale consistent with production process, distribution and a reasonable post marketing surveillance period if necessary.

The advantages of this approach might include :

- Maintenance of physician/patient choice through brand continuity ,
- Minimal market disruption
- Reduced need for patient and health professional education.

The disadvantages of this approach might include:

- It does not address the issue of products which are not reformulated
- Does not consider non MDIs as alternatives
- No incentive for changeover unless linked with some form of “target and timetable”.

2) By Individual Drug Compound (Drug by Drug)

After a new reformulated CFC-free MDI containing a given drug (eg. salbutamol) is launched and a period of post marketing surveillance undertaken , licenses for the sale of any CFC MDIs containing that drug will be withdrawn. after a given period.

The advantages of this approach might include:

- Maintenance of physician/patient choice through drug continuity
- Provides fast removal of CFC MDIs provided the withdrawal period is reasonably short
- Rewards the innovating company.

The disadvantages of this approach might include:

- The patient population may be better served by waiting until at least two CFC free MDIs are available to cover the unlikely event of product failure
- Physicians and patients have potentially no choice of brands and major brand switching will be necessary with consequent market disruption and the potential creation of monopolies
- In drug categories A and B , some drugs may never be reformulated for technical or economic reasons. No incentive for changeover unless linked with some form of “target and timetable.”

3) Category by Category Transition

For each category of drugs A-F, when sufficient CFC alternatives become available in that drug category , the remaining CFC containing products in that category can be phased out within a specified time. (“Sufficient” to be defined and determined by each Party).

The advantages and disadvantages of this approach will depend on the numbers of alternatives determined for safe transition for that category in each country.

The advantages of this approach might include:

- tailoring the policy to individual national needs
- with limited alternatives in a category, fast transition is possible

- with many alternatives in a category patient safety would be maintained

The disadvantages might include:

- CFC-free alternatives may not be available for all drugs in a category before they are phased out
- with limited alternatives in a category patient safety might be compromised
- with too many alternatives in a category transition would be slow.

4) Targets and Timetables

Another strategy might involve setting targets for CFC reduction to zero over a fixed time. Such a strategy should take into account both health and safety issues and provision of a reasonable time frame for CFC withdrawal as and when non-CFC alternatives become available.

A health and safety determined time frame might be based on estimates of expected introduction of CFC MDI alternatives. This estimated timetable might be monitored annually with deviations requiring justification.

Possible advantages of such an approach might be:

- flexibility based primarily on health and safety issues
- co-operative and less prescriptive framework
- permits considerable choice of therapies

Possible disadvantages of this approach might be:

- limited incentive for transition
- that it requires detailed reporting by manufacturers of export and local markets
- that it requires annual adjustment should consumption not reflect forecasts

An alternative strategy might be an arbitrarily set timetable which limits total volumes of CFC MDI production on a year by year basis eg. annual 10% target reductions from 1998 volumes.

Possible advantages of this approach might be:

- rigorous timetable for CFC withdrawal
- rewards innovative manufacturers

Possible disadvantages of this approach might be:

- that it does not allow for unpredicted health and safety issues

- would be difficult to allocate bulk product to individual manufacturers
- that it does not take into consideration unexpected delays in supply of alternatives to CFC MDIs

2.5 Implications of Transferable Essential Use Exemptions and Trade Restrictions on the Transition and Access to Treatment Options

The TOC believes that transfer of essential use exemptions between Parties will facilitate the transition and patient access to treatment options. As transition proceeds MDI manufacturers may choose to rationalise production for economic, technical and logistical reasons. Flexibility in the transfer of rights between Parties will facilitate the transition with no net environmental impact (as discussed in section 3.1).

Under the Montreal Protocol, there is no restriction on movement of finished goods, i.e. manufactured MDIs. The Parties should note that if individual countries develop export bans for CFC MDIs they could disrupt access to treatment options in importing countries. This could impact on national transition strategies.

2.6 International Markets and Fluidity of Trade in CFC MDIs and their Alternatives

CFC MDIs are an internationally traded product which are controlled through product licenses. It is anticipated that once the transition has occurred then CFC alternative treatments will be similarly traded.

Once transition has taken place in a Party, there is potential for imports of CFC containing products from another Party. However, in a number of countries this will be controlled through existing regulations on the import of therapeutic goods and product license approvals.

2.7 Incentives and Impediments to R & D and Market Penetration of Alternatives

The world market for inhaled products is several billion US dollars and is continuing to grow. This provides a clear incentive to develop replacements. The reformulation of CFC MDIs to replace the propellants with a non-CFC began in 1988 and has proved to be much more technically difficult than was originally envisaged. Over 90 laboratories in at least 10 countries are involved in reformulation efforts with a total estimated cost to date of almost US\$1 billion.

There are differences between the CFC and HFC MDIs which have resulted in the need for extensive clinical investigations and revision of long-standing manufacturing methods. In addition the regulatory hurdles for approval of HFC products in some countries may be significantly higher than for the approval of CFC MDIs.

There are over 80 patents or patent applications in the area of CFC-free MDI technologies which could be either an incentive or impediment to R & D. However, at least one company is making its technology available to other companies.

Since salbutamol MDIs are estimated to comprise half the total global use of MDIs the potential exists to significantly reduce consumption of CFCs. 3M's experience in the UK is salutary. Six months after the new MDI was introduced in the UK, usage was less than 1% of all salbutamol MDIs, despite an extensive marketing and educational programme which resulted in at least 50% product awareness in UK physicians. Almost two years after this introduction it had only reached 1.5% market share. It is too early at this stage to comment on market penetration in the US.

Factors influencing uptake of this non-CFC product include: lack of incremental benefit to patients, apathy of physicians to environmental benefits and higher cost than generic CFC salbutamol products. It is important to note that the lack of motivation to physician prescribing and economic considerations makes it unlikely that marketing and education programmes alone will produce a significant switch away from CFC products in the absence of clearly defined and implemented national transition policies.

2.8 The Degree to which DPIs and Other Alternatives May be Considered Medically Acceptable and Affordable Alternatives

Dry Powder Inhalers (DPIs) are now available from a number of companies in many countries and the introduction of new DPIs is foreseen in further countries in the coming year. There is good evidence that the previously noted trend of increased DPI usage continues, although the rate of increase in use and penetration differs from country to country. Only in a few countries have DPIs yet achieved a significant market share (see also Figures in Section 1.2).

Main factors that influence the use of DPIs as alternatives to MDIs include:

- not all substances or substance classes are available as DPIs,
- not all available DPIs are introduced in all countries,
- the currently considerably higher cost in comparison to MDIs in some countries,
- DPIs are not suitable or effective for all age groups, eg. children or some elderly, due to dependence on inspiratory flow rate,
- lack of awareness by physicians and patients of potential benefits of DPIs.

Further, to the above, no other currently available inhalation systems are considered practical alternatives to MDIs. However, the TOC notes with interest that a number of portable, hand-held nebulisers, and similar systems are under development. These may be potential future alternatives to MDIs and DPIs.

Two novel oral compounds (leukotriene modifiers) are unlikely to substitute for current effective inhaled preventative therapy in a large number of asthma patients. For the reasons outlined in the 1994 Technical Options Committee, overall use of inhaled medication is increasingly because of increased disease prevalence. Indeed, the WHO/NHBLI Guidelines on asthma management encourage the inhaled route as the preferred method of administering medication. Thus, the mainstay of therapy for asthma and COPD is likely to remain therapy administered by the inhaled route.

2.9 Implications for Importing Countries of the Transition and Reductions in Essential Use CFC Production

Once transition has occurred in countries which manufacture CFC MDIs for export, some essential use supplies for CFCs will be required to continue manufacture for export to importing countries. This supply will need to be continued until importing countries have completed transition to non-CFC alternatives, or until alternative sources of supply can be secured. It is particularly important that CFC allowances be available for manufacture of CFC MDIs for export to Article 5(1) countries, for Countries with Economies in Transition and Article 2 countries with large disadvantaged communities, until non-CFC MDI alternatives become available in these countries. Otherwise the supply of MDIs will be interrupted, posing risks for patient care.

There has been concern that there will be a significant potential cost differential of non-CFC alternatives from their CFC predecessors. Experience with HFC products already marketed has indicated that this is not significantly different from that of its branded CFC counterpart. This may not be the case with respect to generic MDIs.

The TOC believes that importing nations should not rely on the expectation of continued supply of CFC MDIs but rather should try to expedite their own transition by importing CFC-free alternatives.

The TOC notes that there is substantial manufacturing capacity for CFC MDIs in Article 5(1) countries (in the range of approximately 1000 to 2000 tonnes of CFCs per annum. The TOC will investigate this more thoroughly in 1998 but encourages Parties to provide data to enable this reporting.

2.10 Steps to Facilitate Access to Affordable non-CFC Treatment Options and Technology

As previously noted in this report, the TOC recognises that the transition to non-CFC treatment options may carry a financial burden for many countries and health authorities. Non-CFC MDIs are likely to be introduced at a price similar to existing CFC branded products, but this may be higher than available CFC generics. Transition may, therefore, carry a financial burden for many countries and health authorities. Parties should be prepared to plan budgets and to direct regulatory authorities to review the terms for public procurement and reimbursement so that purchasing policies support appropriate use of non-CFC alternatives.

A second economic consideration is that of the possible inability of some companies to reformulate existing CFC products. To maintain continuity of product supply these companies will need to license such technology from the originating company or acquire the finished product.

2.11 Implications for Patient Sub-Groups with Compelling Medical Needs

Some CFC MDIs are used by distinct patient subgroups such as the elderly. Some niche MDIs are relied upon by some patients although consumption may be relatively small and declining. Reformulation into CFC-free versions of such products is unlikely to be commercially viable or technically possible.

Continuing supplies of CFC-containing MDIs in asthma/COPD may be perceived as necessary for two reasons:

- The efficacy of current alternative products and devices is generally comparable to CFC containing MDIs. However, some patients may have a personal preference for CFC MDIs. This matter is likely to be overcome by educational endeavours and should not be the basis for an essential use nomination.
- Severe side effects from alternative products or devices. In some cases there may be side-effects from alternative products or devices. This will be offset by having an adequate range of alternatives available before CFC MDI withdrawal.

In consultation with interested Parties, the TOC will monitor the continuing medical needs of particular patient subgroups.

3 EVALUATION OF STATUS OF USE OF ODS AND ALTERNATIVES FOR LABORATORY AND ANALYTICAL USES

At their Seventh Meeting, the Parties to the Montreal Protocol requested the Technology and Economic Assessment Panel and its Technical Options Committees to evaluate the current status of use of controlled substances and alternatives and report progress on the availability of alternatives for Laboratory and Analytical Uses.

There is little reported information on the use of controlled substances for analytical and laboratory uses. A number of Parties have adopted licensing systems in order to manage supplies into these applications. These systems generally license supplies to the distributors of controlled substances into the laboratory and analytical sector but do not register the many of thousands of small users in this sector probably due to its impracticality.

The European Commission has published the quantities of controlled substances that it has licensed in 1995 and 1996 in its Official Journal. These data give an indication of the levels requested by the distributors but do not demonstrate the actual levels used. In a number of cases distributors may be building stocks for future sales or have not actually purchased controlled substances against their licences due to a lack of demand in the sector.

Licences issued by the European Commission for Laboratory and Analytical Uses

	1995			1996		
	Controlled Substance			Controlled Substance		
	CTC	CFC	111-TRI	CTC	CFC	111-TRI
No. of companies	34	35	*	21	27	15
Quantity (metric tonnes)		245.3	*	233.95	207.25	104.5

* 1,1,1-Trichloroethane was not controlled for laboratory uses in 1995.

Other data

Although data are not available for other Article 2 countries it can be estimated that use for laboratory and analytical uses in the USA and Japan are unlikely to exceed those used in Europe. It can be estimated that the total global use of controlled substances for these applications will not exceed a maximum of 3,000 metric tonnes.

Recommendations

Parties may wish to consider the issue of the exemption for laboratory and analytical uses at their 9th Meeting in 1997. The global exemption expires at the end of 1997, and little progress has been made toward eliminating this use.

There are four main options that could be considered:

- 1) To not allow a further global essential use exemption for laboratory and analytical uses.
- 2) To not allow a further global exemption for laboratory and analytical uses but request Parties to submit detailed applications for individual use through the annual essential use process. These would then be assessed by the Technology and Economic Assessment Panel and its relevant Technical Options Committee.
- 3) To permit a further global essential use exemption for laboratory and analytical uses for a specified number of years.
- 4) To permit a further global exemption for essential use for laboratory and analytical uses for a specified number of years and encourage Parties, through their National Ozone Programmes, to set reduction targets and timetables for the use of controlled substances in laboratory or analytical uses.

Some of the advantages and disadvantages of the above options are as follows:

Option 1:

The major advantage of this option is that it would minimise emissions to the environment of controlled substances from laboratory and analytical uses.

The major disadvantage is that it could seriously disrupt analysis and research and development in many thousands of laboratories world-wide which are dependent on these substances. The effects would be rapid and the users would have little notice of the change to adapt their standards and procedures where this would be possible. This might lead to:

- lack of uniformity in methods of analysis being developed throughout the world
- consequent increases in costs to industry in complying with different analytical methods that may develop as a result of rapid restrictions.

Option 2

The Parties have already determined the essential uses for 1998 and will determine those for 1999 at the 9th Meeting in Montreal in September 1997. If Parties chose to require specific essential use nominations for these uses, in order to obtain an essential use exemption for laboratory and analytical uses and given the time that would likely be needed by Parties to collect the necessary information, the Parties would be submitting their applications during late 1998/early 1999 for a Decision at the Meeting of the Parties in 1999 for the year 2000. This approach would put an enormous workload on the Parties, TEAP and its TOCs.

Option 3

The advantage of continuing the global exemption would be continuity in the use for laboratories and research establishments where awareness of a phase out is low. The disadvantage of a continued global exemption would be the perception that uncontrolled use would continue and there would be no incentive to encourage the research, development and adoption of alternatives.

Option 4

As discussed in option 3 above the continuation of the global exemption for a specified number of years would allow continuity in use in areas where awareness of a phase out is low. By encouraging targets and timetables for phase-down of uses this would send a signal that the exemption is finite and thereby encourage the research, development and adoption of alternatives with the consequential change in national and international standards. Once these alternatives have been adopted in international standards the previous use of ODS could be eliminated.

The disadvantage of this option would be the possibility that some Parties would adopt more progressive restrictions causing:

- lack of uniformity in methods of analysis being developed throughout the world
- consequent increases in costs to industry in complying with different analytical methods that may develop as a result of rapid restrictions.

Having reviewed the above options, the TOC recommends that the Parties grant a further two year global exemption for the use of controlled substances for laboratory and analytical uses. Furthermore, it is recommended that Parties are encouraged to adopt within their National Ozone Programmes measures designed to reduce these uses.

The TOC also reiterates the importance of:

- organising National Consultative Committees to review and identify alternatives to laboratory and analytical uses and encouraging the sharing of information concerning alternatives and their wider use
- encouraging national standards organisations to identify and review those standards which mandate the use of ODS in order to move to ODS-free alternatives
- developing an international labelling scheme
- reporting data annually under a global essential use exemption framework which allows Parties to monitor the success of reduction strategies, and investigating and reporting published instructions, standards, specifications and regulations requiring the use of ODS.

APPENDIX 1

NATIONAL TRANSITION STRATEGIES FOR MDIs

(A) PROPOSED UNITED STATES

Taken from US Government Printing Office Home Page <http://www.access.gpo.gov/index.htm>, also available at FDA Home Page <http://www.fda.cder.gov>.

[Federal Register: March 6, 1997 (Volume 62, Number 44)]

[Proposed Rules]

[Page 10242-10247]

From the Federal Register Online via GPO Access [wais.access.gpo.gov]

[DOCID:fr06mr97-24]

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DEPARTMENT OF HEALTH AND HUMAN SERVICES

Food and Drug Administration

21 CFR Part 2

[Docket No. 97N-0023]

RIN 0910-AA99

Chlorofluorocarbon Propellants in Self-Pressurised Containers;
Determinations That Uses Are No Longer Essential; Request for Comments

AGENCY: Food and Drug Administration, HHS.

ACTION: Advance notice of proposed rulemaking.

SUMMARY: The Food and Drug Administration (FDA) is seeking public comment on the policy it is considering for adoption on making and implementing determinations that uses of chlorofluorocarbons (CFC's) currently designated essential will no longer be deemed essential under the Clean Air Act due to the availability of safe and effective medical product technology that does not use CFC's. Essential-use products are exempt from FDA's ban on the use of CFC propellants in FDA-regulated products and the Environmental Protection Agency's (EPA's) ban on the use of CFC's in pressurised dispensers. The agency is taking this action because it is responsible for determining which products containing CFC's or other ozone-depleting

substances are an essential use under the Clean Air Act. FDA is soliciting comments on this policy to assist the agency in striking an appropriate balance that will best protect the public health, both by ensuring the availability of an adequate number of treatment alternatives and by curtailing the release of ozone-depleting substances.

DATES: Written comments by May 5, 1997.

ADDRESSES: Submit written comments to the Dockets Management Branch (HFA-305), Food and Drug Administration, 12420 Parklawn Dr., rm. 1-23, Rockville, MD 20857.

FOR FURTHER INFORMATION CONTACT: Wayne H. Mitchell, Center for Drug Evaluation and Research (HFD-7), Food and Drug Administration, 7500 Standish Pl., Rockville, MD 20855, 301-594-2041.

SUPPLEMENTARY INFORMATION:

I. Background

Under Sec. 2.125 (21 CFR 2.125), any food, drug, device, or cosmetic in a self-pressurised container that contains a CFC propellant for a nonessential use is adulterated, or misbranded, or both, under the Federal Food, Drug, and Cosmetic Act. This prohibition is based on scientific research indicating that CFC's reduce the amount of ozone in the stratosphere and thereby increase the amount of ultraviolet radiation reaching the earth. An increase in ultraviolet radiation will increase the incidence of skin cancer, and produce other adverse effects of unknown magnitude on humans, animals, and plants. Section 2.125(d) exempts from the adulteration and misbranding provisions of Sec. 2.125(c) certain products containing CFC propellants that FDA determines provide unique health benefits that would not be available without the use of a CFC.

These products are referred to in the regulation as essential uses of CFC's and are listed in Sec. 2.125(e). Under Sec. 2.125(f), any person may petition FDA to request additions to the list of uses considered essential. To demonstrate that the use of a CFC is essential, the petition must be supported by an adequate showing that: (1) There are no technically feasible alternatives to the use of a CFC in the product; (2) the product provides a substantial health, environmental, or other public benefit that would not be obtainable without the use of the CFC; and (3) the use does not involve a significant release of CFC's into the atmosphere or, if it does, the release is warranted by the consequence if the use were not permitted.

EPA regulations implementing the provisions of section 610 of the Clean Air Act (42 U.S.C. 7671i) contain a general ban on the use of CFC's in pressurised dispensers, such as metered-dose inhalers (MDI's) (40 CFR 82.64(c) and 82.66(d)). These EPA regulations exempt from the general ban "medical devices" that FDA considers essential and that are listed in Sec. 2.125(e). Section 601(8) of the Clean Air Act (42 U.S.C. 7671(8)) defines "medical device" as any device (as defined in the Federal Food, Drug, and Cosmetic Act), diagnostic product, drug (as defined in the Federal Food, Drug, and Cosmetic Act), and drug delivery system, if such device, product, drug, or drug delivery system uses a class I or class II ozone-depleting substance for which no safe and effective alternative has been developed (and, where necessary, approved by the Commissioner of Food and Drugs (the Commissioner)); and if such device, product, drug, or drug delivery system has, after notice and opportunity for public comment, been approved and determined to be essential by the Commissioner in consultation with the Administrator of EPA (the Administrator). Class I substances include CFC's, halons, carbon tetrachloride, methyl chloroform, methyl bromide, and other chemicals not relevant to this document (see 40 CFR part

82, appendix A to subpart A). Class II substances include hydrochlorofluorocarbons (HCFC's) (see 40 CFR part 82, appendix B to subpart A).

Production of ozone-depleting substances is being phased out world-wide under the terms of the Montreal Protocol on Substances that Deplete the Ozone Layer (Montreal Protocol), Sept. 16, 1987, S. Treaty Doc. No. 10, 100th Cong., 1st sess., 26 I.L.M. 1541 (1987). In accordance with the provisions of the Montreal Protocol, under authority of Title VI of the Clean Air Act (section 601 *et seq.*), manufacture of CFC's in the United States was generally banned as of January 1, 1996. To receive permission to manufacture CFC's in the United States after the phaseout date, manufacturers must obtain an exemption from the phaseout requirements from the Parties to the Montreal Protocol. Procedures for securing an essential-use exemption under the Montreal Protocol are described in the most recent request by EPA for applications for exemptions (60 FR 54349, October 23, 1995). Firms that wish to use CFC's manufactured after the phaseout date in medical devices (as defined in section 601(8) of the Clean Air Act) covered under section 610 of the Clean Air Act must receive exemptions for essential uses under the Montreal Protocol.

Faced with the statutorily mandated phaseout of the production of CFC's, drug manufacturers are developing or have developed alternatives to MDI's and other self-pressurised drug dosage forms that do not contain ozone-depleting substances. Examples of these alternative dosage forms are MDI's that use such non-ozone-depleting substances as propellants and dry-powder inhalers (DPI's). FDA has recently approved the first CFC-free MDI, 3M Pharmaceuticals Inc.'s albuterol sulfate product, Proventil<Register> HFA; although a determination has not yet been made on whether this product is a technically feasible alternative to the use of CFC's, this approval gives the subject matter of this advance notice of proposed rulemaking (ANPRM) a particular timeliness. The current or future availability of "technically feasible alternatives to the use of a [CFC]" may mean that the existing listing of a use in Sec. 2.125(e) would no longer reflect current conditions. It is with this situation in mind that FDA is publishing this ANPRM regarding agency determinations that certain uses of ozone-depleting substances are no longer essential.

FDA has determined that it would be most productive to set out the following tentative policy on the elimination of essential uses in an ANPRM. The agency believes that providing an opportunity for the fullest public participation at the earliest possible stage in the agency decision-making process in this matter is appropriate to assist FDA in striking an appropriate balance that will best protect the public health, both by ensuring the availability of an adequate number of treatment alternatives and by curtailing the release of ozone-depleting substances. In striking this balance, FDA intends to assess a number of factors and is interested in public comment on them. In establishing its policy on the elimination of essential uses, FDA will assess the potential beneficial effects of reducing CFC emissions from drug products broadly, based on the amount of CFC emissions that would be avoided, the stratospheric ozone depletion that would be averted, and the resulting decline in incidence of UV-B-related adverse human health effects, including human cancers and cataracts. FDA will also assess the beneficial public health effects of continued availability of CFC-containing drug products broadly, based on the availability, safety, and efficacy of alternatives, in full consideration of differences in patients' medical circumstances, physiological sensitivity, and acceptability of use, among others. FDA is specifically soliciting comments on how it should develop information to assist in striking this balance and how it should further balance the need for timely action. FDA also believes that there is adequate time to publish an ANPRM and respond to comments but will endeavour to complete this rulemaking process in a timely fashion. Because the first potential technically feasible alternatives are just now coming on the market, it will take a significant amount of time for manufacturers to collect and present the post-marketing safety and patient acceptance data that the agency will need to determine if the products are, in fact, technically feasible alternatives (see section II.B. of this document).

II. Proposed Policy

FDA has tentatively determined that certain uses of CFC's, listed in Sec. 2.125(e) as essential, can no longer be considered to be essential. FDA is considering proposing to remove these uses from the list of essential uses in a rulemaking to be initiated soon. Uses no longer considered essential are discussed in section II.A. of this document. FDA also expects that certain uses still considered to be essential will cease to be considered essential as new technology develops. Section II.B. of this document describes the policy that FDA has tentatively determined will be used in making determinations that these uses of CFC's are no longer essential. FDA has worked closely with EPA in developing the following policy and this ANPRM reflects those discussions. This policy will also be the subject of a notice of proposed rulemaking to incorporate the policy into FDA regulations.

A. Listed Uses That Are No Longer Considered Essential

1. Metered-Dose Steroid Human Drugs for Nasal Inhalation

Steroid human drugs for nasal inhalation are currently available using metering atomising pumps rather than nasal MDI's. The availability of such products as Beconase® AQ and Vancenase® AQ (beclomethasone dipropionate monohydrate), Nasarel® and Nasalide® (flunisolide), Flonase® (fluticasone propionate), and Nasacort® AQ (triamcinolone acetonide), and the widespread patient acceptance of these products, indicate to FDA that using CFC's in metered-dose steroid human drugs for nasal inhalation can no longer be considered to be essential and FDA has tentatively determined to remove the use from Sec. 2.125(e).

2. Drug Products That Are No Longer Being Marketed

Several of the essential uses listed in Sec. 2.125(e) exempt only a single approved drug product and, in a few cases, that drug product is no longer being marketed (or is no longer being marketed in a formulation containing CFC's). FDA has tentatively determined that an essential use for which no drug product is currently being marketed should no longer be considered to be essential. The absence of a demand for the product sufficient for even one company to market it is highly indicative that the use is not essential. Therefore, FDA has tentatively determined to remove the following uses from Sec. 2.125(e): Polymyxin B sulfate-bacitracin zinc-neomycin sulfate soluble antibiotic powder without excipients, for topical use on humans; and contraceptive vaginal foams for human use.

B. Criteria for Determination That a Use Is No Longer Essential

1. Therapeutic Classes

In evaluating petitions submitted under Sec. 2.125(f) requesting that a new use be listed as essential, FDA has not required a showing that technically feasible non-CFC alternatives to a product contain the same active ingredient or active moiety¹ as the drug product that would be the subject of the proposed essential use. Thus, if other drug products, containing other active moieties, are available for treatment of the same condition, they may be considered technically feasible alternatives to the proposed essential-use product. Many of the drug products marketed under Sec. 2.125 are pharmacologically closely related, are indicated for the treatment of the same conditions, and may be considered to be treatment alternatives. In evaluating whether a use remains essential, FDA believes that it is appropriate to evaluate these treatment alternatives together as a therapeutic class. In this regard, FDA has tentatively determined that metered-dose corticosteroid human drugs for oral inhalation and metered-dose short-acting adrenergic bronchodilator human drugs for oral inhalation are appropriate therapeutic classes for essential-use determinations. The determination of whether drug products that are not members of either therapeutic class represent essential uses of CFC's will be made under the criteria set out in section II.B.2. of this document.

FDA has tentatively determined that all drugs currently marketed under Sec. 2.125(e)(2) should be considered to be members of the therapeutic class "metered-dose corticosteroid² human drugs for oral inhalation." These drugs contain the following active moieties:

- beclomethasone
- dexamethasone
- flunisolide
- fluticasone
- triamcinolone

FDA has tentatively determined that drugs containing the following active moieties currently marketed under Sec. 2.125(e)(3) should be considered to be members of the therapeutic class "metered-dose short-acting adrenergic bronchodilator human drugs for oral inhalation":

- albuterol
- bitolterol

¹ 21 CFR 314.108(a) defines active moiety as meaning "the molecule or ion, excluding those appended portions of the molecule that cause the drug to be an ester, salt (including a salt with hydrogen or coordination bonds), or other noncovalent derivative (such as a complex, chelate, or clathrate) of the molecule, responsible for the physiological or pharmacological action of the drug substance."

² The active ingredients in all drug products currently marketed under the essential use for metered-dose steroid human drugs for oral inhalation are members of the subclass of substances known as corticosteroids. FDA has tentatively determined that it would be more accurate to use the more specific term corticosteroids rather than the more general term steroids to describe the therapeutic class.

- isoetharine
- isoproterenol
- metaproterenol
- pirbuterol
- terbutaline

Adrenergic bronchodilator drug products containing the active moiety salmeterol are not included in the therapeutic class because of the longer duration of action and different indication of usage of salmeterol as compared to metered-dose short-acting adrenergic bronchodilator human drugs for oral inhalation. Adrenergic bronchodilator drug products containing the active moiety epinephrine are also not included in the class because epinephrine is the only active moiety used in drug products sold over-the-counter (OTC). These OTC drug products are available to patients who may not have access to prescription drugs. Therefore, FDA has tentatively determined that prescription drug products should not be considered as alternatives to drug products containing epinephrine. The determination of whether a drug product containing salmeterol or epinephrine constitutes an essential use would be considered under the criteria for an individual active moiety discussed in section II.B.2. of this document.

The use of CFC's in any drug product that is a member of a therapeutic class described above would no longer be considered essential if, for each therapeutic class:

1. Three distinct alternative products, representing at least two different active moieties, are being marketed, with the same route of delivery, for the same indication, and with approximately the same level of convenience of use as the products containing CFC's. At least two of the three alternative products must be MDI's.
2. Adequate supplies and production capacity exist for the alternative products to meet the needs of the population indicated for the therapeutic class.
3. At least 1 year of post-marketing use data for each product are available. There should be persuasive evidence of patient acceptance in the United States of each of the alternative products.
4. There is no persuasive evidence to rebut a presumption that all significant patient sub-populations are served by the alternative products.

FDA believes that making essential-use determinations for an entire class of closely related drug products will expedite the elimination of drug products that release ozone-depleting substances. FDA recognizes that there may be limited incentives to develop alternative products containing every active moiety currently marketed under essential-use exemptions. By eliminating the essential use by therapeutic class, FDA will ensure that these drugs do not remain on the market longer than necessary.

FDA also hopes that the knowledge that the essential use covering a given product may be eliminated, even though no alternative product exists containing the same active moiety as that product, may provide added incentive for the manufacturer of that product to develop an alternative product containing the same active moiety. In addition, the agency believes that requiring multiple alternative drug products containing multiple active moieties should ensure that all significant patient populations have safe and effective alternatives to CFC-containing drug products.

A discussion of the application of these criteria can be found in section II.B.3 of this document.

Under the proposed policy being considered for elimination of the essential-use status of the therapeutic classes, the essential-use status for individual members of a therapeutic class would only be eliminated when the essential-use status for the therapeutic class as a whole is eliminated. FDA recognizes that this approach may allow the essential-use status of an individual member of a therapeutic class to be retained despite the marketing of one or more technically feasible alternatives containing the same active moiety, pending elimination of the essential-use status for the therapeutic class as a whole. In addition to the policy FDA is considering for elimination of the essential-use status of the therapeutic classes described above, FDA is considering a policy for elimination of the essential-use status of individual members of a therapeutic class in advance of elimination of the essential-use status for the therapeutic class as a whole. Under this proposed policy, the essential-use status of an active moiety within a therapeutic class would be eliminated when one alternative product that contains the same active moiety is being marketed. All other elements of the policy regarding therapeutic classes would apply, including: The alternative product is delivered by the same route of administration, for the same indication, and with approximately the same level of convenience of use; there are adequate supplies and production capacity; at least 1 year of post-marketing use data are available; and there is no persuasive evidence to rebut a presumption that all significant patient sub-populations using that active moiety are served by the alternative product. Therapeutic classes would still be evaluated under the proposed therapeutic class policy, and alternative products used in the evaluation of the essential-use status of a member of the therapeutic class under the proposed additional policy would also be used in the evaluation of the class as a whole. FDA requests public comment on these approaches, and other possible approaches, for the elimination of the essential-use status of individual members of the therapeutic classes and the therapeutic classes as a whole.

2. Individual Active Moieties

In examining the essential-use status of drug products when FDA has not already made a tentative determination that a currently listed essential use can no longer be considered to be essential, or when the drug is not a member of one of the therapeutic classes described in section II.B.1. of this document, FDA will look at other drug products containing the same active moiety as possible technically feasible alternatives. The use of CFC's in any drug product that is not a member of a therapeutic class described in section II.B.1. of this document would no longer be considered essential if:

1. One alternative product containing the same active moiety is being marketed, delivered by the same route of administration, for the same indication, and with approximately the same level of convenience of use compared to the product containing CFC's.

2. Adequate supplies and production capacity exist to meet the needs of the population indicated for the alternative drug product containing the active moiety.
3. At least 1 year of post-marketing use data for the product are available. There should be persuasive evidence of patient acceptance in the United States of the alternative product.
4. There is no persuasive evidence to rebut a presumption that all significant patient sub-populations are served by the alternative product.

A discussion of the application of these criteria can be found in section II.B.3. of this document.

Drug products marketed under the following current essential uses would generally be evaluated under the above “individual active moieties” criteria:

- Metered-dose ergotamine tartrate drug products administered by oral inhalation for use in humans.
- Intrarectal hydrocortisone acetate for human use.
- Anesthetic drugs for topical use on accessible mucous membranes of humans where a cannula is used for application.
- Metered-dose nitroglycerin human drugs administered to the oral cavity.
- Metered-dose cromolyn sodium human drugs administered by oral inhalation.
- Metered-dose ipratropium bromide for oral inhalation.
- Metered-dose atropine sulfate aerosol human drugs administered by oral inhalation.³
- Metered-dose nedocromil sodium human drugs administered by oral inhalation.
- Metered-dose ipratropium bromide and albuterol sulfate, in combination, administered by oral inhalation for human use.
- Sterile aerosol talc administered intrapleurally by thoracoscopy for human use.

As discussed in section II.B.1. of this document, the essential-use status of drugs containing the active moieties epinephrine and salmeterol will also be evaluated under the “individual active moieties” criteria.

FDA requests public comment on the appropriateness of potentially eliminating such essential uses and criteria outlined here.

³ The evaluation of the essential use status of drug products containing atropine sulfate may be an exception to the application of the criteria set out in section II.B. of this document. Drug products containing atropine sulfate were never commercially marketed under Sec. 2.125, but were manufactured for the U.S. Army for use by armed services personnel. The unique status of this use may require that other criteria be applied to it.

3. Discussion of Criteria

In arriving at the tentative criteria for evaluating the essential-use status of the two therapeutic classes, FDA has kept in mind that the MDI is the most widely accepted delivery system for administering drugs by oral inhalation for the treatment of asthma and chronic obstructive pulmonary disease. Physicians and patients value an MDI's compact size and ease of use. Because these factors are important and help ensure that patients receive appropriate medical treatment, FDA would require that at least two of the alternative products be available as an MDI. FDA is also aware that not all patients may tolerate a given drug product. Accordingly, FDA has reached the tentative conclusion that there must be products representing at least two different active moieties before FDA will consider that there are technically feasible alternatives to the therapeutic class. FDA is proposing that there be three distinct drug products. FDA wishes to ensure that there are substantial differences among the alternative products in order to give patients a wide variety of therapeutic options. Therefore, a drug product and a second generic drug product that refers to the first drug product to gain approval, under section 505(j) of the Federal Food, Drug, and Cosmetic Act (21 U.S.C. 355(j)), would not generally be considered to be two distinct drug products for purposes of evaluating the essential-use status of the drug.

For most of the essential uses that would be evaluated under the "individual active moieties" criteria, there is only one product being marketed under each essential use. Therefore, requiring the availability of more than one alternative would appear to be inadvisable.

Because of their larger size and relative lack of convenience of use, FDA does not consider currently available nebulisers to be technically feasible alternatives to MDI's. Currently available delivery systems that FDA considers to be technically feasible alternatives to MDI's using CFC's are multiple-dose DPI's⁴ and MDI's that do not contain CFC's. Continuing changes in technology may give FDA reason to revisit this tentative determination.

In evaluating whether adequate supplies and production capacity exist for the alternative product or products to meet the needs of the patient population indicated for drug products covered by an essential use, FDA's analyses will be flexible, but with one overarching principle: To ensure that there are no significant shortages of drug product that could harm the public health of the United States. Factors such as multiple production sites, to secure a steady supply if there is an interruption at one site, would be considered favourably in this regard.

In evaluating post-marketing use data and evidence of patient acceptance under the third criterion, FDA anticipates that it may be useful for sponsors of alternative products to conduct large post-marketing studies, preferably in the U.S. clinical practice setting, directly comparing their product which does not contain CFC's to the CFC-containing product for which it would be considered an alternative. It may also be possible for several sponsors to jointly commission a large post-marketing clinical study of their common products. In addition to the formal studies described above, manufacturers of alternative products, or other persons requesting the elimination of an essential use, may wish to submit to FDA a review of post-marketing surveillance data from FDA's MEDWATCH programme, the spontaneous reporting systems of other countries, and all other available post-marketing data after a potential alternative product has been marketed in the United States for a period of 1 year. FDA has tentatively concluded that

⁴ Single-dose DPI's that are currently marketed in the United States would not be considered technically feasible alternatives to MDI's using CFC's. The agency has tentatively determined that these single-dose DPI's do not approximate the convenience of MDI's because patients must carry both the single-dose DPI device and a supply of the drug. The patient must also load the device prior to each use. The comparative inconvenience of single-dose DPI's does not warrant their being considered technically feasible alternatives. The agency also believes that these single-dose DPI's have not shown adequate levels of patient acceptance.

foreign data would not be considered acceptable as the sole evidence of patient acceptance, but these data will be considered in addition to U.S. post-marketing use data in cases where U.S. formulations and foreign formulations have been shown to be the same or substantially similar. The term “patient acceptance” here assumes that the alternative products have adequate safety, tolerability, effectiveness, and compliance. Because information regarding patient acceptance is not routinely captured by post-marketing surveillance, such assessments should be incorporated into the proposed formal clinical studies.

In evaluating the last criterion, that there is no persuasive evidence to rebut a presumption that all significant patient sub-populations are served by the alternative product, FDA believes that there should be a strong presumption that, if the first three criteria are met, then all relevant sub-populations will be adequately served by alternative products. If FDA is not already in possession of evidence indicating the presence of a sub-population served only by a product containing CFC's, then the burden of producing compelling scientific evidence that there is a sub-population served only by a product containing CFC's would be placed on anyone opposing the determination that a use is no longer essential.

C. Implementation

FDA currently intends to publish a notice of proposed rulemaking after the comment period for this ANPRM closes. That proposed rule would eliminate essential uses for steroid human drugs for nasal inhalation and for drugs that are no longer marketed. The proposed rule would also codify the criteria for elimination of essential uses discussed in section II.B. of this document. FDA intends to use the preamble of the proposed rule to respond to comments on this ANPRM.

As the criteria for eliminating essential uses are met, FDA will propose elimination of essential uses for the appropriate therapeutic classes or individual active moieties. FDA intends that such proposals will be published and finalised in an expeditious manner.

FDA is aware that the proposed policy contained in this ANPRM is, to a certain degree, predicated on the assumption that drug manufacturers are aggressively developing alternatives to products containing CFC's. If this assumption is less than fully met, FDA recognises that it may have to take an even more active role in encouraging the development of technically feasible alternatives. Furthermore, FDA contemplates re-examining the effectiveness of the policy set out in this ANPRM 1 to 3 years after the publication of the first final rule implementing the policy set out in this ANPRM. If this re-examination reveals that alternatives to CFC's are not being aggressively developed, FDA will consider eliminating essential uses where manufacturers of drug products covered by those uses have not demonstrated due diligence in developing alternative products.

D. Analysis of Impacts

FDA is required to examine the impacts of its proposed rules under Executive Order 12866 and the Regulatory Flexibility Act (5 U.S.C. 601- 612). Executive Order 12866 directs agencies to assess all costs and benefits of available regulatory alternatives and, when regulation is necessary, to select regulatory approaches that maximise net benefits (including potential economic, environmental, public health and safety, and other advantages; distributive impacts; and equity). The Regulatory Flexibility Act requires agencies to analyse regulatory options if the proposed rule is expected to have a significant impact on a substantial number of small entities. FDA is soliciting information and data to help it examine the impacts that a proposed rule based on this advance notice would have. In order to help the agency prepare these analysis, FDA requests comments on the following impact questions:

1. Are the incentives discussed in the ANPRM adequate to spur the needed market innovation? Are there alternative means of introducing appropriate market incentives?
2. Assuming that an alternative product is approved for marketing, what is the estimated cost of obtaining post-marketing data supporting the new product as a technologically feasible alternative? How much time would be necessary? What other costs should the agency consider?
3. How much would it cost to obtain the data including the post-marketing study discussed in the ANPRM? How much would it cost to obtain the data excluding such a post-marketing study? What are the components of this estimate (e.g., person-hours, contract dollars, etc.)?
4. How much time should be allowed for phasing out a CFC-containing product no longer considered essential?
5. Are there other alternative policies that the agency should consider that would achieve the stated goals and be less burdensome to patients that use these products and/or to the industry that provides the products?

III. Other Rulemaking Proceedings Regarding CFC's

In the very near future, FDA intends to propose a rule regarding criteria to be applied in agency determinations to add new essential uses to Sec. 2.125(e). The agency is not soliciting comments on this separate rulemaking proceeding, and is only mentioning the matter here to provide a more complete picture of FDA's current plans regarding the regulation of CFC-containing drug products. FDA does not intend to respond to any comments regarding this issue at this time; those persons wishing to comment on this issue should wait until the proposed rule is published.

Consistent with the phaseout provisions of the Clean Air Act, the proposed rule regarding the addition of new essential uses will provide new and substantially more stringent criteria for determining that a use is essential. Specific criteria will be proposed for both investigational drugs and commercially marketed drugs.

FDA currently intends that this proposed rule will provide a restructuring of Sec. 2.125(e) to eliminate essential uses that cover an entire class of drugs, such as current Sec. 2.125(e)(3) "metered-dose adrenergic bronchodilator human drugs for oral inhalation." In their place, FDA will propose to list the use of every active moiety currently marketed under the current class essential use. This will mean that an individual wishing to market, for example, an adrenergic bronchodilator where the active moiety is not listed will need to petition FDA to amend Sec. 2.125(e) to add the use of the active moiety.

The proposed rule would also eliminate out-of-date transitional provisions, and make other similar non-substantive housekeeping changes.

The agency has determined to go directly to a proposed rule on these provisions of the agency's policy, rather than requesting comment on them in this or another ANPRM, in order to accelerate consideration of the new more stringent criteria for determining when new uses are essential. FDA believes that as the agency will soon be eliminating essential uses, it would be a waste of scarce agency resources, as well as inconsistent with the general policy favouring the phase out of ozone-depleting substances, to create new essential uses unless an extraordinary showing of public benefit can be made.

Interested persons may, on or before May 5, 1997, submit to the Dockets Management Branch (address above) written comments regarding this ANPRM. Two copies of any comments are to

be submitted, except that individuals may submit one copy. Comments are to be identified with the docket number found in brackets in the heading of this document. Received comments may be seen in the office above between 9 a.m. and 4 p.m., Monday through Friday.

Dated: February 28, 1997.

William B. Schultz,

Deputy Commissioner for Policy

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(B) INTERIM APPROACH AUSTRALIA

Below is an interim report forwarded by Australia which provides a broad outline of Australia's general approach to the phaseout of CFC-based asthma treatments. Consultations are continuing with industry, users and regulatory authorities. It was advised that this report represents an initial indication of the direction being taken within Australia, rather than a final strategy.

BROAD OUTLINE OF AUSTRALIA'S GENERAL APPROACH TO THE TRANSITION TO NON-CFC TREATMENTS OF ASTHMA AND CHRONIC OBSTRUCTIVE PULMONARY DISEASE

Introduction

Australia is committed to the timely elimination of CFCs and all other ozone-depleting substances and fully recognises the need to reduce and remove the current exemption which allows for the production and import of CFCs for Metered Dose Inhalers (MDIs). Australia also recognises the need for a national strategy for the phaseout of CFC-based MDIs in order to ensure a smooth and efficient transition to non-CFC treatments of asthma and Chronic Obstructive Pulmonary Disease (COPD) in a way which will protect the health and safety of patients. To develop this strategy, consultation has commenced with health professionals, respiratory medicine companies, health regulatory bodies and major user groups. This process has already resulted in broad agreement on a number of issues. The aims of the on-going consultative process are to:

- ensure that the interests and welfare of all patients are protected during and after the transition process;
- ensure that environmental objectives are met as speedily as possible, consistent with the first objective;
- ensure that the health professionals are fully informed of all relevant issues before and after the transition process; and
- establish policies for government and industry in Australia to facilitate a seamless transition to non-CFC treatments of asthma and COPD.

Australia is pleased to provide a broad outline of the general approach that is currently being developed for the transition to non-CFC treatments of asthma and COPD. As the consultation process is continuing with industry, users and regulatory authorities this report represents an initial indication of the direction being taken in Australia, rather than a final strategy. Australia hopes to be in a position to provide additional information as the consultation process continues throughout the year.

Broad Regulatory Approach to Phaseout

In considering ways to achieve a smooth and efficient transition which also protects the health and safety of patients, two broad approaches have been considered in Australia. These were:

1. regulations on a substance-by-substance basis, whereby substances are required to be removed from the market following the approval of one or more equivalent CFC-free alternatives; or
2. an agreed reduction timetable, with percentage reductions against a baseline, for the import of bulk CFCs for MDI production purposes, possibly with a complementary timetable for total quantities of CFCs contained in finished products.

The first approach of regulating on a substance-by-substance basis is not supported by most stakeholders in Australia. The primary reasons are because this type of regulation was seen to be incredibly complicated and would require detailed administration and regulation with large associated costs. It was recognised that substance-by-substance regulation does not in itself provide incentives for speedy formulation of alternatives for the whole range of CFC-based products.

A reduction timetable for the import of quantities of CFCs was favoured for a number of reasons. This approach is relatively simple and provides incentives for ongoing research, development and approval of non-CFC treatments. A reduction timetable is consistent with the supply-control approach normally taken under the Protocol and is likely to achieve similar environmental benefits to the more complicated substance-by-substance approach. It also provides greater flexibility to national governments in developing implementation arrangements which will suit the circumstances of each country.

As part of the process of considering possible reduction timetables, companies operating in Australia were asked to provide estimates of the percentage reductions in imports of CFCs for MDI purposes that may be achievable by the year 2000. Similarly, companies were also asked to indicate in what year a virtual phaseout was likely to be achievable. In developing these estimates, industry was asked to take into account the time necessary for research, development, approval and market penetration of CFC-free alternatives. Industry was also asked to take into account the time required for the necessary educational programmes for health professionals and patients.

On the basis of the estimates provided by industry, it is suggested that a reduction of between 60 and 70 per cent against a 1996 baseline could be achieved by the year 2001. Similarly it is suggested that a virtual phaseout may be achievable by 2005. The term 'virtual phaseout' is used as there are some specialised products which, due to small quantities used, are not viable for reformulation.

Due to uncertainties involved in developing these estimates, the suggested reduction percentages and virtual phaseout date should be considered as an indicative target only at this stage and will need to be reviewed regularly as the transition proceeds.

Product Review and Approval

As an important element of the development of an appropriate national transition strategy, national environmental and health authorities in Australia are engaged in detailed and ongoing consultation. In accordance with paragraph 2 of Decision VIII/11, these authorities are discussing the possibility of expediting the review of marketing, licensing and pricing applications of CFC-free treatments in Australia. Industry stakeholders also agree that they need to consult regularly with regulatory authorities in the interest of expediting processing of CFC-free product applications. Consideration is also being given to the possibility of establishing some form of priority review system for CFC-free products.

As part of the strategy to phaseout CFC treatments of asthma and COPD, Australia would like to stop the introduction of any new products containing CFCs at an appropriate time. However, under current Australian legislation, regulatory authorities cannot refuse to accept new applications for MDIs containing CFCs. In the interim, industry is being advised that the process of transition is underway and that essential use exemptions will not be available indefinitely.

Reimbursement Policies

Paragraph 3 of VIII/11 requests that national authorities review the terms for public MDI procurement and reimbursement, so that purchasing policies do not discriminate against non-CFC alternatives. Australia is working to ensure that there are no financial disincentives to the introduction or use of non-CFC alternatives. To do this it is recognised that pricing authorities will need to consider factors such as the sale price requested by industry, the actual cost of manufacture, overseas pricing experience, the availability and pricing of alternative products (such as Dry Powder Inhalers) and the relative efficacy and safety of the new product as compared to the CFC equivalent.

The national pharmaceutical pricing authority is encouraging early consultation with industry well before any product is released on the market in an attempt to ensure that pricing structures for MDIs do not impact negatively on the phaseout.

Controls on Advertising

Paragraph 4 of Decision VIII/10 requests that Parties encourage companies not to engage in false or misleading advertising targeted at either non-CFC alternatives or CFC MDIs. In Australia there are no additional specific actions required in response to this decision as:

- all companies believe that the Australian Pharmaceutical Manufacturer's Association already has adequate mechanisms in place, through its Code of Conduct, to prevent false or misleading product advertisement, promotion or representation by sales representatives; and
- the Australian Trade Practices Act also provides protection against false and misleading claims.

Packaging and Marketing of CFC-free Products

Paragraph 3 of Decision VIII/10 requires Parties to request that companies selling MDIs will differentiate packaging between CFC-containing and CFC-free MDIs and apply other appropriate marketing strategies to encourage patient acceptance of CFC-free alternatives.

Australian companies have different views on the best way to encourage patient acceptance. Some companies feel that consistency in product name and packaging would be the most effective way to encourage acceptance. There is, however, general agreement that there would be value in CFC-free products carrying a uniform logo announcing these products as CFC-free. The National Asthma Campaign, Australia's leading asthma advisory body, is attempting to develop a universally acceptable logo in consultation with all industry stakeholders.

Ongoing Education Campaign

Paragraph 2 of Decision VIII/10 requests that Parties undertake efforts to educate health-care professionals and patients about other treatment options and the transition to non-CFC alternatives.

Stakeholders in Australia generally agree that the National Asthma Campaign, in collaboration with industry stakeholders, should conduct national advertising campaigns for health professionals and patients throughout the changeover period. All stakeholders agree that continued participation by Environment Australia will be very important to reinforce the environmental messages in the ongoing education campaign.

Minimising Unnecessary Emissions of CFCs

Paragraphs 6 and 7 of Decision VIII/10 require Parties to request companies manufacturing MDIs to take all economically feasible steps to minimise CFC emissions during manufacture and to encourage the responsible disposal of unusable MDIs. In Australia there is no additional specific action required in response to this decision as:

- Australian manufacturers of MDIs already have in place procedures to recover CFCs from MDIs which have been returned or have expired; and
- the value of the CFCs used in manufacture is high and companies have advised that they already take all feasible steps to minimise emissions.

APPENDIX 2

TIMESCALES AND TECHNICAL ISSUES RELATING TO THE BUILDING STOCKPILES OF PHARMACEUTICAL CFC PROPELLANT

Background

This Appendix reviews a possible option of the construction of a “stockpile” of pharmaceutical quality CFCs, to cover the reduced needs in the last few years of demand, when production of new (just in time) material becomes impractical through limited demand, and outlines the main technical issues that would need to be addressed, and attaches some ballpark timescales.

Steps in Creating a Stockpile

Based on recent experience the steps required for the construction and use of such a stockpile are outlined below. Before such a process could commence, the volume to be stored would have to be clearly and unambiguously determined.

1. Identification of Storage Facilities

Available facilities must be surveyed, to determine whether they are available and potentially suitable for use for bulk pharmaceutical grade propellant storage. Reach agreement with the owners for lease and use. (2 months)

If sufficient suitable storage volume is not available (it must be understood that the requirements for the storage of pharmaceutical grade propellants are extremely stringent, and many tank storage facilities will be intrinsically unsuitable), it will become necessary to provide additional new capacity at a suitable location.

2. Provision of Storage Facilities

In the following steps, route A assumes sufficient capacity can be found, route B assumes that at least some new capacity will be needed.

A. Only Using Existing Facilities

A1. Commence an overhaul programme that will contain some or all of the following elements (All: 9 months)

Detoxify and make safe for entry and detailed inspection

Full specification of overhaul cleaning, modifications, changes to pipework

Let and commence contracts for above work

Inspection of finished works

Rough Cleaning, vacuuming, inspection of cleaning

Seal tank manways

Purge air, fill with dry air or nitrogen

A2. Validate and Commission for pharmaceutical Propellant Storage:

Flush each tank with suitable solvent to remove welding traces, etc. (eg. methylene chloride)

Remove solvent, evacuate, purge with dry nitrogen

Flush each tank with CFC (11 or 12 depending on intended use), monitoring level of particulates and traces of previous solvent in the washings, until pre-set acceptance criteria are met. Reject the flushings for other uses/destruction

Flush with final wash of medical grade CFC, analysing the washings for all tests and comparing (against pre-set acceptance criteria) with the analysis of the input material.

If test passed, tank accepted. All washings downgraded for other uses/destruction

(2 months)

B. At Least Partly using Newly Constructed Facilities

B1. Pre-construction

Identify site

Design and specify

Seek planning permission

Let construction contracts (6 months)

B2. Construction

Level and prepare site

Lay foundations. Construct tank stillages

(Tanks constructed off-site by contractor)

Bring tanks to site, place on stillages

Install and connect all pumps, pipework, and. equipment

Remove debris and vacuum

Seal manways (6 months)

B3. Flushing

As A2 above (2 months)

3. *Import of Pharmaceutical Grade CFC*

The storage facilities can then be filled with CFC. Rate of filling is limited by CFC production, transport, and analysis limitations. Whilst pharmaceutical analysis is always performed with great care, analysis of the material before acceptance to the stockpile would be carried out with even greater stringency, as the risk of contamination by an off spec. batch must be eliminated.

Time taken will obviously be a function of the size of the stockpile, but typically an import period of 4-6 months should be considered.

Overall Timelines

Totalling up the foregoing, the following lead times from clearance to completion of stockpile can be obtained:

1. Using existing storage only: 17-19 months
2. Using some new storage: 20-22 months

**MONTREAL PROTOCOL
ON SUBSTANCES THAT DEplete
THE OZONE LAYER**



Technology and Economic Assessment Panel

PART II: REPORT OF THE PROCESS AGENTS TASK FORCE

**April 1997 Report
Volume II**

**Montreal Protocol
On Substances that Deplete the Ozone Layer**

UNEP Technology and Economic Assessment Panel

PART II: REPORT OF THE PROCESS AGENTS TASK FORCE

April 1997 Report, Volume II

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PREAMBLE - TEAP COMMENTS

Use of Controlled Substances as Process Agents

The TEAP thanks the Process Agents Task Force (PATF) for their efforts in preparing a report that provides clear technical information and detailed data on use and emissions of controlled substances used as process agents.

Non-Article 5(1) Findings

Emissions in Non-Article 5(1) countries from the use of controlled substances as process agents are comparable to the insignificant and inadvertent emissions of ODSs from feedstock uses. Further significant reductions in use and emissions are projected for the coming five years. Additional controls in Non-Article 5(1) countries may shift production to Article 5(1) countries, where ODS emissions may be significantly higher. Such a shift of production could substantially increase the ultimate cost of the Article 5(1) phaseout. Therefore, TEAP unanimously recommends that Parties consider the advantages of henceforth treating chemical process agents in the same manner as feedstocks.

Article 5(1) Findings

Emissions in Article 5(1) countries from use of controlled substances as process agents are significant and, without assistance, will continue to grow. However, proven technologies are commercially available to convert some facilities to non-ODS processes and to minimise emissions from those processes where alternatives have not yet been proven. Therefore, TEAP unanimously recommends that Parties consider the advantages of technology co-operation and financing of emission reduction and process conversion projects in Article 5(1) countries.

Notice

The United Nations Environment Programme (UNEP), the UNEP Process Agents Task Force chairs and members and the companies and organisations that employ UNEP Process Agents Task Force chairs and members do not endorse the performance, worker safety, or environmental acceptability of any of the technical options discussed. Every industrial operation requires consideration of worker safety and proper disposal of contaminants and waste products. Moreover, as work continues -- including additional toxicity testing and evaluation -- more information on health, environmental and safety effects of alternatives and replacements will become available for use in selecting among the options discussed in this document.

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Process Agents Task Force
is available on the Internet
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REPORT OF THE PROCESS AGENTS TASK FORCE

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The opinions expressed are those of the committee and do not necessarily reflect the views of any sponsoring or supporting organisation.

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Katsuyuki Takei

Japan Association For Hygiene Of Chlorinated Solvents
Japan

Helen Tope

Victoria Environment Protection Authority
Australia

Rob Van Den Bor

Aramid Products (Akzo-Nobel)
Netherlands

F.A. Vogelsberg

DuPont
U.S.A.

John Wilkinson

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Beijing University Of Chemical Technology
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EXECUTIVE SUMMARY

Products

Process agents are used to produce a wide variety of products that are considered to be useful to society. Some products can be produced without the use of ODS. For other products the ODS used as a process agent cannot be replaced for reasons of health, safety, environment, quality, yield, cost effectiveness, commercial viability, commercial availability, and technical feasibility.

Example uses identified in the report of the PATF are summarised in the following table:

Examples of Products Made Using Process Agents

Process	Product Uses
Chlorine	Necessary for production of 60% of the chemicals produced and 80% of the pharmaceuticals produced, also used to produce polymers, solvents and thousands of other products. Chlorine is also used as a water treatment chemical to maintain the safety of public water supplies.
Caustic Soda	Used to produce paper and as an intermediate in the production of other products.
Chlorinated Rubber	Used as a binder in corrosion resistant paint for ships, bridges and off-shore structures. Due to very high durability used as a major component of highway marking paints. Also used as a component of heavy duty adhesives - e.g. bonds rubber to steel in automobiles.
Endosulphan	A broad spectrum biodegradable insecticide-acaricide used in the control of pests in cotton and other crops.
Ibuprofen	A basic drug used in the manufacture of analgesic formulations for use as pain killers.
Dicofol	A broad spectrum non systemic acaricide with little insecticidal activity. Used on tea and many fruits, vegetables, ornamentals and field crops for the control of various species of mites.
Chlorosulphonated polyolefin (CSM)	It is used in automobiles for timing and fan belts. Also used as a sheathing for wire and cable, as a gasket in the doors of microwave ovens and as a roofing membrane. Many inflatable whitewater rafts and rescue boats are fabricated with this material.
PPTA polymer	Bullet proof vests, lightweight armoured vehicles, motorcycle and bicycle helmets and containers for the transportation of dangerous goods are examples of products made using the material.
Fluoropolymer resins	Used as a sheath for aircraft and computer electrical wiring. Also used as a non-stick coating for cookware.
Fine Synthetic Fibre Sheet Structure	Typical uses are for medical instrument packaging (allows sterilisation after packing), air infiltration barriers for buildings, protective clothing for workers handling toxic or dangerous chemicals and high strength, light weight packaging materials.

Definitions

In order to clarify uses of controlled substances as process agents the PATF recommends that Parties consider the following definitions:

Feedstock: A controlled substance that undergoes transformation in a process in which it is converted from its original composition except for insignificant trace emissions as allowed by Decision IV/12.

Process Agent: A controlled substance, that because of its unique chemical and/or physical properties, facilitates an intended chemical reaction and/or inhibits an unintended chemical reaction.

Controlled substances are typically used in chemical processes as process agents for at least two of the following unique chemical and/or physical properties:

- 1.) Chemically inert during a chemical reaction
- 2.) Physical properties, e.g.
 - boiling point
 - vapour pressure
 - specific solvency
- 3.) To act as a chain transfer agent
- 4.) To control the desired physical properties of a process, e.g.,
 - molecular weight
 - viscosity
- 5.) To increase plant yield
- 6.) Non-flammable/non-explosive
- 7.) To minimise undesirable by-product formation

Note 1: Refrigeration, solvent cleaning, sterilisation, aerosol propellants and fire fighting are not process agents according to this definition.

Note 2: Parties need not consider use of ODS for foam blowing, tobacco puffing, caffeine extraction, or fumigation because these uses are already covered in other Decisions and/or by Technical Options Committee Reports.

Where the term “Process Agent” is used in this report it refers to the use of a controlled substance used as a process agent.

The Montreal Protocol defines “consumption” as:

Consumption = production + imports - exports

Parties should be aware that if process agent applications are considered differently than feedstock applications the quantities of controlled substances required would then have to meet the definition of consumption. However, in the case of ODS used as process agents the supply of ODS used to replenish loss of process inventory may not equal emissions.

In the case of ODS used as process agents, the ODS consumption would be utilised to replenish process inventory losses resulting from transformation, destruction and emissions to the atmosphere from the process and/or trace quantities slowly emitted from the product. However, the existing definition of consumption, when applied to process agent use of ODS, disregards transformation and destruction and could result in a disincentive to reduce emissions.

The Parties may wish to carefully consider the emission reductions achieved to date and expected in the foreseeable future and develop appropriate actions to recognise the transformation and destruction that may occur in process agent use of ODS.

For the purpose of this report the supply required for replenishment of lost inventory is referred to as “make-up” and defined as follows:

Make up quantity: The quantity of controlled substance per year, needed to continue the manufacture of products in a plant, due to transformation, destruction and inadvertent losses (i.e. emissions and residual amounts in final product).

Identified Uses of ODS as Chemical Process Agents

Where possible case studies have been developed for identified process agent uses (see Appendix C of the complete PATF report). The studies elaborate on the use and consumption of controlled substances, availability and feasibility of alternatives, products produced and other relevant information.

Case Study	Application
1	Use of CTC in the elimination of NCl ₃ in the production of chlorine and caustic soda
2	Use of CTC in the recovery of chlorine in tail gas from production of Chlorine
3	Use of CTC in the Chlorinated Rubber Process
4	Use of CTC in Endosulphan production
5	Usage of CTC in Ibuprofen production
6	Use of CTC in Dicofol production
7a	Use of CTC in Chlorosulphonated polyolefin (CSM) production in a Non-Article 5(1) country
7b	Use of CTC in Chlorosulphonated polyolefin (CSM) production in an Article 5(1) country
8	Production of Poly-Phenylene-Terephthal-Amide with the aid of CTC in an intermediate raw product
9	Use of CFC-113 in manufacturing a family of fluoropolymer resins
10	Use of CFC-11 in manufacture of a fine synthetic fibre sheet structure
No Case Study	Use of CTC in Styrene Butadiene Rubber (SBR) production
No Case Study	Use of CTC in Chlorinated Paraffin production

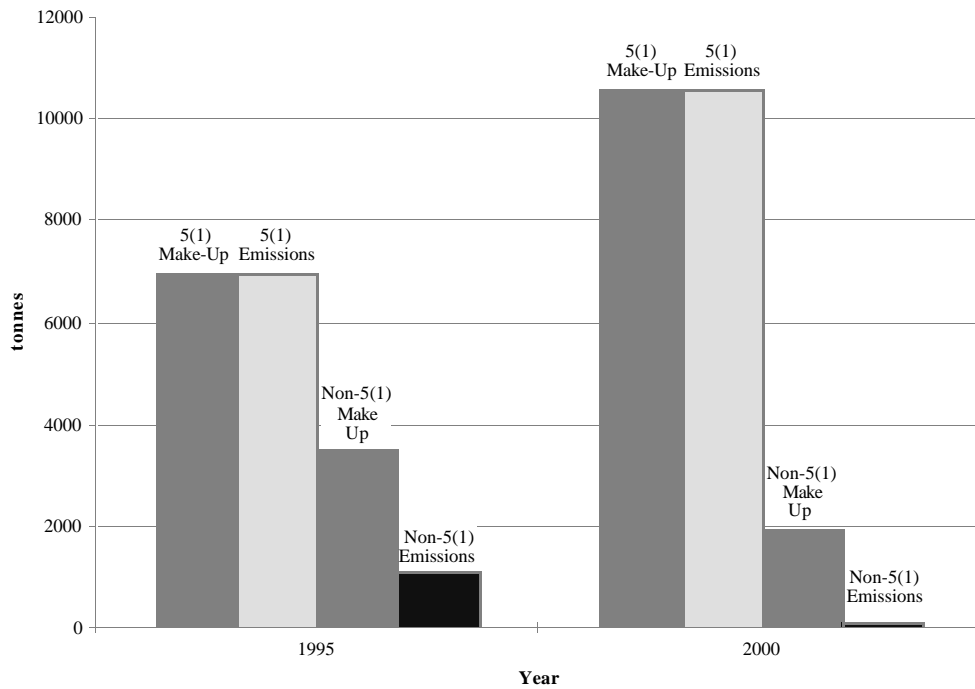
Feedstock Applications

Noting the definition of feedstock the PATF considers the following to be feedstock applications rather than process agent applications.

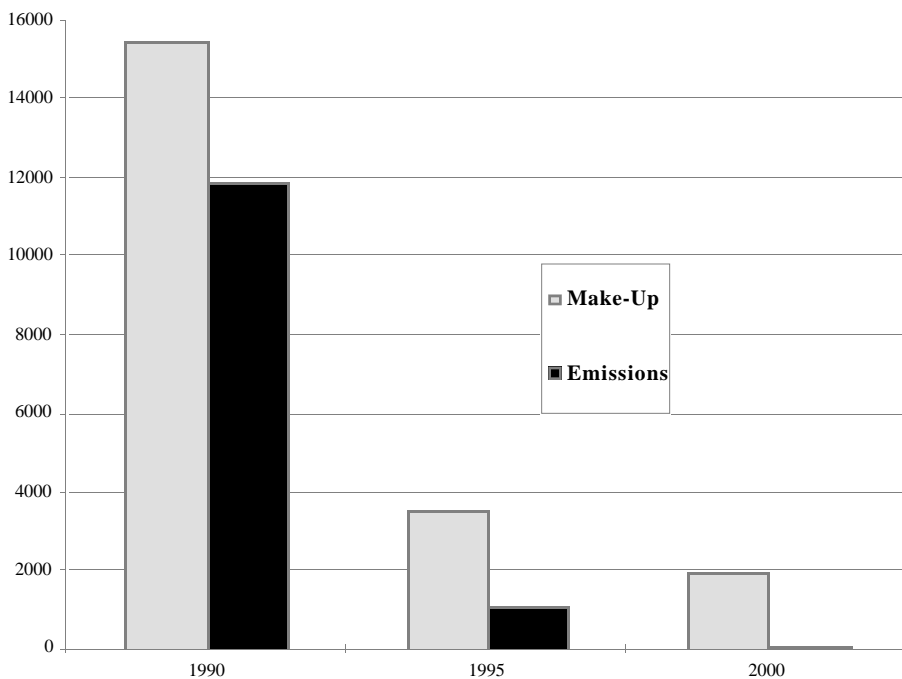
Case Study	Application
C-11	Use of Trichloroethane in the production of semiconductors
C-12	Use of CFC-12 in the purification of graphite

Estimates of Emissions of ODS Used as Process Agents

Global estimates of make-up and emissions for 1995 and 2000 (tonnes/year)



Make up and emissions of ODS used as process agent for Western Europe, North America and Japan - 1990, 1995 and 2000 (tonnes/year)



Emissions Associated with the Different Control Technologies and other Process Conditions under which Chemical Process Agents are Used

The preceding graphs clearly indicate the progress that has been made in Western Europe, Japan and North America in reducing use and more importantly emissions of ODS process agents up until now and for the foreseeable future. The new technologies that have made it possible to convert to the use of non-ODS process agents and the now proven technologies that have been employed to significantly reduce emissions are available for use elsewhere.

In general the various case studies have illustrated that emissions of controlled substances used as process agents can be minimised to “insignificant or trace levels” similar to that allowed for feedstock use where a process with adequate control technology and destruction capability are employed.

Minimisation of emissions can be achieved by use of practical control technologies to contain, destroy, or abate potential ODS emissions, i.e.

- carbon adsorption of gas streams
- steam stripping of aqueous wastes
- fugitive emission monitoring system
- leak detection monitoring
- destruction by means of technologies approved by the Parties to the Montreal Protocol.

However emissions of controlled substances used as process agents in simple batch processes are sometimes much more difficult to control. Simple batch type processes without advanced emission control technologies are typically used in Article 5(1) countries.

Alternative Process Agent Technologies or Products Available to Replace ODS in Such Uses.

Appendix C of this report provides case studies for most of the uses of controlled substances used in process agent applications identified by the PATF. Where alternative technologies or substitutes exist they have been identified in the case studies and summarised in Chapter 4. Some alternative products have been identified in the case studies, however, the information provided should not be considered as exhaustive.

All of the case studies illustrate clearly that the development and introduction of possible alternatives to ODS use in process agent applications depends on the following criteria:

- health and/or safety aspects
- environmental impacts other than ozone depletion
- quality and/or yield of the end product
- cost effectiveness and commercial viability
- commercial availability and restrictions due to proprietary technology
- technical feasibility

General Conclusions

Although the Non-Article 5(1) countries have significantly reduced and will continue to reduce their emissions, global emissions are expected to rise as the result of growth in Article 5(1) countries.

From an examination of the case studies of the identified processes the following conclusions are offered:

In most cases emissions from the use of ODS as process agents in Non-Article 5(1) countries are similar to the insignificant quantities emitted from feedstock uses.

For all of the identified processes, programmes are underway to find and/or develop alternatives to the use of ODS as process agents.

Depending on the difficulties of the process under investigation there is a diversity of progress ranging as follows:

- phaseout achieved or achievable
- expected phaseout within the next few years subject to solution of final technical issues
- those processes with extreme difficulty to find an alternative.

Realising that these results been achieved in a period of 5 to 6 years, together with measures to significantly reduce emissions, there has been remarkable progress and further progress is expected in foreseeable future.

The expectation is that in the coming 10 years a substantial portion of the use of ODS as process agents will be virtually phased out in Non-Article 5(1) countries and that these new technologies can be applied in Article 5(1) countries. Adequate technical and financial assistance will facilitate the implementation of these technologies.

Conclusions Regarding Non-Article 5(1) Countries

The PATF has found that emissions from use of ODS as process agents in Non-Article 5(1) countries have been reduced significantly and could be considered as similar to the insignificant quantities emitted from feedstock uses. Use of ODS as process agents in the manufacture of pharmaceuticals and crop protection products was not fully investigated in the limited time period available to prepare this report.

Conclusions Regarding Article 5(1) Countries

The PATF found that emissions of ODS used as process agents are significantly higher in Article 5(1) countries including China, India and Brazil. In Article 5(1) countries those processes that utilise ODS as process agents are mostly of a simple batch type. In general, these batch type processes do not employ approved destruction technologies and may employ only rudimentary other types of emission control. As such the PATF found that the emissions from use of ODS as process agents resulted in much higher emission levels than use of ODS as feedstock. Significant opportunities exist to accomplish near phaseout of the use of ODS in Article 5(1) process agents by conversion of processes to the use of non-ODS process agents or processes.

For CSM and chlorinated rubber an alternative to conversion would be to employ emission reduction measures and reduce ODS emissions to insignificant levels. This may also be an appropriate strategy for use in some facilities that produce chlorine and for use in some cases of chlorine tail gas scrubbing.

The chemical process industries in Article 5(1) countries have the following options to reduce use and/or emissions:

- Modify production facilities to reduce their emissions to minimum possible levels;
- Changeover from CTC use to alternative non-ODS solvent use or alternative process/product;
- Shutdown and/or consolidate small scale plant/facilities.

The implementation of the above stated options by enterprises in Article 5(1) countries requires:

- availability of skilled manpower and their appropriate training;
- access to technology; and
- adequate financing.

Onetime changeover to an alternative non-ODS process/product has the distinct advantage of bringing about the near total phase out of the ODS and would be a sustainable solution.

Conclusions Regarding Countries with Economies in Transition (CEITs)

The PATF was unable to thoroughly investigate the use of ODS as process agents in countries with economies in transition. However, Poland has reported use of CTC for the recovery of tail gas from production of chlorine and use of CTC in the production of three pharmaceuticals; antical, disulfiram and ketofen.

1 INTRODUCTION AND DEFINITIONS

1.1 Background

Pursuant to Decision VII/10 of the Parties, the Technology and Economic Assessment Panel (TEAP) constituted the Process Agents Task Force (PATF). PATF has endeavoured to further develop and improve upon the work completed by the Process Agents Working Group (PAWG) in 1995.

This report was developed by members of the PATF during meetings held in Toronto, Geneva, San José and Mumbai. During the Mumbai meeting a joint session was held with members of the Indian Chemical Manufacturer's Association (ICMA). The meeting with ICMA was a useful opportunity for PATF members to gain insight into the typical issues facing Article 5(1) users of process agents and to share the new technologies that have been employed to significantly reduce emissions in the non-Article 5(1) countries.

1.2 Decisions

The following Decisions of the Parties to the Montreal Protocol have been used as the basis for the work of the Process Agents Task Force (PATF):

Decision I/12B: Clarification of terms and conditions: Controlled substances produced

The First Meeting of the Parties decided in Dec.I/12B:

- (a) to agree to the following clarification of the definition of "controlled substances produced" in Article 1, paragraph 5:

"Controlled substance produced" as used in Article 1, paragraph 5 is the calculated level of controlled substances manufactured by a Party. This excludes the calculated level of controlled substances entirely used as a feedstock in the manufacture of other chemicals. Excluded also from the term "controlled substances produced" is the calculated level of controlled substances derived from used controlled substances through recycling or recovery processes;

- (b) each Party should establish accounting procedures to implement this definition.

Decision IV/12: Clarification of the definition of controlled substances

The Fourth Meeting of the Parties decided in Dec.IV/12:

1. that insignificant quantities of controlled substances originating from inadvertent or coincidental production during a manufacturing process, from unreacted feedstock, or from their use as process agents which are present in chemical substances as trace impurities, or that are emitted during product manufacture or handling, shall be considered not to be covered by the definition of a controlled substance contained in paragraph 4 of Article 1 of the Montreal Protocol;

2. to urge Parties to take steps to minimise emissions of such substances, including such steps as avoidance of the creation of such emissions, reduction of emissions using practicable control technologies or process changes, containment or destruction;
3. to request the Technology and Economic Assessment Panel:
 - (a) to give an estimate of the total emissions resulting from trace impurities, emission during product manufacture and handling losses;
 - (b) to submit its findings to the Open-ended Working Group of the Parties to the Montreal Protocol not later than 31 March 1994.

Decision VI/10: Use of controlled substances as process agents

The Sixth Meeting of the Parties decided in Dec. VI/10, taking into account:

That some Parties may have interpreted use of controlled substances in some applications where they are used as process agents as feedstock application;

That other Parties have interpreted similar applications as use and thereby subject to phase-out;

That the Technology and Economic Assessment Panel has been unable to recommend exemption, under the essential use criteria, to Parties submitting applications of such uses nominated in 1994; and

The pressing requirement for elaboration of the issue and the need for appropriate action by all Parties;

1. To request the Technology and Economic Assessment Panel:
 - (a) To identify uses of controlled substances as chemical process agents;
 - (b) To estimate emissions of controlled substances when used as process agents and the ultimate fate of such emissions and to evaluate emissions associated with the different control technologies and other process conditions under which chemical process agents are used;
 - (c) To evaluate alternative process agents or technologies or products available to replace controlled substances in such uses; and
 - (d) To submit its findings to the Open-ended Working Group of the Parties to the Montreal Protocol not later than March 1995, and to request the Open-ended Working Group to formulate recommendations, if any, for the consideration of the Parties at their Seventh Meeting;
2. That Parties, for an interim period of 1996 only, treat chemical process agents in a manner similar to feedstock, as recommended by the Technology and Economic Assessment Panel, and take a final decision on such treatment at their Seventh Meeting.

Decision VII/10: Continued uses of controlled substances as chemical process agents after 1996

The Seventh Meeting of the Parties decided in Dec.VII/10, recognising the need to restrict emissions of ozone-depleting substances from process-agent applications,

1. To continue to treat process agents in a manner similar to feedstocks only for 1996 and 1997;
2. To decide in 1997, following recommendations by the Technology and Economic Assessment Panel and its relevant subgroups, on modalities and criteria for a continued use of controlled substances as process agents, and on restricting their emissions, for 1998 and beyond.

Decision VII/30: Export and import of controlled substances to be used as feedstock

The Seventh Meeting of the Parties decided in Dec.VII/30:

1. That the amount of controlled substances produced and exported for the purpose of being entirely used as feedstock in the manufacture of other chemicals in importing countries should not be the subject of the calculation of “production” or “consumption” in exporting countries. Importers shall, prior to export, provide exporters with a commitment that the controlled substances imported shall be used for this purpose. In addition, importing countries shall report to the Secretariat on the volumes of controlled substances imported for these purposes;
2. That the amount of controlled substances entirely used as feedstock in the manufacture of other chemicals should not be the subject of calculation of “consumption” in importing countries.

- end of Decisions -

1.3 Information Required by the TEAP

The critical information required of the PATF by the TEAP is to:

- (a) identify uses of controlled substances as chemical process agents;
- (b) estimate emissions of controlled substances when used as process agents
- (c) report on emissions associated with the different control technologies and other process conditions under which chemical process agents are used;
- (d) report on alternative process agents or technologies or products available to replace controlled substances in such uses; and
- (e) provide guidance and examples to differentiate between process agent, feedstock and other uses of ODS.

1.4 Definitions

In order to clarify uses of controlled substances as process agents the PATF recommends that Parties consider the following definitions:

Feedstock: A controlled substance that undergoes transformation in a process in which it is converted from its original composition except for insignificant trace emissions as allowed by Decision IV/12.

Process Agent: A controlled substance, that because of its unique chemical and/or physical properties, facilitates an intended chemical reaction and/or inhibits an unintended chemical reaction.

Controlled substances are typically used in chemical processes as process agents for at least two of the following unique chemical and/or physical properties:

- 1.) Chemically inert during a chemical reaction
- 2.) Physical properties, eg.
 - boiling point
 - vapour pressure
 - specific solvency
- 3.) To act as a chain transfer agent
- 4.) To control the desired physical properties of a process, eg.,
 - molecular weight
 - viscosity
- 5.) To increase plant yield
- 6.) Non-flammable/non-explosive
- 7.) To minimise undesirable by-product formation

Note 1: Refrigeration, solvent cleaning, sterilisation, aerosol propellants and fire-fighting are not process agents according to this definition.

Note 2: Parties need not consider use of ODS for foam blowing, tobacco puffing, caffeine extraction, or fumigation because these uses are already covered in other Decisions and/or by Technical Options Committee Reports.

Where the term “Process Agent” is used in this report it refers to the use of a controlled substance used as a process agent.

The Montreal Protocol defines “consumption” as:

Consumption = production + imports - exports

Parties should be aware that if process agent applications are considered differently than feedstock applications the quantities of controlled substances required do not always fit this definition of consumption as consumption may not equal emissions.

In the case of ODS use as process agents, the supply is utilised to replenish process inventory lost as the result of transformation, destruction and emissions to the atmosphere from the process and/or trace quantities slowly emitted from the product.

Therefore the supply required for replenishment of lost inventory is referred to as “make-up” and defined as follows:

Make up quantity: The quantity of controlled substance per year, needed to continue the manufacture of products in a plant, due to transformation, destruction and inadvertent losses (i.e. emissions and residual amounts in final product).

1.5 General Considerations

Estimates of emissions of controlled substances when used as process agents and the ultimate fate of such emissions will be found in Chapter 2 of this report.

Chapter 3 discusses various regulatory approaches and the use of voluntary guidelines in achieving emission reductions.

Chapter 4 of the report summarises identified alternatives to the use of controlled substances as process agents.

Chapter 5 presents identified uses in Article 5(1) countries and provides helpful insight into current and future emissions as well as a discussion of options to encourage conversion to non-ODS process agents and/or emission minimisation.

Appendix A of the report outlines the typical considerations necessary to develop and implement an emission reduction programme.

Appendix B supplements information found in Chapter 3.

Appendix C of this report provides case studies for most of the uses of controlled substances used in process agent applications identified by the PATF. It was difficult to identify all uses of controlled substances, however major uses have been carefully detailed in the case studies. The structured approach used in each case study provides the following information about each process examined:

- type of process
- products made
- reason for use of controlled substance as a process agent
- emission estimates
- emission reduction measures
- possible alternatives

The structure of the case studies and the type of information provided may prove useful to Parties in evaluating other uses that may come to their individual attention.

A glossary of terms used in the report will be found in Appendix D.

2 PROCESS AGENT USE AND EMISSIONS

2.1 Identified Processes

The table below summarises major identified processes.

*Table 2.1 - Major Identified Processes**

Process (P.A.)	Application	Reason used	Product use
Chlor-alkali (CTC) (Case Study C-1)	Elimination of NCl_3	Safety and quality of product	Chlorine is a universal chemical used for more than 60 % of all chemical synthesis.
Chlor-alkali (CTC) (Case Study C-2)	Chlorine recovery by tail gas absorption	Safety, Yield	Chlorine is a universal chemical used for more than 60 % of all chemical synthesis.
Chlorinated Rubber CTC) (Case Study C-3)	Chemical inert solvent for high quality product	Inert solvent	Heavy duty anti-corrosives and adhesives
Endosulfan production (CTC) (Case Study C-4)	Chlorination reaction	Inert solvent	Biodegradable insecticide
Ibuprofen production (CTC) (Case Study C-5)	Solvent for Friedel-Crafts synthesis	Inert solvent	Anti-inflammatory drug
Dicofol (Case Study C-6)	Solvent	Inert solvent	Broad spectrum acaricide
Chlorosulfonated Polyolefin (CTC) (Case Studies C-7a&b)	Chlorination solvent	Inert solvent, safety	High tech coatings, protective materials.
Aramid Polymer PPTA (CTC) (Case Study C-8)	Chlorination specific solvent	Quality, safety waste reduction	Asbestos replacement, public and military safety products
Fluoropolymer resins (CFC-113) (Case Study C-9)	Specific solvent	Specific dispersant, chemical inert	Extreme temperature electric insulation, inert coatings
Synthetic fibre sheet (CFC-11) (Case Study C-10)	Spinning solvent	Quality, safety yield	Protective wrappings, very strong sheets
SBR (CTC) (No Case Study)	Solvent	Chain transfer agent	Synthetic rubber, strong and resistant to extreme temperatures and climate
Chlorinated Paraffin (CTC) (No Case Study)	Solvent	Inert solvent	Lubricant additive, flame retardant for plastics, plasticiser in rubber paints

* for more details see case studies in Appendix C

The preceding table shows that for more than 90% the usual process agent is CTC, two processes use CFC-11 and CFC-113. The widest use of CTC as a Process Agent is in the field of chlorine production. Other uses vary and consist of manufacture of polymers, chlorinated (intermediate) products, pharmaceuticals, pesticides and other agricultural chemicals.

Some process agent uses listed have no known or feasible alternatives at present. However, this knowledge is not static; much progress has been made and will continue in finding solutions or alternatives that reduce or eliminate use of ODS.

2.2 Emissions of Process Agents in Non-Article 5(1) Countries

To show the development of "make up" and emissions of the identified manufacturing processes for Europe, North America and Japan the data are condensed in the following table for the relevant years 1990, 1995 and predictions for 2000.

Table 2.2 - Make up and Emissions of ODS Used as Process Agents for Western Europe, North America and Japan (tonnes/year)

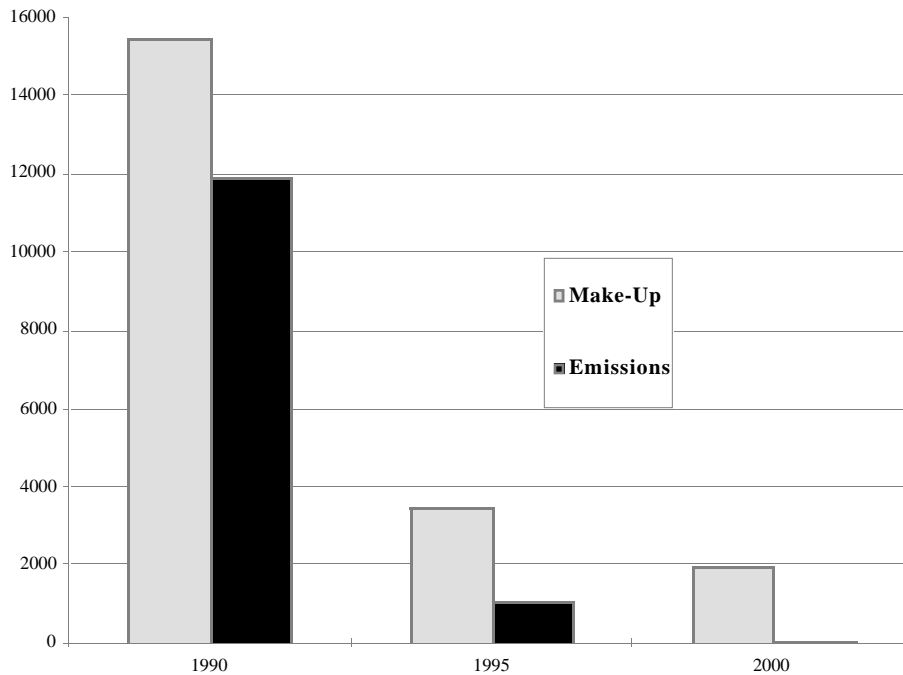
Country	Processes	Make up			Emissions		
		1990	1995	2000	1990	1995	2000
Japan*	All estimated use of CTC as PA	5,321	1,140	0	4,098	750	0
North America	Chlorine production (CTC)	633	633	633	129	4.6	4.6
North America	CSM (CTC)	3,564	717	717	2,847	64	64
North America	Fine synthetic fibre (CFC-11)	2,323	131	0	2,300	130	0
North America	Fluoropolymer (CFC-113)	400	250	0	220	120	0
Western Europe	Chlorine production (CTC)	765	528	500	77	10.5	5
Western Europe	Chlorinated Rubber (CTC)	2,300	27	20	2,200	6.8	4.8
Western Europe	PPTA polymer (CTC)	200	72.5	70	38	2	1
Total		15,506	3,498.5	1,940	11,909	1,087.9	79.4

- use of ODS other than CTC for Japan has not been reported

Comparison between 1990 and 1995 quantities for both make up and emissions demonstrates that substantial reductions have been achieved. These reductions have been achieved as the result of various measures such as plant closure, addition of emission control measures and change in process to use of non-ODS process agents or better utilisation of ODS process agents. Further reductions will likely be achieved as a result of continuing research and development efforts.

The role of voluntary industry standards and national health and environmental regulations is discussed in Chapter 3.

Figure 2.1 - Make up and Emissions of ODS Used as Process Agent for Western Europe, North America and Japan (tonnes/year)



The choice in using 1995 as a starting point was selected as data was not available for 1990. The estimated make up and emissions at present were provided as the result of a survey of the countries for which data is shown. The estimates are lower than those previously estimated in the 1994 PAWG report. The PAWG report based estimates on assumed market growth rather than the survey technique employed in this report.

The potential to reduce emissions in Article 5(1) countries exists using similar measures employed in non-Article 5(1) countries. However, the most cost effective measures will likely be substitution to non-ODS process agents and other changes in processes to eliminate dependency on the use of ODS process agents, where available. The potential for substitution to non-ODS process agents is especially applicable in the production of pharmaceuticals and agricultural chemicals. Process changes to reduce ODS emissions may be effective in large scale facilities, however, for small scale operations such techniques may be difficult to implement.

2.3 Make Up and Emissions in Article 5(1) Countries

The situation for Article 5(1) countries is shown in the table below.

Table 2.3 - Make up and Emissions of CTC as a Process Agent in Article 5(1) Countries for 1995 and 2000*(tonnes/year)

Application	Brazil	China***	India	Indonesia	South Korea	Others	Total
Chlorosulfonated Polyolefin (CTC)		894					894
Chlorinated Rubber		1,200	800				2,000
Chlorinated Paraffin (70% solid grade)		1,250					1,250
Pharmaceuticals	10	228	**584	150			972
Agricultural Chemicals	10	228	700				938
Chlor-Alkali	100						100
SBR	47				600	200	847
Total 1995	167	3,800	2,084	150	600	200	7,001
Estimate 2000	200	6,120	3,354	150	600	200	10,624

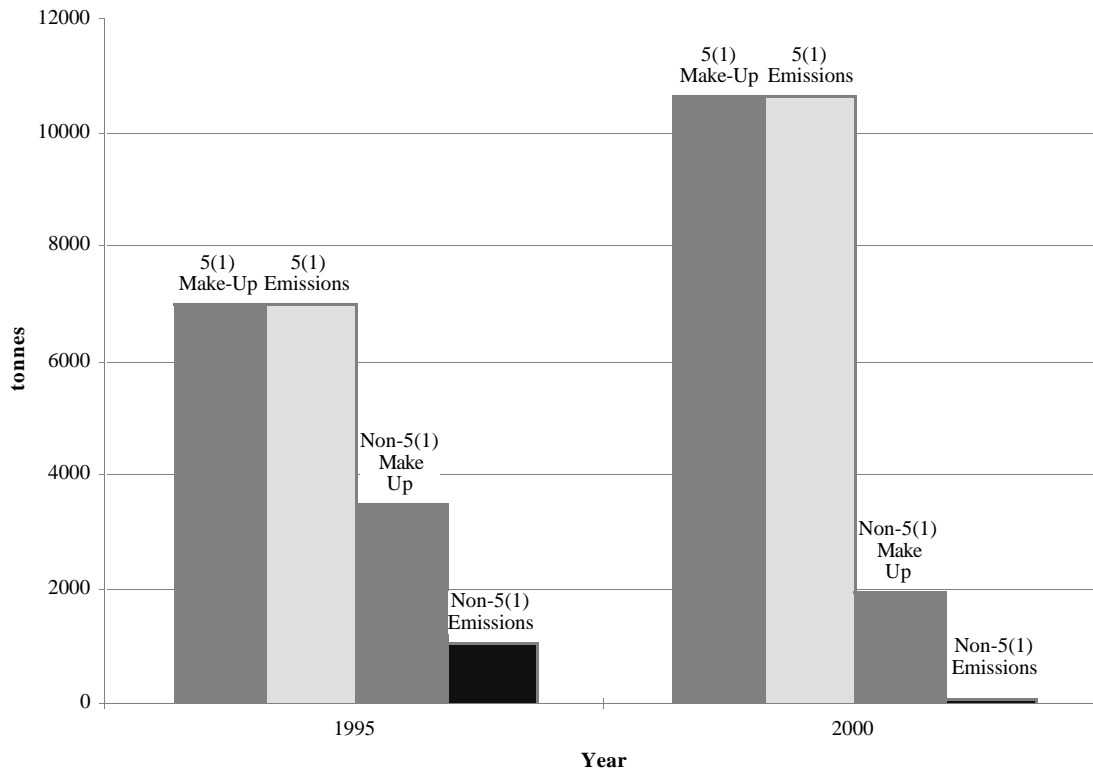
* Make up and emissions are virtually the same. The estimates for 2000 are based on the assumption of 10% annual growth of production volume for China.

** Emissions were previously higher.

*** Figures for China are estimates provided by Dr. Zhang Zhiqun. It was not possible to provide definitive figures for China as a full investigation could not be carried out in the time available.

2.4 Global Estimates

Figure 2.2 - Global Estimate of Emission of ODS Used as Process agents (tonnes/year)



Although the non-Article 5(1) countries have significantly reduced their emissions, global emissions are expected to rise as the result of growth in Article 5(1) countries.

3 MINIMISING AND MONITORING EMISSIONS

3.1 Introduction

This chapter provides an overview of approaches currently in use to minimise and monitor emissions of ozone-depleting substances in process agent applications. As indicated by the Case Studies in Appendix C, all process agent industries operating in non-Article 5(1) countries are subject to specific domestic emission regulations or negotiated government-industry targets which have resulted in the elimination or significant reduction of ODS emissions. In addition to pressure for elimination because of its ozone depletion potential, CTC use in non-Article 5(1) countries has historically been subject to rigorous regulatory control because it is highly toxic.

In the Article 5(1) countries emission standards for CTC and other ODS vary from stringent to non-existent. Widespread knowledge of the health and safety issues of CTC has resulted in reduced emissions, contributing to the goal of the Montreal Protocol. No information is available from CEIT countries.

3.2 Governmental Approaches

The unique legal and industrial circumstances of individual non-Article 5(1) countries have resulted in a broad array of successful approaches for minimising emissions from process agent applications. One Scandinavian country has allowed ODS use only with payment of monetary penalties. Other countries in the EU and North America have adopted more traditional command-and-control measures or negotiated limits established in collaboration with the affected industry or facility. In general, the PATF identified four levels of regulatory approaches used in non-Article 5(1) that have resulted in the very low ODS emissions observed in process agent applications. Although there is a descending order of administrative hierarchy, each of these types of regulations are equally effective. Due the high toxicity of CTC, health and safety standards have often been a driving force behind the rapid emission achievements observed in non-Article 5(1) countries.

3.2.1 Supra-national and Regional Approaches

For example the European Union issues regulations and directives that are applicable in the member states. EU regulations have the force of law; directives mandate more general guidelines and requirements. Member states are required to change national laws and regulations to implement directives but they are free to tailor programmes to meet their needs as long as the programmes provide compliance with the EU regulations.

3.2.2 National Approaches

In many countries national legislation on air, water and waste provide legal authority to meet standards on emission controls and monitoring/reporting requirements for toxic and hazardous chemicals.

3.2.3 Sub-national Approaches

In order to implement national regulatory programmes or through prefecture, departmental, provincial or state legislation, specific sub-national regulations are developed. Often these regulations are more stringent than nationally-set regulations.

Local authorities have a delegated or mandated authority to issue licenses, permits and other controls which limit emissions.

3.3 Voluntary Standards to Reduce Emissions

In some countries and for some applications, voluntary efforts by industry have led to significant reductions in emissions. For example, in Japan the goal of industry has been to voluntarily eliminate all use of ODS as process agents. Industry and trade associations have generated “codes of good practice” as support for members in meeting voluntary standards. Technical directives and guidelines based on proven techniques have facilitated moving process agent applications toward lower emissions. Individual companies using non-toxic ODS have also initiated corporate policies to minimise ODS emissions. Some Article 5(1) process agent users also rely on corporate policies, that may be more stringent than applicable regulatory standards, to minimise ODS emissions in the absence of regulatory standards.

Further details on practical measures to reduce emissions can be found in Appendix A.

4 SUBSTITUTES AND ALTERNATIVES

Identified alternatives to the use of ODS, as shown in the case studies provided in Appendix C of this report, are summarised in the table below:

Table 4.1 - Identified Alternatives to the Use of ODS*

Industry (P.A.)	Application	Alternatives
CS-1 : Chlor-alkali (CTC)	Elimination of NCl_3	No general alternatives. Some plant specific alternatives.
CS-2 : Chlor-alkali (CTC)	Chlorine recovery by tail gas absorption	Plant specific alternatives only
CS-3 : Chlorinated Rubber (CTC)	Chemical inert solvent for high quality product	Aqueous process
CS-4 : Endosulfan production (CTC)	Chlorination reaction	Alternatives available
CS-5 : Ibuprofen production (CTC)	Solvent for Friedel-Crafts synthesis	Alternatives available.
CS-6 : Dicofol	Chlorination reaction	Alternatives available
CS-7a & 7b Chlorosulfonated Polyolefin (CTC)	Inert solvent to achieve desired product quality	Non-ODS alternative for portion of products. No viable alternative to date for others.
CS-8 : Aramid Polymer PPTA (CTC)	Chlorination specific solvent	Plant specific alternatives only.
CS-9 : Fluoropolymer resins (CFC-113)	Specific solvent	Alternative for portion of products. Ongoing programme.
CS-10 : Synthetic fibre sheet (CFC-11)	Spinning solvent	Conversion to non-ODS Process Agent underway.
SBR (CTC) No case study	Chain transfer agent	Mercaptans
Chlorinated paraffin (CTC) - No case study	Inert solvent	Non-ODS process agent.

* for more details see case studies in Appendix C

4.1 Chlor-Alkali Production

CTC is the traditional and efficient agent to extract nitrogen trichloride (NCl_3) from liquid chlorine. NCl_3 is a highly explosive substance inadvertently produced in chlor-alkali plants when the electrolysed salt contains nitrogen derivatives. When production of liquid chlorine is necessary, NCl_3 can build-up to a dangerous concentration.

The obvious ODS free solution is the use of very pure salt. However the availability and/or the transportation of salt of required purity to an existing plant site is often not technically or economically feasible. As a result research efforts for existing plants are focused on:

- selection of a non-ODS process agent
- elimination of the nitrogen derivatives from the salt solution before electrolysis
- destruction of NCl_3
- dilution of NCl_3 in liquid chlorine

The first technique has been abandoned because no alternative process agent has the unique set of required properties (with the exception of chloroform, which is not a true substitute since it is transformed to CTC by reacting with chlorine).

For the latter three possibilities, the question of applicability must be answered case by case as plant design and equipment, nitrogen derivatives and purity requirements for chlorine are very different from one facility to another. For a particular plant, one technique might be a suitable solution, only a partial one, or cannot be safely used at all.

4.2 Recovery of Chlorine in Tail Gas from Production of Chlorine

CTC is the only practical solvent suitable for use in the tail gas recovery process. Strict requirements for stability in the presence of chlorine, corrosivity, acceptable toxicity, mutual solubility with chlorine, and vapour pressure have excluded the use of alternate substances. The absorption/stripping tail gas process allows for essentially complete recovery of all of the chlorine as liquid product. Other technologies do exist for partial recovery of the tail gas chlorine or for conversion of the tail gas to a different product.

One substitute technology is to react the tail gas chlorine with hydrogen to form hydrogen chloride vapour, which is then absorbed in water to form hydrochloric acid. This requires specialised equipment at a substantial cost, and produces a product different from the intended original. This equipment also adds additional safety risk from the standpoint of explosion potential.

Another substitute technology is to install additional liquefaction equipment as a partial alternative to the CTC tail gas process. Additional drying steps using sulphuric acid may be necessary to prevent excessive corrosion in this case. Equipment to perform a neutralisation step with an alkali (or other treatment) must then also follow due to the practical limits to which chlorine can be recovered through liquefaction alone. The product from this neutralisation step must then be disposed of in an appropriate manner.

4.3 Chlorinated Rubber

The search for alternatives has been on many possibilities as there are different processes. Depending on the role of CTC in quality of product and differences in process two main routes can be distinguished:

- Although CTC use is maintained in the process the emissions have been virtually eliminated.
- After 5 years of research and development a water based process has been developed.

The reduction of more than 99.9% in CTC emissions from CR production in the non-Article 5(1) countries, in less than 5 years, shows that CR can be produced by either process in an environmentally responsible manner and represents an enormous success.

4.4 Endosulfan Production

The solvent in the reaction is originally carbontetrachloride. The substitute ethylene dichloride has been developed by one company while another company reports successful use of an aromatic solvent. The adoption of the alternatives requires a change in the production process.

4.5 Ibuprofen Production

It is reported that ethylenedichloride (EDC) is an acceptable substitute for CTC.

4.6 Dicofol Production

It is reported that dichloroethane (DCE) is an acceptable substitute for CTC.

4.7 Chlorosulfonated Polyolefin (CSM)

In North America, no viable alternative has been found for the full range of products and processes of commercial significance. Of the many investigated possibilities chloroform seemed promising, however it leads to a 40% reduction of production capacity and large unavoidable quantities of CTC are inadvertently produced.

In China the possibility of using chlorobenzene as a process agent was investigated, however this option was abandoned for the following reasons:

- Energy consumption is much higher than use of CTC due to the higher boiling point of chlorobenzene;
- Chemical stability to chlorine and sulphur dioxide is lower than that of the CTC process;
- Plant safety was unacceptable due to the flammability, explosivity and toxicity of chlorobenzene.

In Japan, manufacture of fluoropolymer resins has been converted to a non-ODS process utilising a proprietary technology, however the facility does not produce the full range of CSM products.

4.8 Aramid Polymer PPTA

A commercial non-ODS process for the production of the raw material TDC is known. This is however based on a different chemical reaction and the process is carried out with the use of phosgene as a raw material. Such use is only technically and commercially viable when phosgene is already present or is used for more than one product. A research and development programme to find a better corresponding, ODS free, alternative to the existing production process is showing promising progress.

4.9 Fluoropolymer Resins

In North America, close to fifty potential process agents have been explored over the past eight years as part of a research and development programme. It is expected that much of the product line will be converted away from CFC-113 during 1997 and 1998. However, there are still specific critical use applications that have not yet been able to accept the non-ODS products. Efforts are continuing to find an acceptable process agent or suitable processing conditions for these products.

In Japan, manufacture of fluoropolymer resins has been converted to a non-ODS process utilising a proprietary technology, however the facility does not produce the full range of CSM products.

4.10 Fine Synthetic Fibre Sheet

No simple, safe, drop-in candidate has been identified to replace CFC-11 in the existing facilities, despite a continuing (more than four years) programme that has examined over one hundred possible process agents. A non-ODS process agent is in development, but it requires completely new spinning and recovery facilities to use it. Although the first new commercial lines were started up in 1995, it is uncertain when all products will be converted from CFC-11 due to necessary approvals required for some products (e.g. packaging of sterilised medical instruments).

4.11 Conclusions

From an examination of the case studies of the identified processes the following conclusions are offered:

- In most cases emissions from use of ODS as process agents in non-Article 5(1) countries are similar to the insignificant quantities emitted from feedstock uses.
- For all of the identified processes, programmes are underway to find and/or develop alternatives to the use of ODS as process agents.
- Depending on the difficulties of the process under investigation there is a diversity of progress ranging as follows:
 - phaseout achieved or achievable
 - expected phaseout within the next few years subject to solution of final technical issues
 - those processes with extreme difficulty to find an alternative.
- Realising that these results have been achieved over a period of 5 to 6 years, together with measures to significantly reduce emissions, there has been remarkable progress and further progress is expected.

The expectation, is that in the coming 10 years, a substantial part of the use of ODS as process agents will be virtually phased out in non-Article 5(1) countries and that these new technologies can be applied in Article 5(1) countries. Adequate technical and financial assistance will facilitate the implementation of these technologies.

5 ARTICLE 5(1) COUNTRIES

5.1 Emissions of ODS from Chemical Process Industries in Article 5(1) Countries

5.1.1 Use of controlled substances in chemical processes

In Article 5(1) countries, Carbon tetrachloride (CTC) is the main ODS which finds extensive use in chemical processes as an inert solvent medium in carrying out the chemical reactions.

No data came to light on the use of any other ODS e.g. Methyl Bromide in Bromine based processes in Article 5(1) countries. All references in this chapter, therefore, relate to the usage of CTC.

5.1.2 Survey of CTC usage

Country programmes of some major Article 5(1) countries were reviewed in order to identify CTC use and its emissions. On the basis of this study, inquiries were initiated with the relevant government authorities, dealing with ozone matters, in China, Malaysia, Indonesia, Thailand, Egypt, Brazil, Mexico, Argentina and India. Assistance was also sought from Prof. Zhang Zhiqun from China and Mr. Caio Sedenio from Brazil, members of the PATF.

Response was received from the above listed countries except Thailand, Indonesia, Egypt and Mexico. Since the country programmes of Thailand and Mexico did not include any CTC consumption, it has been assumed that the position remains the same. For Indonesia, the CTC consumption of 150 MT which is stated in the country programme for the pharmaceutical manufacture has been maintained.

The position in South Korea was investigated during personal visit, however, it may not be a complete picture.

5.1.3 Industries using CTC in chemical processes

The chemical industries using CTC, excluding those using it as feedstock, in Article 5(1) countries are as follows:

- Chlorosulphonated Polyethylene (CSM)
- Chlorinated Rubber (CR)
- Chlorinated Paraffin (solid, 70% content grade)
- Pharmaceuticals
- Agricultural chemicals
- Chlor-Alkali
- Styrene Butadiene Rubber (SBR)

The survey revealed for the first time that CTC is also being used as a chain transfer agent in the emulsion polymerisation process of SBR in South Korea. Reported CTC consumption for SBR production in South Korea in one industrial unit of 600 MT is quite high and it has been taken into account. A more detailed investigation is needed, including that in other Article 5(1) countries, to further check possible use of CTC for this application.

5.1.4 CTC usage in chemical processes

In Article 5(1) countries, CTC is widely used as a process agent. In the identified chemical applications, CTC is not transformed chemically, as in the case of feedstock use, except to the extent of an unintended transformation/conversion in trace or insignificant quantity. Use of CTC in the aforesaid chemical industries is generally by means of batch operation/process. The quantity of CTC used in the production cycle (i.e. inventory contained within the process equipment) in such operations is large and the bulk of it is recovered and recycled in the system, yet annual loss is significant relative to non-Article 5(1) countries.

The survey shows that in 1995, 72,800 MT of CTC was estimated to be in use in 1995 in the production cycle, as per details given in Table 5.1 hereunder. China and India are the main users of CTC in chemical process industries in Article 5(1) countries.

Table 5.1 - CTC Process Inventory in Chemical Process Industries in Article 5(1) Countries (in metric tonnes)

Country	Year 1995	Year 2000 Projected*
Brazil	447	535
China**	43,400	69,895
India	27,660	44,015
Indonesia	300	300
South Korea	600	600
Others***	393	408
Total use	72,800	115,753

* unconstrained cycle use

** the figures for year 2000 for China are worked out on the basis of 10% growth per annum

*** these figures are indicative only as the survey may not have covered the assessment of CTC use in all Article 5(1) countries concerned

Table 5.2 - Make-up and Emissions of CTC as a Process Agent in Article 5(1) Countries for 1995 and 2000*(in metric tonnes)

Country	Year 1995	Year 2000 Projected**
Brazil	167	200
China***	3,800	6,120
India	2,084	3,354
Indonesia	150	150
South Korea	600	600
Others****	200	200
Total Emissions	7,001	10,624

* Make up and emissions are virtually the same.

* * Unconstrained use

*** The figures for year 2000 for China are on the basis 10 % annual growth

**** These figures are indicative only as the survey may not have covered the assessment of CTC use in all Article 5(1) countries concerned

5.1.5 Emissions of CTC from chemical processes in Article 5(1) countries

The survey shows that in 1995 in Article 5(1) countries, the emissions of CTC from the industries listed under 5.1.3. were about 7,001 MT as given in Table 5.2. However, as further information becomes available, the actual quantities of usage and of emissions of CTC in Article 5(1) countries may be higher.

5.1.6 Application-wise emissions of CTC in Article 5(1) countries

Table 5.3 - Application-wise Emissions of CTC in Chemical Processes in Article 5(1) Countries in 1995 (in metric tonnes)

Application	Brazil	China	India	Indonesia	South Korea	Others	Total
Chlorosulphonated Polyethylene (CSM)		894					894
Chlorinated Rubber (CR)		1,200	800				2,000
Chlorinated Paraffin (Solid, 70% Chlorine content)		1,250					1,250
Pharmaceuticals	10	228	584**	150			972
Agricultural chemicals	10	228	700				938
Chlor-Alkali	100	unkno wn					100
SBR	47				600	200	847
Total	167	3,800	2,084	150	600	200	7,001

** Consumption was higher in the earlier period (see Table 5.5)

A major source of CTC emissions is from CSM and from Chlorinated Rubber production facilities operating in China and India. According to the information available, there exist two plants for CSM production in China. For chlorinated rubber production, there exist eight plants in China and four plants in India.

The amount of CTC use and of its emissions in pharmaceutical and agricultural chemical industries comes next in order of magnitude to that of CSM and CR production facilities.

In the pharmaceutical sector, CTC is being used in India for the following products and its estimates of consumption(emissions) for each product are shown in Table 5.4.

- Bromhexine hydrochloride.
- Cloxacilin.
- Chlorophenesin.
- Diclofenac sodium.
- Ibuprofen.
- Isosorbid mononitrate.
- Omeprazol.
- Phenyl glycine.

A case study on the status of CTC usage in the production of Ibuprofen in India, of which the manufacture is the largest amongst the above pharmaceutical products, is appended in Appendix C-5.

In the agricultural chemicals sector, CTC use in India is in the manufacture of the following products and estimates of consumption(emissions) of CTC in each case are given in Table 5.4.

- Endosulfan (insecticide)
- Dicofol (an acaricide)

Case studies on the status of CTC usage in the production of Endosulfan and Dicofol in India can be found in Appendices C-4 and C-6.

Table 5.4 - Application-wise Usage and Emissions of CTC in India (in metric tonnes)

Product	1995 Process Inventory	1995 Emissions	2000 Projected Process Inventory	2000 Projected Emissions
Chlorinated Rubber (CR)	8,100	800	22,000	1,800
Agricultural Chemicals				
Endosulfan	14,400	590	14,715	604
Dicofol	1,200	110	2,500	250
Pharmaceuticals				
Bromhexine hydrochloride	100	10	500	50
Diclofenac sodium	100	12	160	16
Cloxacilin	100	10	130	13
Chlorophenesin	200	20	200	20
Ibuprofen **	850	271	1,000	320
Phenyl glycine	2,400	240	2,500	250
Isosorbid mononitrate	70	7	100	10
Omeprazol	140	14	210	21
Total	27,660	2,084	44,015	3,354

** About 800 MT of CTC use was phased out in Ibuprofene production in India during the period 1993-1995

5.1.7 Changing pattern of CTC usage in chemical process applications in India

Table 5.4 shows that in India, an estimated quantity of 27,660 MT of CTC was used in the production cycle in 1995 and an estimated quantities of 2,084 MT of CTC emissions resulted from such use.

At the time of preparation of the India Country Programme in 1993, the main source of emission of CTC was identified to be from the production of pharmaceutical product, Ibuprofen. This was estimated at 1,060 MT in the base year 1991. There are, at least, 14 producers of Ibuprofen in India and a number of them have phased out use of CTC and converted their processes using non-ODS solvents. As a result, CTC emissions from Ibuprofen production has already been reduced by about 800 MT, representing the quantity of CTC phased out in period 1993 to 1995.

Currently, other uses of CTC for production of Chlorinated Rubber, Endosulfan and Dicofol are the main sources of emissions of CTC, which are increasing in India.

For the year 2000, the projected unconstrained CTC use is 44,015 MT and the corresponding emissions are projected at 3,354 MT. The profile of the changing pattern of CTC use and emissions in India is given in Table 5.5.

Table 5.5 - Changing Pattern of CTC Emissions in Chemical Process Applications in India (in metric tonnes)

Product	1991	1995	2000 (Projected)
Chlorinated Rubber (CR)	320	800	1,800
Agricultural Chemicals	800	700	854
Pharmaceuticals**	1,060	584	700
Total Emissions	2,180	2,084	3,354

** About 800 MT of CTC use was phased out in Ibuprofen production in India during the period 1993-1995

5.2 Plan for Restricting Use and Emissions of CTC in Article 5(1) Countries

5.2.1 Status of emissions of CTC in Article 5(1) countries in chemical processes

Table 5.2 summarises CTC emissions in Article 5(1) countries, in the identified chemical processes. Use is large and is increasing.

In view of the large emissions, it is inappropriate to consider the use of CTC as a process agent in Article 5(1) countries as analogous to feedstock use.

5.2.2 Reasons for high level of CTC emissions in Article 5(1) countries

The principal reasons for the high level of CTC emissions are:

- (i) The plants and facilities of the user industries in Article 5(1) countries are generally simple batch operations. The effective implementation of emission minimisation strategies to significantly lower down the emissions of CTC is not attainable without carrying out major modification of plants/facilities and installation of new equipment for monitoring, control systems and destruction technologies.
- (ii) There is residual CTC entrapped in the end-products of some processes.

5.2.3 Options for Article 5(1) countries to reduce CTC emissions

Recognising the need to restrict emissions of ozone depleting substances from process-agent applications, the Parties to the Montreal Protocol adopted the Decision VII/10.

In order to comply with their obligations to the Protocol, the chemical process industries in Article 5(1) countries have the following options:

1. Modify production facilities to reduce their emissions to minimum possible levels;
2. Change-over from CTC use to alternative non-ODS solvent use or alternative process/product.
3. Shut-down and/or consolidate small scale plant/facilities.

The implementation of the above stated options by enterprises in Article 5(1) countries requires:

- (i) availability of skilled manpower and their appropriate training
- (ii) technology transfer, wherever warranted.
- (iii) adequate financing

One-time change-over to an alternative non-ODS process/product as per option 2 above, wherever possible, would have a distinct advantage of bringing about the near total phase out of the ODS and would be a lasting solution.

5.2.4 Availability of alternatives

Alternatives to use of CTC in most of the chemical process applications are identified and described in Chapter 4.

The position with regard to conversion to these alternatives in Article 5(1) countries is as follows:

- Producers of Agricultural chemicals, Pharmaceuticals and SBR have more or less identified the suitable non-ODS alternatives which they can use in substitution to the use of CTC.
- The aqueous process for the manufacture of Chlorinated Rubber now in commercial operation, merits consideration for adoption by producers of Chlorinated Rubber in Article A5(1) countries.
- Alternative non-ODS solvents or processes are also now available for some CSM and Chlorinated Paraffin manufacture which can be adopted by A5(1) countries in due course.

5.2.5 Barrier to CTC phaseout in Article 5(1) countries

Conversion from CTC to alternative non-ODS solvents or processes requires capital investment. Several conversion projects have been submitted to the Multilateral Fund. However, as the Parties have not yet established a long term policy for ODS process agents no decision has been taken by the fund.

5.2.6 Phaseout cost

An accurate estimate of the cost of conversion from CTC to available alternative non-ODS solvents or processes can be made only after preparation of project reports.

However, as a general indication, the cost of conversion in pharmaceutical and pesticide industries is of a low order. As an example, the estimated incremental cost of phasing out CTC in Endosulfan manufacture in India with a non-ODS solvent works out to about USD 1.0-2.0 per kg ODP as unit abatement cost. Similarly, for pharmaceutical products also, the conversion cost is likely to be of a modest order.

In the case of chlorinated rubber, the cost of acquisition of technology of the aqueous process and the needed changes/alterations as well as installation of required equipment suiting to the aqueous process would need higher investment. However, the large quantity of CTC emissions from chlorinated rubber manufacture, which are of the order of 2000 MT and which would be abated by adoption of the aqueous process, is expected to bring the unit abatement cost per kg ODP to a fair level.

As a rough and general indication, it may be stated that total phase-out cost of over 10,624 MT of CTC would be of much lesser amount than estimated in the PAWG report which based its assumption on emissions of over 11,737 MT.

5.3 Acknowledgements

This chapter of the report was compiled based on information gathered with the assistance of the following:

- i) Indian Chemical Manufacturer's Association.
- ii) Indian Institute of Chemical Technology (Authors of the draft report on Strategy for the Phase-out of ODS in Solvent Sector prepared for the Ministry of Environment and Forests, Government of India and presented to the World Bank).
- iii) Mr. Liu Yi, China National Environmental Protection Agency, China.
- iv) Professor Zhang Zhiqun, member PATF, Beijing University of Chemical Technology, China.
- v) Mr Caio Sedeno, member PATF, Dow Latin America, Brazil.
- vi) Mr.Y.S.Joh, General Manager-Purchasing, M/s.Korea Kumho Petrochemical Co.Ltd., S.Korea.
- vii) Ms. Maria L. Gomez, Instituto Nacional de Tecnologia Industrial, Argentina.
- viii) Mr. Amer Sofian Mustafa, Dept. of Environment, Ministry of Science, Technology & Environment, Malaysia.

APPENDIX A

EMISSION ABATEMENT TECHNIQUES

The purpose of this appendix is to provide a brief explanation of the function and the general experience of emission reduction techniques and the way they can be introduced successfully.

The first part (A.1) concerns the management aspects and the second (A.2) practical recommendations.

A.1 Developing a Programme

A.1.1 Organisation

Being aware that the problem may grow complex and to secure full co-operation of everyone involved it is wise to inform all company personnel and the authorities concerned about the course of action.

An Environmental Mission Statement should be developed as a first step to clearly communicate the goal and commitment of the programme.

Within the organisation it is necessary to assign responsibility for the programme and its execution. To be informed about the activities and progress, a reporting system is needed.

A.1.2 The situation at the starting point

To avoid confusion it is necessary to fix the starting point as well as possible. Begin by gathering knowledge about the process and all of its emissions.

Where measurements cannot be taken or data are lacking we must proceed by assessments from material balances. Perfection is not necessary at this stage, some 90 % (including the main emissions) will do for developing a first plan of action. Although knowledge about the plant emissions may still be incomplete, a start must be made to avoid undue loss of time.

Recording the progress at this stage is essential for looking back, filling discovered gaps and maintaining the right course.

A.1.3 Establish an action plan

Set out a course to achieve minimal emission. It may be concluded that sophisticated techniques such as end of pipe treatment are unavoidable. However at this stage do not forget that this is a first incomplete impression of the problem and that this may change. Practically it often is observed that more data is required. Make arrangements for measurements to improve the data available. The cost of extra measurements normally outweighs the extra cost of over design. Some surprising results may come up (positive and/or negative).

Continue and give monitoring of waste streams and records of performance a thought because they will be needed in the end. Records of performance can be semi-quantitative, for instance levels of contamination, number of disturbances etc.

At this stage a skilled engineer should begin to look for first step in-house measures based on proven techniques and process conditions and using the concepts of recycling and pollution source elimination. These measures have a good chance to pay for themselves and they help to reduce the magnitude of end of pipe treatments.

A.1.4 Final goals

After this work, which sometimes has to be repeated because of new ideas or new data, it will be clear what final goals must be set. The estimated quantitative emission that remain must be set as a goal, otherwise the goal will become elusive. Next the costs are calculated to evaluate financing so that a final decision can be made for the next steps.

A.1.5 Emissions

A side step to emissions, abating techniques and possible results. There are some 5 mechanisms with which ODS can be emitted to the atmosphere and reach the ozone layer.

1. Direct discharge into air from vents, stacks, process gas outlets
2. From wastewater - slowly emitted into air
3. From products - emission depends on use
4. From (semi)solid waste - emitted from landfill or reclaim
5. From leakage - (small) direct into air

Every mechanism has a number of possibilities in a plant, a checklist will be helpful to identify the sources as exhaustively as possible. Do not neglect the flanges! Have you ever seen a mechanic assembling/unfitting pipelines? Be aware.

A.1.6 Types of abatement techniques

The practical, proven abatement techniques are coupled to the emitting mechanisms. For every mechanism there is more than one abatement technique available.

Abatement techniques for the five sources of emissions are as follows:

1. Air: absorption, scrubbing, condensation, congealment and incineration
2. Water: separators, stripping, adsorption and extraction
3. Product: distillation, crystallisation, stripping and adsorption
4. Waste: incineration
5. Leakage: maintenance

A.1.7 What reductions are possible?

- Air purification: 90 - 99 %
- Water purification: 90 - 99 %

- Product purification: (Product specific)
- Waste destruction: 99.9 %
- Good maintenance: up to 90 %
- Good housekeeping: No incidents

These figures are guidelines and are not meant as a guarantee. The possible reductions are ten to thousandfold. The differences originate from the nature of the process and the type of product produced. Fluid products are simpler to purify than solids. As well, the revenue generated by sale of the final product establishes an important element of the cost effectiveness of the choice of abatement measures. The challenge for the engineers is to select a design that uses the minimal number of techniques, offers lowest operating and maintenance costs and yet satisfies the environmental conditions.

A.1.8 Essentials for achieving emission reduction

The essentials for achieving an acceptable reduction lie in the knowledge of the process and a quality design. The design study is not easy because constraints exist in a working plant which complicate solutions. Assistance of professionals can provide better solutions. For planning projects and project cost therefore enlist the experienced help of an engineering company and the producers of the abatement technologies.

A.1.9 Types of constraints

The possible constraints, as mentioned, are high in number and sometimes complex. To look for a way out a scheme is presented in the practical guide (see A.2); a short summary is presented here.

Physical constraints: originate from temperature, pressure, humidity etc.

Technical constraints: originate from operational safety, type of operation, maintenance.

Organisational: space, facilities, integrated or stand alone.

Economical: investment, operating cost, processing cost of waste.

Environmental: are the standards met?

A.1.10 How to deal with the constraints

In the scheme the selections, that are made, are in ascending order. Every selection narrows the number of possible solutions. (See the scheme in A.2)

The knowledge that zero solutions are unacceptable stimulates the involved engineer. The reward is the proof of compliance.

A.1.11 Engineering characteristics

There are no standard best solutions. Much depends on the skill of the engineer and his knowledge of the process. Generally, sometimes with help, a ready-made solution is found thereby reducing the cost. The involvement on every level provides an assurance that viable solutions will not be overlooked.

A.1.12 Assistance

The proof of the pudding is in the eating. Assistance and advice can be useful when the plan is implemented. Use offered assistance of:

- Successful companies (co-operating process agent users)
- Chemical and Pharmaceutical Institutes
- Trade Associations

A.2 Practical Guide to Emission Abatement Techniques

A.2.1 Losses and loss control

The use of (volatile) chemicals in plants fundamentally leads to losses to the environment. To what extent these losses are acceptable, depends on various factors such as:

- the nature of the chemical (toxic - non toxic),
- the capacity of the plant (losses relative to..),
- the location of the production site (safe to surroundings),
- safety (no explosion hazard),
- the influence on air quality in the plant.

In the case of ozone depleting substances (ODS) this also means that such losses to the atmosphere should be minimised to insignificant levels.

Depending on the situation there are widespread techniques and practices to keep losses to a minimum.

Although this is true, the difference is gradual and depends on the attention that is paid to this subject. Therefore, a general survey of technical measures and techniques is presented here as a stimulus.

A.2.2 Sources of emissions

The losses during production in a plant are emissions to the atmosphere, from water, from products, from soil and from solid wastes.

- Direct losses to the atmosphere can originate from vents, stacks, leaks and spills.

- In wastewater streams losses are possible by dissolved or dispersed ODS, spills, process clean-outs and leaks to cooling water or even to steam condensates.
- In products volatilisation of residual ODS may occur depending on use.
- In soil, contamination may take place by leaks, spills and lack of collecting facilities.
- Process waste may contain ODS in a moderate concentration.

A.2.2.1 Emissions to the atmosphere.

A chemical plant normally has:

- a relief system.
- one or more vent gas systems.
- one or more process gas outlets.

The relief system by design must provide access to the atmosphere to give immediate pressure relief for safety reasons in case of unacceptable over-pressure. This limits the possibilities of emission control. The impact on emissions is negligible when attention is given to:

- A relief system with a header to a blow down vessel and/or a high capacity cooler.
- Design of pressure vessels that allow sufficient pressure interval between action level alarm and relief pressure, thereby reducing the frequency of relief activation.
- Control of relief valve leakage.

The vent gas systems and the process gas outlets can be subjected to ODS capturing techniques; other conditions in the process determine whether this is feasible or not.

There are also losses through flanges, seals, samplers etc. (leakage losses). These losses are readily overlooked but may contribute to a great extent to the total of emissions by the number. In erecting a plant, piping is typically prefabricated to design specifications and dimensions. Erection will show the fit which is never perfect due to the inequalities of fabrication and construction. These inequalities are overcome by gaskets between the flanges that have a limited compressibility. Forcing by high strength bolting leaves strain in the system leading to closure at one side of the gasket but possible leak at the other side. A random check with an organic vapour analyser (or even a well trained dog) will produce an estimate of such losses. Equalising unbridgeable strain by cutting and welding in the field may sometimes be necessary. A maintenance programme, based on emission control after mounting, can reduce these losses to a minimum.

A.2.2.2 Emissions to water

Not only the wastewater but also intermediate flows in the plant may be purified depending on the goal that even may be water re-circulation. The permitted level is according the national or local rules. Treatment of wastewater can bring the remaining concentration down to 0.1 to 0.01 mg/l of the ODS.

A.2.2.3 Losses in products

In products the specification always leaves some room for contamination with other products because the separation techniques are not perfect. In general the specification of contaminants is below a certain limit i.e. 0.1 % or even lower in the case of ODS. Fluid products allow a better purification than solid ones since handling fluids is easier than that of solids. Moreover the rate of chemical and physical processes in solids is considerable lower than in corresponding fluids.

A.2.2.4 Losses in soil

Soil contamination is only reversible at very high cost with techniques in development. Prevention is therefore the best way. Spills and incidents can provide knowledge for correction. Manual handling operations deserve special attention.

A.2.2.5 Losses in waste

Process waste may contain ODS in a moderate but unrecoverable concentration. Also leaks and spills of ODS contaminate solid wastes. These losses only lead to (gradually emerging) ODS emissions when they are in landfill or are reclaimed. Incineration that complies with UNEP guidelines doesn't lead to any significant emission.

A.2.3 Purification techniques and constraints

A number of techniques are available (Table A.1). These can be bought as commodities but a successful application is another thing. There are a lot of constraints that must be taken in account and a thorough check is needed (see Table A.2)

This is neither meant to discourage nor to suggest avoidance. Professional skill can be used to find excellent solutions.

A.2.3.1 Conditions for successful application of purification techniques.

The success of every process, technique or reaction depends on the quality of the knowledge about the materials and the parameters of the physio-chemical system.

Therefore the choice of a purification treatment or system should always be preceded by a thorough study of the range of physio-chemical properties of the materials such as solubility, temperature-pressure relationships, corrosive properties, possible reactions, contamination's etc. and of a study of the physical phenomena like type of flow, magnitude of flow, temperature, pressure, phase transitions etc. The knowledge of these enables one to evaluate the effect of the different unit operations that govern the techniques under study.

Table A.1 - Purification Techniques (not exhaustive)

Waste Stream	Purification Technique
Water	Steam stripping Air stripping Adsorption Extraction Coalescing Filtration
Product	Distillation Stripping Adsorption Crystallisation Heat treatment Vacuum drying
Air	Ventilation control (isolation and vapour recycle) Blanketing Absorption Scrubbing Condensation Stripping Deep cooling (congealment) Incineration
Waste	Incineration Decomposition Transformation

Table A.2 - Constraints

Process	Safety (explosion limits) Composition Pressure Temperature Humidity Particulate matter Corrosion
Technical	Reliability Yield Feasibility Contamination Operation Co-production Recycling possible? Continuous/discontinuous
Organisation	Space for positioning Facilities Integration in process
Economic	Investments Operational cost Energy consumption
Environmental	Meet the standards Unwanted by-products

A.2.4 The quality of knowledge

The better the physical phenomena and properties are known, the better the effect of "in house measures" can be predicted and the better the design of "end of pipe" techniques can be. So knowledge pays more than the cost of it. As an example: when a flow has an uncertainty of 40% an engineer could calculate the design 40% in excess to be sure it will work. The cost of some extra measurements to provide better accuracy is usually less expensive than over sizing.

A.2.5 Looking into the future

With the knowledge at hand the first steps should be the study of the "in-house measures" without any end of pipe (EOP) techniques. Also when EOP techniques are to be installed, this study is a must to reduce the dimensions of the EOP technique and thereby to reduce the cost.

The reduction of ODS emissions with "in house" measures may already be appreciable and sufficient under the circumstances.

However when an EOP technique must be chosen the process of in-house measures must be repeated with the aim to get the best and less costly solution of in-house measures and "end of pipe" technique together. The in-house measures may differ then from the foregoing because another choice of collecting flows for the treatment is necessary.

To give a guide for this process with its different steps and criteria in which technical, economical, environmental and organisation factors play a role a scheme is given at the end of this chapter.

A.2.6 Human factors

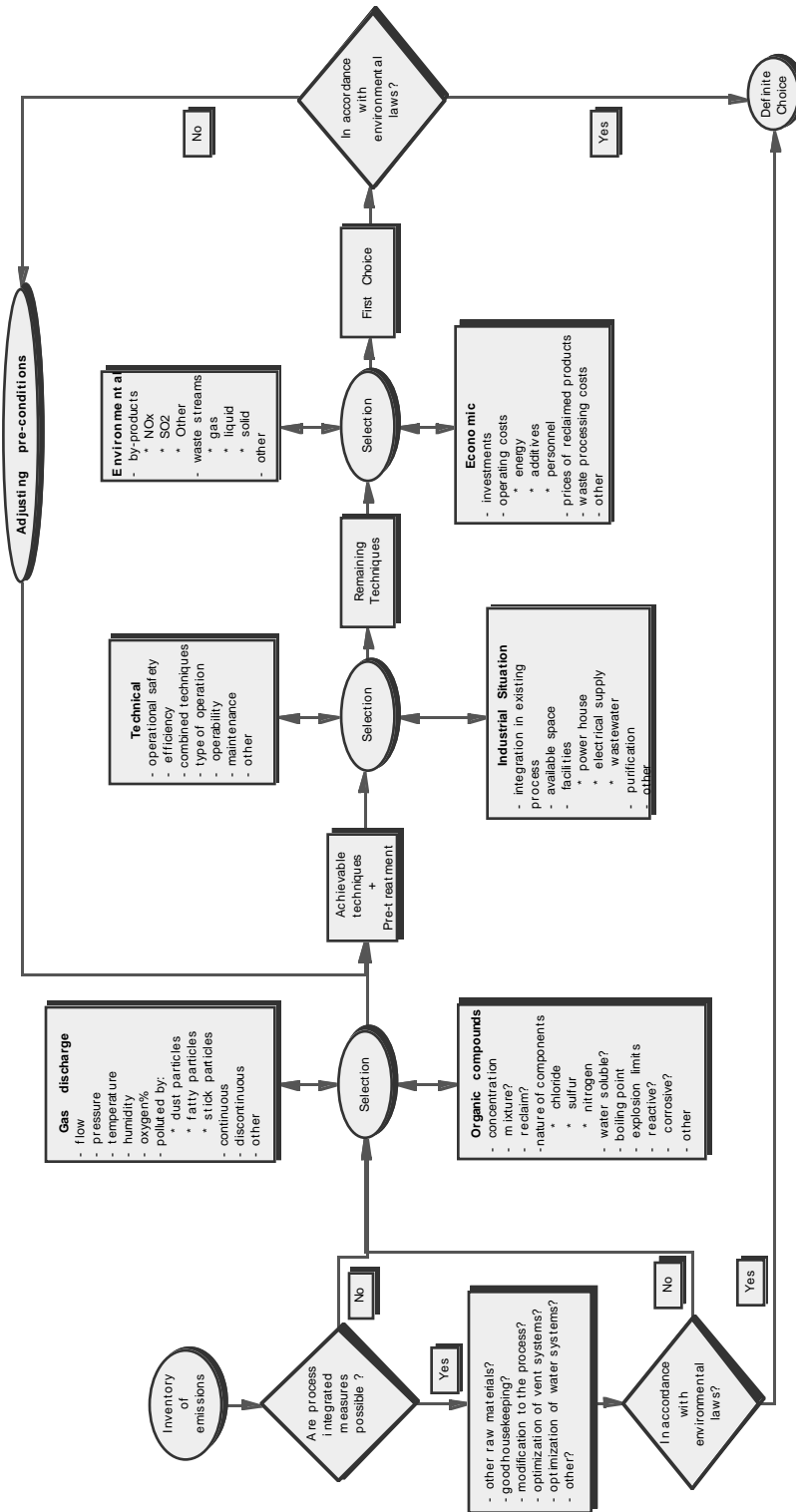
Beside the quality of design and construction the result will be dependent on human operating factors such as:

- operator training on the new part of the job.
- commitment of all plant personal
- (computer aided) assistance
- monitoring and rapid response on deviations
- maintenance according pre-set rules

"The craftsmanship lies in handling the tool smartly."

A.2.7

Scheme of consecutive steps as a guide



A.2.8 Survey of purification techniques for gases

We will differentiate between:

- Systems without "end of pipe" techniques and
- System with "end of pipe" techniques

In both cases there is a difference in achievement of reduction of emission between existing plants and plants to be designed.

In existing plants many choices have been made for other reasons than ODS emission control, so there are generally more limitations in the use of methods of controlling ODS emissions than with plants under design. In practice this will lead to different results with the same techniques in various plants.

A.2.8.1 Without "end of pipe" techniques

Generally the best results can be achieved with integrated systems by fully exploiting the possibilities of:

- selection of flows
- reduction of flows
- recycling of flows
- choosing the optimal conditions to avoid vaporisation of the ODS
- using existing low temperature sources for condensation purposes
- using closed systems containing the ODS
- scrubbing

For every item more than one example can be given but the application is in the hands of the engineer who has also to take in consideration: safety, efficiency, fouling, cost, influence on other process steps, etc.

Examples are:

Selection of flows:	avoid mixing concentrated flows with other flows and look for recycling or cooling and condensing possibilities.
Reduction of flows:	Look for conditions to minimise the flow by proper design of the flow conditions.
Recycling:	Re-circulation of a part of an outlet reduces the end stream with that amount.
Vaporisation retarding :	one can have to do with time sequences in bath processes, temperature and pressure changes. There may be some free or acceptable choices to suppress or prevent vaporisation.

Low temperature sources:	can be used for condensing ODS from gas streams or can be used to get a more favourable temperature for scrubbing etc. The use of the low temperature of liquid Nitrogen, already installed for inerting purposes, is an example.
Collecting systems:	that contain fluids with volatile ODS should be closed to avoid direct vaporisation into the atmosphere here prior to treatment.
Scrubbing:	If ODS is used in a mixture of compounds, scrubbing the outlet gas with a less volatile compound of the mixture, followed by recycling, can lower the loss.

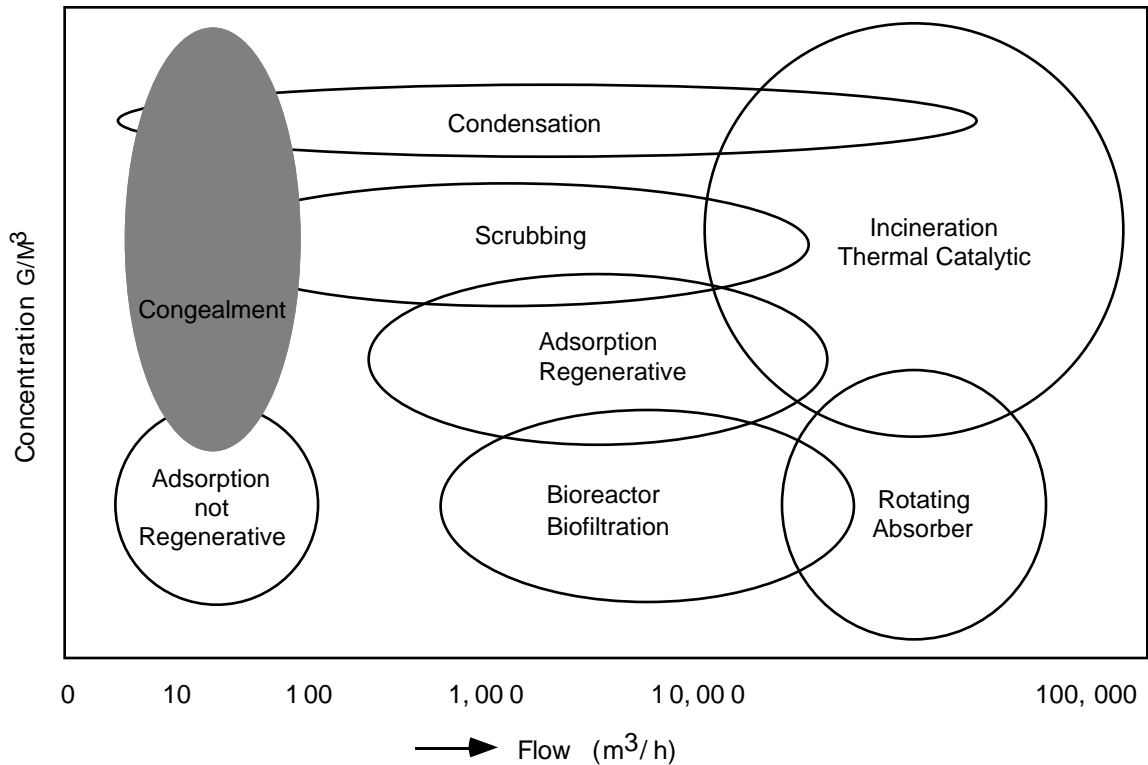
A.2.8.2 End of pipe techniques

Some of these techniques are based on the principles mentioned in 3.1. The difference lies generally in the design properties of the technique and in the conditions that have to be met in using these techniques. (tailor-made design)

These techniques are:

- Adsorption by activated carbon or Macro Porous Polymer
- Absorption by scrubbing
- Condensation by aftercooling or deep cooling
- Incineration (high temperature or catalytic)
- Bioreactor/biofiltration

Global areas in which these techniques normally are applied



A.2.9 Gas purification

A short description of the gas purification techniques:

A.2.9.1 Adsorption by activated carbon

Gases and/or vapours are removed from gas discharges by a physical or chemical binding on the activated carbon. The quality of the activated charcoal determines the efficiency of removal. Also other adsorbents can be used like macro porous polymers, silicagel, mol sieves and alum oxides. Activated charcoal is the most common. Reactivation after saturation is possible with hot air (up to 140°C), nitrogen or steam. The organic components can be reclaimed by condensation (eventually followed by distillation).

Installing of at least two beds makes a continuous adsorption and regeneration possible. A rotating adsorber is also continuous and has its merits with larger gas flows.

The efficiency is generally 90 % when the temperature of the gas discharge is kept between 30 and 40 °C and the humidity at ca 50 %. Feed gases with concentration above 5 mg/m³ should be avoided.

The presence of other components may interfere and lead to a more frequent replacement of activated carbon.

When oxygen is present the temperature of regeneration must be kept under control to avoid a fire by self ignition. Fresh coal must for this purpose always be regenerated with steam to provide enough humidity.

Normal replacement of activated carbon is between 2 and 4 years. Those operations with a regeneration-adsorption unit should be automated to diminish the operating time.

A.2.9.2 Scrubbing

Scrubbing is a common technique to eliminate compounds from gas flows by absorption in a fluid. There are various forms; the difference lies mostly in the way a good gas-liquid contact is secured under operating conditions. Fouling may be a problem and a pre-filter can save a lot of trouble. The efficiency can reach up to 90 %

The technique is suitable for highly concentrated flows. A demister is needed to avoid entrainment. The most profitable operation is when the scrubber liquid can be applied directly in the process; otherwise distilling as a way of separation is common.

In case of oxygen containing flows the explosion limits must be taken in account. Maintenance and operation have often to do with clogging due to dust or sticking particles.

A.2.9.3 Aftercooling and deepcooling

There are two types of condensation apparatus's:

- with direct condensation
- with indirect condensation

With direct condensation the gas flow is cooled by mixing with the cold fluid followed by a separator for the condensate. The condensate is circulated in a loop with a purifying step and an inter-cooler. Lower temperatures can be achieved than with indirect cooling.

While the contact area (the fluid droplets) is constantly refreshed, moisture content to a certain degree (in non aqueous solvents) doesn't interfere at temperatures below zero °C.

Indirect condensation may be a must for reasons of purity or others. The process with humid solvents suffers from ice layer forming on the contact surface so a double system with regeneration is needed for continuous operation. An integrated system, in which a process flow containing the components is cooled and used for direct cooling may be the best solution in this case.

Carbon tetrachloride (CTC) for instance can be cooled down to - 20 °C for reasons of lowering the vapour pressure. (Melting point - 23 °C) In choosing these low temperatures in case of moisture ice crystals may form which can be filtered. The energy consumption can be lowered by taking advantage of already present low temperature sources as for instance liquid nitrogen.

To meet stringent regulations a second purifying technique may be necessary. In that case an optimum on energy consumption can be designed.

A.2.9.4 Incineration.

Incineration is preferred for the high destruction yield of unwanted components. The technique is a powerful one but not without complications (i.e. gas purification). Only combinations for incineration of process tails, unwanted by-products and gases combined with energy conservation (i.e. steam generation) can give a solution at bearable cost at the price of complicated control and/or attention.

A.2.9.5 Bioreaction/biofiltration

For reasons of toxicity for the biomass under the purifying conditions these systems are not used although a lucky combination may be possible. The systems can be characterised as a scrubbing technique with a biomass that decomposes the components absorbed. In case of a disturbance of the conditions the biomass must be reactivated or built up again. These operations are time consuming and for this reason these techniques are avoided in chemical plant operation.

A.2.10 General aspects on wastewater purification in plants

Wastewater purifying techniques are common and well developed. There are however some principles that govern a successful result.

The first of all is quantitative knowledge of the water flows in the plant (i.e. a water balance). The second is a system to keep the flows to be purified within certain limits. If not, the observation is soon made, that the wastewater unit has too low capacity. The reason is that the sewer has always been used as a convenient utility to level out unbalanced flows. The attention for this aspect can hardly be underestimated. Good housekeeping and reuse are the basic means.

The techniques have their own conditions and a basic one is to stay below certain concentration limits to secure the wanted result. Also a selection of flows to be purified is one of the elementary steps. If the wastewater unit then has double the capacity of the prediction there is a fair chance on success.

A.2.10.1 Wastewater purifying techniques.

The unit operations that are common for this purpose are:

- settlers, coalescers, separators.
- clarifiers
- steam strippers, air strippers
- Adsorption coal or macroporous polymer
- distillation
- extraction (mixer/settler)
- filtration

End of pipe techniques are stripping, adsorption and filtration. The best result is achieved by a combination of techniques that complete each other for instance a settler or separator (a trap for droplets in a two phase system) followed by a stripper or an adsorption unit.

It is necessary to keep the pollution concentration in the feed as low as possible when using adsorption columns while the saturated column must be discarded as solid waste. The reactivation techniques in this field are first of its kind.

Intermediate filtration can save a lot of clogging trouble in using an adsorption technique.

Generally the operations are not limited on capacity. However energy consumption and supply of adsorption material are factors in operational cost.

All these unit operations are offered on the market by a variety of companies so no further description is given here.

A.2.11 Rough guidance for choice

The cost of the purifying techniques are dependent of a lot of factors (degree of integration, old or new plant etc. etc.) Therefore no cost figures can be given. However there are some yardsticks for a global indication.

A.2.11.1 Gas purification

If the concentration of the polluting component rises from 1 g/m^3 to 10 g/m^3 the cost is roughly doubled. The same holds for a rise in capacity from $5000 \text{ m}^3/\text{h}$ to ca $30,000 \text{ m}^3/\text{h}$.

With the apparatuses of smaller capacity there is a definite influence of the type of apparatus. Scrubbers are cheapest, followed by adsorbs; incineration is expensive. In the higher capacity region the differences are gradually levelled out by the economy of scale.

A.2.11.2 Wastewater purification

Simple settlers are cheapest followed by more sophisticated separators (tilted plate separator, clarifier)

Stills and strippers are comparable, the availability of cheap energy (low pressure steam or compressed air) can make them more profitable than adsorption techniques.

APPENDIX B REGULATORY REVIEW

B.1 Introduction

This Appendix provides an overview of approaches currently in use in Article 5(1) and non Article 5(1) countries to monitor and minimise emissions of ozone-depleting substances in process agent applications. Differences in national, regional and local standards complicate efforts to compare standards or to estimate the overall burden placed on process agent facilities located in different countries or within a specific country. However, as indicated by the Case Studies, all non-Article 5(1) countries must currently meet specific regulations to minimise emissions of ODS used in process agent applications. In the Article 5(1) countries emission standards for CTC and other ODS vary from stringent to non-existent. Similar to the non-Article 5(1) countries, widespread knowledge of the health and safety issues pertaining to CTC has resulted in some lowering of emissions, and thereby contributing to the goals of the Montreal Protocol. The PATF also considered institutional/regulatory barriers to emission reductions.

B.2 Types of Standards

B.2.1 Regulatory

A number of countries currently restrict ODS emissions in process agent applications through the use of licensing, industry- or chemical-specific control standards or use bans. Mandatory reduction strategies were identified that control direct emissions to air, water, waste and to limit occupational exposures. Specific emission or concentration limits and technical control requirements (e.g. maximum achievable control technologies) are commonly imposed on process agent applications. Ambient release standards and general emission concentration limits are generally linked to the toxicity of the ODS rather than the ODP. Some countries vary emission standards depending on whether production processes are continuous or batch. One country has, however, banned emissions of ODS including uses in process agent applications.

In addition to ambient emission controls, some countries regulate equipment leaks or mandate leak detection and repair programmes that include such control mechanisms as mandated leak detection and repair programmes, periodic monitoring, visual inspections, and instrument monitoring.

Reporting and record keeping requirements are mandated in a number of countries to support the enforcement of emission reduction strategies. In some countries penalties can be applied to both an individual offender within a corporation and the corporation as an entity. Compliance orders outlining activities and a schedule for compliance are other common means of enforcement.

B.2.2 Voluntary and industry set standards to reduce emissions

Several facilities with licensing or other partnerships with non-Article 5(1) based companies reported implementation of corporate-dictated ODS emission initiatives.

Some non-Article 5(1) governments have developed ordinances or guidelines in lieu of or to supplement regulatory requirements. One country reported negotiated but non-binding agreements with process agent sources in order to identify specific control commitments. One country also reported the use economic incentives such as grants or tax concessions to reduce the burden of environmental regulation and encourage environmentally friendly actions.

B.3 Institutional/Regulatory Impediments to Emission Reduction

For pharmaceutical and agricultural chemical products, some countries require additional regulatory review for any formulary change.

C-1 USE OF CTC IN THE ELIMINATION OF NCl_3 IN THE PRODUCTION OF CHLORINE AND CAUSTIC SODA

C-1.1 Introduction

The products made by electrolysis of sodium chloride are:

- Chlorine
- Caustic soda (or potash by electrolysis of potassium chloride)
- Hydrogen

The main uses of these products are shown in the following table:

Chlorine	Necessary for 60% of chemicals and 80% of pharmaceuticals. Water treatment (4%), solvents (6%), chlorinated polymers (41%), non-chlorinated polymers (19%), inorganic chemistry (18%), intermediate chemicals for thousands of products (7%), paper (5%)
Caustic soda	Paper (13%), consumers products (7%), chemicals (54%), others (25%)
Potash	glass manufacture, chemistry, food and cosmetics industries
Hydrogen	very pure product used for chemical synthesis, in food industry or as combustible

Notes to table: % of North American and West European total production where available

C-1.2 Description of overall manufacturing process

Most chlorine and caustic soda are produced by electrolysis of sodium chloride brine. The brine is produced by dissolving sodium chloride crystallised salt (from the sea or mines) or by injecting and pumping water into underground salt veins. The proximity of the source of salt and the availability of adequate electrical power are critical factors in selecting the location of production plants.

The brine undergoes various purification treatment processes. However, the purification processes cannot remove ammonium and nitrogen derivatives present in the salt or in additives (such as calcium ferrocyanide, an anti-caking agent). Ammonium and nitrogen derivatives are typically present in quantities ranging from a few ppm to more than 1000 ppm.

Sodium chloride in the brine solution is split by electric current into chlorine and sodium. Sodium reacts with water of the brine giving caustic soda and hydrogen. Different technologies (mercury, diaphragm, or membrane cells) are used to separate the final products.

Chlorine coming into contact with nitrogen compounds leads to the formation of chlorinated nitrogen derivatives, including nitrogen trichloride NCl_3 .

In certain applications, chlorine must be partially or totally liquefied. It is within this liquefaction process, where chlorine is purified as there is potential for build-up of NCl_3 .

C-1.3 Why CTC is used as a process agent

Quality of final product	XX
Safety	X
Necessity for the chemical reaction	
Yield	
Cost	
Other	

Notes to Table: X signifies the main purpose, XX signifies a secondary purpose

C-1.3.1 Quality of final product

CTC is used to extract the nitrogen trichloride (NCl_3) from the chlorine. Other impurities, both inorganic and organic, are also extracted. Consequently, the liquid chlorine produced from such processes has a high purity level (>99%), with only a few ppm of CTC (<10 ppm).

C-1.3.2 Safety in production, transport and use of liquid chlorine

At concentrations above approximately 3%, NCl_3 has a high explosion potential. Explosion can result from even low physical impact, from exposure to heat or flame, or from spontaneous chemical reaction. Some common materials initiate the decomposition of NCl_3 , particularly when it contains impurities.

NCl_3 has a higher boiling point (+71°C) than chlorine (-34 °C) and as liquid chlorine evaporates, the concentration of NCl_3 increases in the liquid chlorine remaining in vessels from which gaseous chlorine is withdrawn.

Many severe accidents, including fatalities, resulting from NCl_3 explosions have been recorded. To avoid any risk of concentration higher than 1%, Euro Chlor specifically recommends that maximum levels of NCl_3 in liquid chlorine must be maintained below

20 ppm during chlorine production and not exceed 2 ppm for large storage tanks and transport containers of liquid chlorine.

To produce liquid chlorine complying with this recommendation, the distinctive physical and chemical properties of CTC facilitate the efficient extraction of NCl_3 when the total nitrogen in the brine is not sufficiently low, or cannot be reduced to a safe level.

C-1.3.3 Unique properties of CTC required for this application

Carbon tetrachloride :

- is an excellent solvent of chlorine and NCl_3 ;
- has a boiling point (+77°C) much higher than chlorine (-34 °C), but near the boiling point of NCl_3 (+ 71°C), which is important to keep NCl_3 in solution with CTC and separate chlorine;

- is stable in the presence of chlorine;
- is inert and not corrosive.

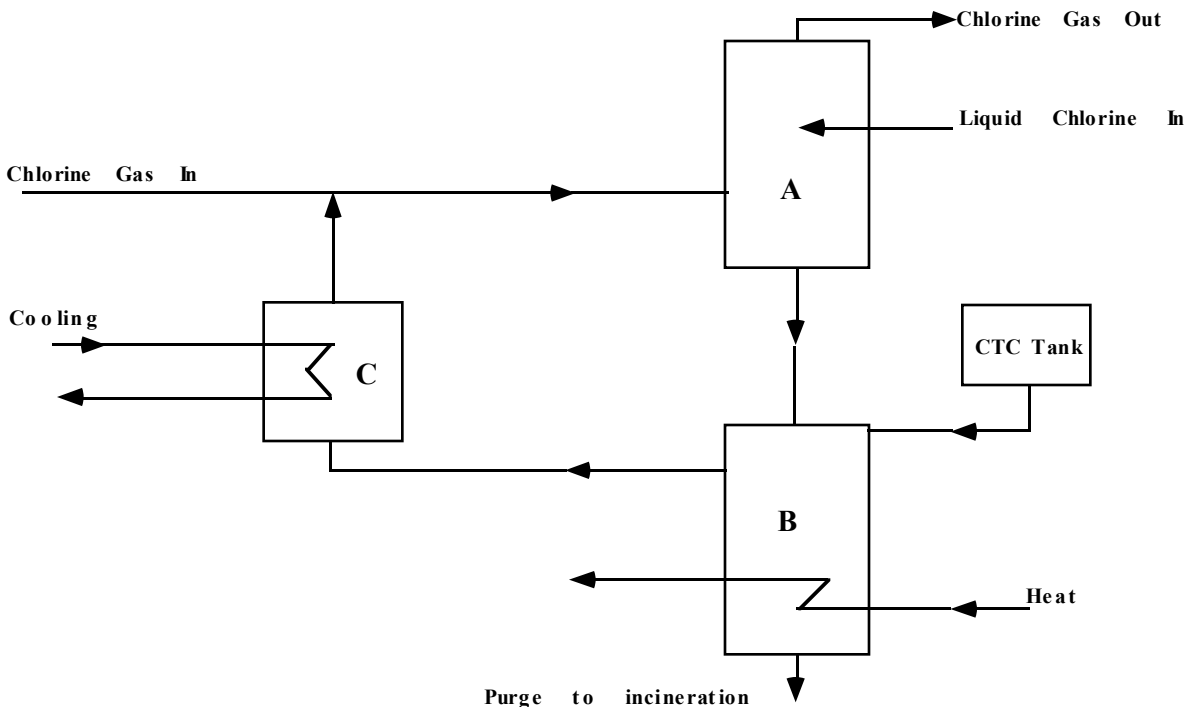
C-1.4 How CTC is used as a process agent

The process used to eliminate NCl_3 with CTC depends on many factors: level of nitrogen derivatives in the salt sources and its variation, electrolysis and liquefaction processes, design and equipment of the facilities, chlorine purity required, etc. The general scheme is as follows:

Before compression to get liquid chlorine, chlorine gas is washed in a column (A in the flow diagram) with liquid chlorine in order to extract heavy impurities such as NCl_3 . Impurities accumulate in liquid chlorine at the bottom of the column. To avoid achieving explosive concentrations of NCl_3 , chlorine with the diluted impurities, including NCl_3 , is drained periodically into a separation tank B where CTC is used as an inert diluent of NCl_3 . From this vessel, chlorine evaporates to go back through a cooler C to the cooling/compression process. In some plants, NCl_3 is slowly decomposed by heat (around 50-60 °C) in the tank B (then called reboiler or destruction reactor).

In both cases, the CTC contaminated with some NCl_3 and other impurities is periodically drained and destroyed.

As an alternative, the mixture of chlorine, CTC and NCl_3 can be evaporated from the separation tank into a caustic soda solution: NCl_3 decomposes into nitrogen and chlorine, chlorine reacts to form sodium hypochlorite and CTC is incinerated.



C-1.5 Quantity of CTC required for make-up

In 1990, the yearly make up of CTC to compensate for the quantity destroyed when used for eliminating NCl_3 was 810 tonnes for 21 plants using this process.

In 1995, the make -up quantity fell to 650 tonnes: 550 tonnes in non-Article 5(1) countries and 100 tonnes in Article 5(1) countries. A further decrease is expected in the near future.

C-1.6 Pollution abatement

C-1.6.1 Emissions

The emissions of CTC were 273 tonnes in 1990 for 21 plants using this process. In 1995 emissions had been reduced to 112.4 tonnes: 12.4 in non-Article 5(1) countries and 100 tonnes in Article 5(1) countries. A further substantial decrease is expected in the near future in non-Article 5(1) countries.

C-1.6.2 Technology (generally used, or to be used in the near future in non-Article 5(1) countries).

The removal of NCl_3 by CTC is conducted in sealed vessels and under permanent operator monitoring. The traces of CTC in chlorine (a few ppm) cannot be emitted as any minute leak of chlorine is detected and eliminated.

The recovered contaminated CTC is transformed to hydrogen chloride and carbon dioxide in a special chlorinated products incinerator. The destruction efficiencies of such incinerators is at least 99.99% to comply with the Montreal Protocol.

C-1.6.3 Regulations affecting operations

Numerous regulations promulgated and implemented in the different countries apply to the operations of this application, as chlorine and carbon tetrachloride are subject to strict controls independently of the ozone depleting potential of CTC. These regulations include monitoring and reporting provisions, the frequency and detail of which depends upon the regulation, the location of the facility and its regulatory status.

For example, in the United States of America, these regulations include the National Emissions Standard for Hazardous Air Pollutants established under the Clean Air Act and incineration standards established under the Resource Conservation and Recovery Act.

The US EPA requires that permits be granted to operate such facilities. The permits require emission control technology for all facilities and set maximum allowable CTC emissions.

C-1.7 Opportunities for Substitutes without CTC and Limitations

C-1.7.1 Identical products produced without the use of CTC

C-1.7.1.1 Elimination of nitrogen compounds from the brine

Such processes which include stripping, oxidising or heating the brine, only affect the ammonia and other volatile impurities. Depending on the nature and contents of the various nitrogen derivatives in the brine, these processes can eliminate NCl_3 , or they can lead to a preliminary and partial purification. The latter makes it possible to reduce the consumption of CTC.

C-1.7.1.2 Elimination of NCl_3 by destruction

Process specific reduction of NCl_3 to a safe concentration may be achieved by: U.V. radiation, thermal decomposition, chemical destruction and catalytic decomposition. According to the variety of the parameters, experimentation of such processes in some plants entails major operating problems or shows limited efficiency raising thereby safety concerns.

C-1.7.1.3 Elimination of NCl_3 by extraction with other solvents:

A survey of 226 other solvents scanned for solubility and physical parameters selected 21 products fitting such criteria, but none satisfied the criteria of inertness to chlorine. A specific case is chloroform, which could be used but which is in fact converted to CTC after reaction with chlorine.

A few facilities where NCl_3 levels are relatively low are using liquid chlorine to dilute NCl_3 . Such system is specific to process and equipment and must be purged more frequently with significant increase of waste streams and of risk of chlorine exposures for plant personnel.

As the configuration of chlorine facilities, nitrogen derivatives in the brine and purity requirement for chlorine vary considerably across the world, the above substitutes —C-1.7.1.1 - C-1.7.1.3— are only feasible and used in some plants but cannot be implemented in other plants.

C-1.7.1.4 Supply of very pure salt

This alternative is used in some countries. But a long term experience shows that sea salt is not, in all countries, pure enough to get the very low level of nitrogen derivatives required i.e. <1 mg/kg.

Chlorine facilities in North America and Europe have been specifically located next to salt mines or brine sources to make them commercially viable. The downstream facilities were settled in close proximity of chlorine production to avoid the risk of transportation. Changing the location of chlorine facilities will upset a lot of industries.

In Europe, it has been estimated that for a 200,000 tonne s/year capacity plant, transportation of pure salt from far away sources would require for unloading, storing and dissolving shops an investment of (US \$) 8 M and extra operating costs would reach (US \$) 36 M annually.

C-1.7.2 Alternative products for the same application produced without the use of CTC

There is presently no direct substitute of chlorine. For some derivated products, substitutes are under development, but they will eventually represent only a small percentage of chlorine uses.

Substitution of caustic soda by soda ash could only cover a limited number of applications of caustic soda.

C-2 USE OF CTC IN THE RECOVERY OF CHLORINE IN TAIL GAS FROM PRODUCTION OF CHLORINE

C-2.1 Introduction of Process

This description applies to the use of CTC as a process agent in an absorption/stripping process in the recovery of chlorine from tail gas produced in the chlorine manufacturing process.

C-2.2 Products Made, Use of the Products

The process agent use of CTC described below is associated with production of liquid chlorine (Cl_2). Chlorine has many essential uses including the purification of drinking water and the production of countless commercially important materials and products.

C-2.3 Description of Overall Manufacturing Process

Sodium chloride salt (NaCl) is dissolved in water and this brine is electrically decomposed into chlorine gas (Cl_2), sodium hydroxide liquid (NaOH) and hydrogen gas (H_2).

Hot, wet chlorine vapour is cooled, dried, compressed and refrigerated until the majority of the chlorine condenses to a liquid product. Uncondensable gases such as oxygen and hydrogen limit the liquefaction rate to avoid reaching an explosive ratio of H_2 / Cl_2 in the gaseous phase. According to specific process design the liquefaction must be limited to between 70 to 95% of the production. The uncondensed vapours, or tail gas, contains 50 to 60% chlorine by volume. Essential safety and good recovery of chlorine requires additional processing steps to separate the chlorine from the inert gases.

C-2.4 Why CTC is Used as a Process Agent

CTC is used as a process agent to separate the residual chlorine from the inert vapours present in the chlorine tail gas, and recover it in a usable form.

The use of CTC as a process agent in tail gas recovery has several advantages when used in conjunction with other equipment that limits emissions to the environment. The CTC based process is proven, reliable, safe, and has minimal environmental impact.

CTC is the only practical solvent suitable for use in this tail gas recovery process. Strict requirements for stability in the presence of chlorine, corrosivity, acceptable toxicity, mutual solubility with chlorine, and vapour pressure have excluded the use of alternate substances.

C-2.4.1 Quality of final product

The CTC process can produce a high purity product. One North American company uses the CTC based tail gas process to produce a custom chlorine product of greater purity than the standard chlorine product. The CTC content of this product is typically less than 10 ppm.

C-2.4.2 Safety with in-plant production

The safety of the CTC based process for the recovery of tail gas has been demonstrated in over than thirty years of reliable and effective service.

This CTC technology also provides the capability to recover the chlorine from equipment to be repaired or serviced.

The CTC process is also more dependable than a substitute technology of combusting the tail gas with hydrogen. The flame safety control systems required to prevent the explosion of the Cl_2/H_2 combustion equipment also result in less reliable operation. The combustion substitute also cannot be used for depressurizing and evacuation of equipment under repair.

C-2.4.3 Cost of use

Properly operated and maintained CTC based tail systems are a low cost method of recovering tail gas chlorine as usable chlorine product. The cost of the substitutes depends on the value of other end products and disposal costs of any wastes produced using substitute technologies.

For facility expansions, modification of existing tail gas systems would likely be considerably less expensive than conversion to an alternate technology. With proper controls, facility expansions would likely not result in any significant increase in atmospheric emissions of CTC.

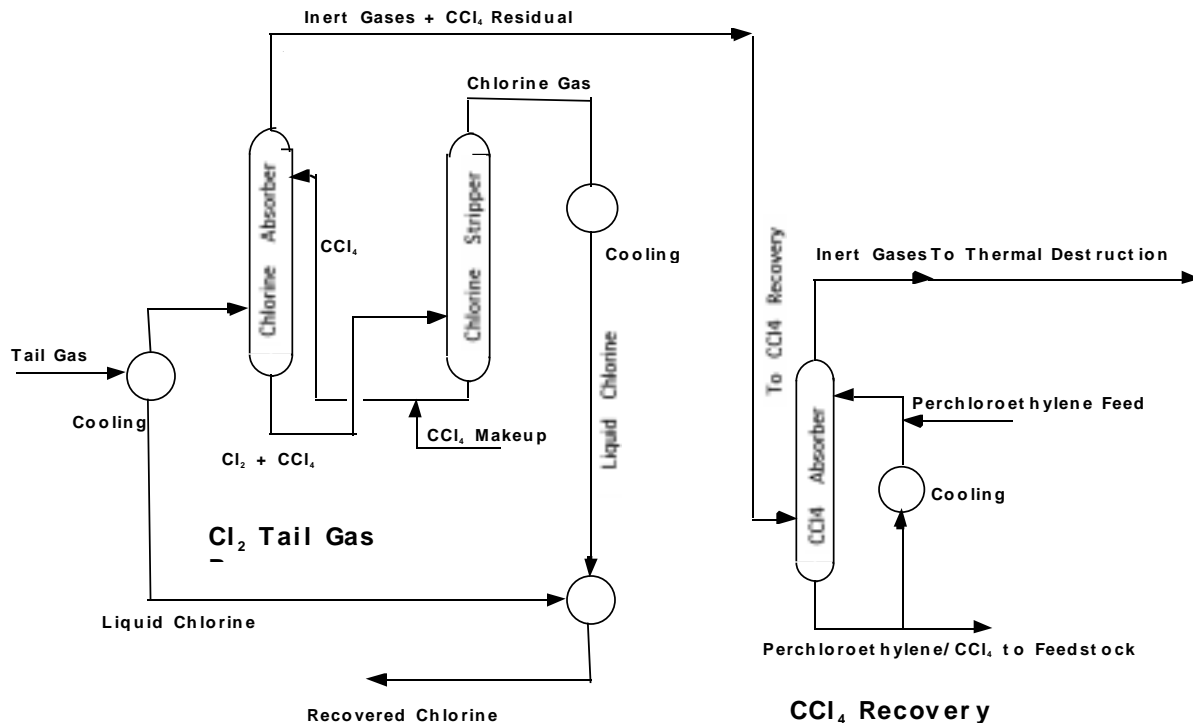
C-2.5 How CTC is Used as a Process Agent

In the tail gas recovery process, the chlorine is first compressed and cooled further to recover some additional chlorine. The remaining inert gas and chlorine vapour mixture is then scrubbed with cold liquid CTC in the chlorine absorber tower. The CTC absorbs the chlorine, and the chlorine-free inert gases are discharged from the top of the tower. The liquid CTC containing the chlorine is removed from the bottom of the absorber and is sent to the chlorine stripper tower. In this tower, the cold CTC/ Cl_2 mix is distilled. The chlorine is vaporised, purified, and condensed to a liquid product. The CTC, now free of chlorine, is cooled and recycled to the chlorine absorber for re-use.

C-2.6 Flow Diagrams

A general process flow drawing describing both the use of CTC as a process agent as well as the downstream treatment to limit CTC emissions follows:

Chlorine Tail Gas and CTC Recovery



C-2.7 Pollution Abatement

C-2.7.1 Efficiency of recovery of the CTC after use

The overall CTC recovery efficiency of a tail gas recovery system combined with downstream processing is extremely high, with approximately 0.25% of the annual CTC make-up potentially being emitted to the atmosphere.

Refrigeration is used to both enhance the recovery of the tail gas chlorine as well and prevent the loss of solvent. The percentage of recovery of CTC on each pass through the system is extremely high. However, due to the large number of cycles, a measurable loss of solvent does eventually occur, and make-up CTC must be added to the system.

C-2.7.2 Final Disposal of CTC

The majority of the CTC leaving tail gas recovery process is present in the inert purge vent(s) from the chlorine absorber tower.

The inerts purge vent is then processed further to recover or destroy the CTC content of the vent stream. The vent is either incinerated at high temperature or otherwise destroyed, or the CTC is extracted using a heavier solvent and recovered or transformed.

C-2.7.3 Quantity required for make-up

The amount of CTC used for make-up in the described tail gas process is approximately 290,000 kg (290 MT) per year. The CTC make-up quantity is much larger than the actual atmospheric emission that occurs as a result of this process agent use.

For one chlorine manufacturer's application of the CTC tail gas process agent technology, the direct atmospheric emissions after vent processing are estimated at 700 kg (0.7 MT) per year, only 0.24 percent of the CTC make-up. The process agent use described here recovers the tail gas from the generation of over 500,000,000 kg (500,000 MT) of chlorine per year.

C-2.8 Opportunities for Substitutes without CTC and Limitations

CTC is the only practical solvent suitable for use in the tail gas recovery process. Strict requirements for stability in the presence of chlorine, corrosivity, acceptable toxicity, mutual solubility with chlorine, and vapour pressure have excluded the use of alternate substances. The absorption/stripping tail gas process allows for essentially complete recovery of all of the chlorine as liquid product. Other technologies do exist for partial recovery of the tail gas chlorine or for conversion of the tail gas to a different product.

One substitute technology is to react the tail gas chlorine with hydrogen to form hydrogen chloride vapour, which is then absorbed in water to form hydrochloric acid. This requires specialised equipment at a substantial cost, and produces a product different from the intended original. This equipment also adds additional safety risk from the standpoint of explosion potential.

Another substitute technology is to install additional liquefaction equipment as a partial alternative to the CTC tail gas process. Additional drying steps using sulphuric acid may be necessary to prevent excessive corrosion in this case. Equipment to perform a neutralisation step with an alkali (or other treatment) must then also follow due to the practical limits to which chlorine can be recovered through liquefaction alone. The product from this neutralisation step must then be disposed of in an appropriate manner.

C-2.8.1 Cost comparison

For one manufacturer alone, replacement of the existing CTC based tail gas systems is estimated to have a capital cost of (US) \$10-\$15M. This expenditure, which does not include any increase in operating expenses, would reduce process agent use of CTC by about 290,000 kg/yr (290 MT). The atmospheric impact would be minimal due to process controls already in place. Atmospheric emissions of CTC would be reduced by only 700 kg/yr (0.70 MT)/

The capital expenditure to reduce CTC emissions are estimated to be a (US) \$14,000 - \$21,000 per kilogram of annual CTC emissions reduction, using either of the substitute technologies discussed above. In comparison, a recent vent incinerator installation at one of the sites using this process agent technology had a capital cost of about \$100 per kilogram of annual emissions reduction.

C-3 USE OF CTC IN THE CHLORINATED RUBBER PROCESS

C-3.1 General

Chlorinated rubber (CR) type resins are a group of resins prepared by chlorination of aliphatic hydrocarbon polymers, such as polyethylene, polypropylene, polybutadiene, and synthetic or natural rubbers. The chlorination degree is about 30 to 70 % (low to high chlorine content).

The resulting resins are thermoplastic, odourless and non-toxic. They are freely soluble in organic solvents and are compatible with various other resins such as alkyds, vinyl's or chloroparaffines. When the resultant coatings are applied to the surface of metal, concrete, paper, wood etc., they leave a transparent, hard and lustrous glass-like film, which resists the permeation of moisture, oxygen gas, salt, acids and alkalis. These characteristics have made CR type resins ideal for use as the binder of corrosion-resistant paint, (e. g. ships, especially underwater and anti-fouling paint, containers, bridges and other steelwork), highly durable road marking paint, gravure printing ink and as a component of various types of adhesives (especially for heavy duty adhesives connecting rubber and steel in automotive constructions). This wide field of different applications can be achieved by changing the raw material, the viscosity of the polymer, and the degree of chlorination.

Further advantages of CR-based resins are the easy formulation and wide variety of the resins; simple reparability even after many years; the easy application by brush, roller or spraying (e. g. airless) under even unfavourable climatic conditions (high or low temperatures or humidity); the fast drying and recoatability and last but not least the especially favourable ratio of price to performance. This is why CR is especially used in Article 5(1) countries.

To manufacture CR, the raw material is first dissolved in carbon tetrachloride (CTC). Chlorine gas is introduced into this solution and reacts with the raw material to form CR. The solution is then introduced into boiling water. The CR is precipitated, and the solvent vaporises. The CR is separated from water, rinsed, dried and ground to form a white powder which is the saleable product. After removal of the water, chlorine, hydrochloric acid and other impurities the solvent is reused.

C-3.2 Why CTC is Used as a Process Agent

CTC is used as the process agent because, of all the many solvents which are compatible with both the reaction components and the end product, it is the only one which is not attacked by chlorine. The special configuration of CTC allows smooth chlorination conditions (short time, low temperature) and results in a uniformly chlorinated polymer. At the recovery of chlorine and separation from hydrogen chloride it is also a unique and safe medium, preventing an explosive reaction between hydrogen and chlorine.

C-3.3 CTC Emissions

In 1990, CTC emissions from CR-production in non-Article 5(1) countries totalled 4,300 tonnes. By 1995, emissions had fallen to approximately 6.8 tonnes. Further reductions are planned. One plant in Germany was able to reduce emissions to 300 kg/year.

Chlorinated Rubber Production with CTC

Country	Number of production sites	1995 CR production (tonnes)	1995 CTC-emissions (tonnes)
Germany	1	7,000	0.3
Italy	1	2,000	6.5
China	8	1,000	1,200
India	4	1,600	800
Total	14	11,600	2,006.8

In Article 5(1) countries, the situation is completely different: CTC-emissions are 0.5 to more than 1 tonne per tonne of CR-production. The investment and operating costs of the environmental technology for a modern CR plant account for more than one-third of the total costs. The expenditure for a sustainable reduction of emission from these plants is very high.

C-3.4 Bayer Chlorinated Rubber Process

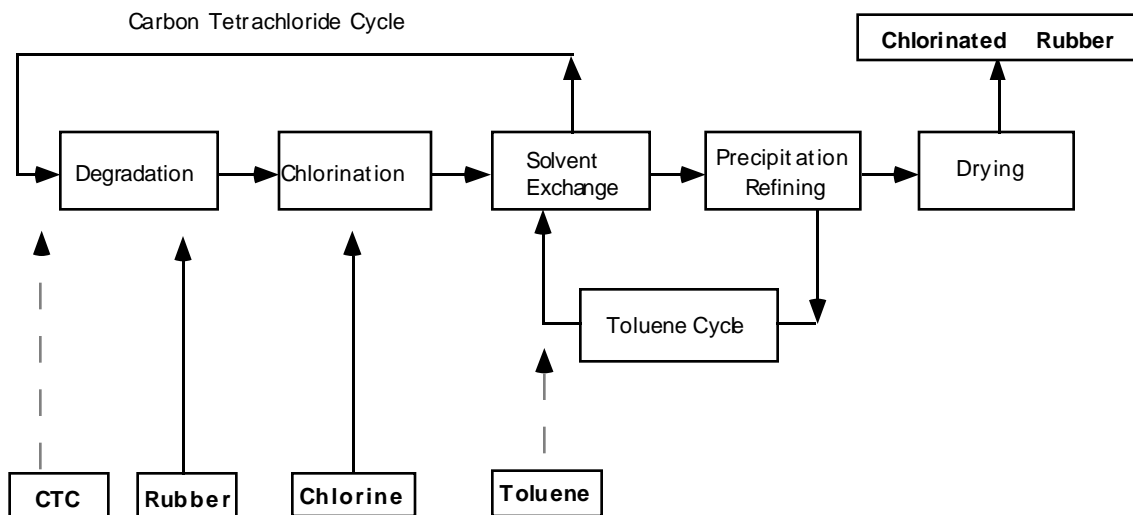
C-3.4.1 Process

In Germany, Bayer has been producing chlorinated rubber (CR) for almost 70 years. As a raw material, it uses a special natural rubber, polyisoprene and polybutadiene. As the molecular chains are too long, the chains first have to be split. This is done in a radically initiated degradation step. As CTC is not flammable, this can be performed safely in the presence of oxygen which improves the process. After that, chlorine gas is introduced into this solution and reacts with the raw material to form CR.

Due to the strong affinity of CTC for solid CR, 1 - 10 % of CTC would remain in the CR leading to high CTC losses and emissions. Bayer therefore designed a solvent exchange process in which, after chlorination, CTC is completely exchanged with toluene in a distillation column. Thus, virtually no CTC is emitted from the washing and drying process or carried away in the CR itself, which contains an average of less than 10 ppm CTC - this is only 70 kg/y at a production of 7,000 t/y. After removal of the water, chlorine, hydrochloric acid and other impurities, the CTC is completely reused.

The toluene solution is then introduced into boiling water. The CR is precipitated and the toluene vaporises. The CR is separated from the water, rinsed, dried and ground to form a white powder which is the end product (see flow chart). The toluene is recycled to the solvent exchange unit.

C-3.4.2 Flow chart



C-3.5 Pollution Abatement

German environmental regulations provide stringent requirements to continuously reduce emissions. Thus, CTC-emissions from the Bayer-CR-plant were reduced from about 450 tonnes/year in 1989 to about 300 kg/year in 1993 and thereafter. They are much lower than German regulations require. Installations using CTC require a license which includes special construction, operating, safety, monitoring and environmental reporting measures. For this reason, Bayer established a closed and highly contained process system. Specific emission figures are:

Offwater (22nd Offwater Regulation):	2.00 mg/l
Bayer (after stripping and sewage plant):	0.05 mg/l
Offgas (Technical Instruction Air):	20.00 mg/m ³
Bayer (after adsorption on activated carbon):	0.25 mg/m ³
Product and Residue (Hazardous Substances' Regulation):	≤ 0.1 % = 1,000 ppm
Bayer (after solvent exchange):	0.001 % = 10 ppm
Max. concentration in air inside the plant (MAK)	65 mg/m ³
Bayer:	< 0.1 mg/m ³

The Bayer site at Dormagen where CR is produced, is certified according to the European ECO-Audit-Regulations. The CR process is continuously monitored and audited. Local and governmental authorities are regularly informed about the CR process. Thus, after the improvements of the process in the last few years, a completely new and elaborate description of the process and its safety and environmental installations was submitted to the authorities. After checking the process the license was renewed. Figures detailing the amount of CTC and its concentration in off-gas are sent to the local government every two years.

Although CTC is inert to chlorination, it slightly reacts in the presence of moisture by chlorinating the rubber. The moisture is introduced with the CTC itself and especially with the rubber. The decomposed amount of CTC must be replaced but is not emitted, of course. The annual make-up of CTC for this process is about 20 tonnes/year, only 0.3 tonnes/year of which

are emitted. With additional small portions of water, the consumption of CTC for the chlorination of rubber would increase substantially and its feedstock use would be more evident.

Further reduction of emissions below 300 kg/year would be extremely difficult and expensive to achieve, however, an increase of production could be achieved in the facility without any increase in emissions.

C-3.6 Substitutes and Alternatives

In general, the Bayer production process has been used world-wide by many companies with insignificant variations. Its advantage is that the reaction and solvent recovery are simple. On the other hand, it requires a high technical standard to prevent emission of CTC. CTC vaporises very readily, not only from open containers but also from small leaks in flanges, mixer shafts, pumps, etc.

These difficulties have prompted many attempts to modify the production process or to find alternatives to CTC as the process agent. Between 1949 and 1951, for example, a number of patent applications were made in which aqueous latex dispersions were chlorinated instead of the CTC solution. In spite of many efforts at that time there were poor results.

In 1989 when it became known that CTC depletes the ozone layer, the major CR manufacturers formed the Chlorinated Rubber Environmental Working Group to develop measures to reduce CTC emissions. However, their starting positions and the regulatory frameworks in which they operated varied so widely that each of the companies achieved the objectives set in very different ways:

- Almost 50% of the world's production capacity of some 40,000 tonnes/year was shut down (UK, USA), because companies felt that any investment in improving old plants or building new plants would not be cost effective.
- Japanese manufacturers stopped using CTC and succeeded in developing the aqueous process.
- Due to the strong affinity of CTC for solid CR, 1 - 10% of CTC would remain in the CR leading to high CTC losses and emissions, Bayer therefore designed a solvent exchange process in which, after chlorination, CTC is completely exchanged with toluene in a distillation column. This, virtually no CTC can be emitted from the washing and drying process or carried away in the CR itself which contains an average of less than 10 ppm. Thus, CTC emissions were virtually eliminated.
- For the production of low chlorinated polyolefins other Japanese manufacturers switched to the use of a non-ODS solvent.

It should be noted that CTC can be inadvertently produced in a chemical process when simple hydrocarbons react with chlorine to form CTC. The aqueous process for the manufacture of chlorinated rubber produces inadvertent, trace quantities of CTC. However as CTC is not used as a raw material for the aqueous process this inadvertent production of CTC is neither a feedstock or process agent use.

The reduction of more than 99.9 % in CTC emissions from CR production in the industrial nations within less than five years shows that CR can be produced under environmentally safe conditions both with the CTC and the aqueous process. This reduction represents an enormous success.

- Plants with a replacement value in excess of US \$150 million were shut down.

- The installation of closed systems and solvent exchange and the change to the aqueous process together cost some US \$100 million.
- Formulations had to be revised and customers for 50,000 to 100,000 tonnes of end product had to switch to alternative products such as polyurethanes, epoxides or acrylates.

C-4 USE OF CTC IN ENDOSULFAN PRODUCTION

C-4.1 Introduction

Endosulfan is an organochlorine insecticide. It is a broad spectrum biodegradable insecticide - acaricide widely used in the control of pests in cotton and other crops.

There are three medium size manufacturers of Endosulfan in India; two of them are using CTC as solvent in their process. This report describes the process of one of the two CTC users but provides CTC consumption and emission levels for both the plants.

C-4.2 Endosulfan Manufacturing Process

HET DIOL is reacted with thionyl chloride with CTC as an inert solvent. During reaction HCl is formed which is scrubbed. After the reaction the mass is neutralised with alkali. This neutralised mass is then distilled to recover the CTC solvent which is recycled for the process. Molten Endosulfan mass is then flaked by cooling and flakes are packed as per requirement.

C-4.3 CTC Consumption and Emission

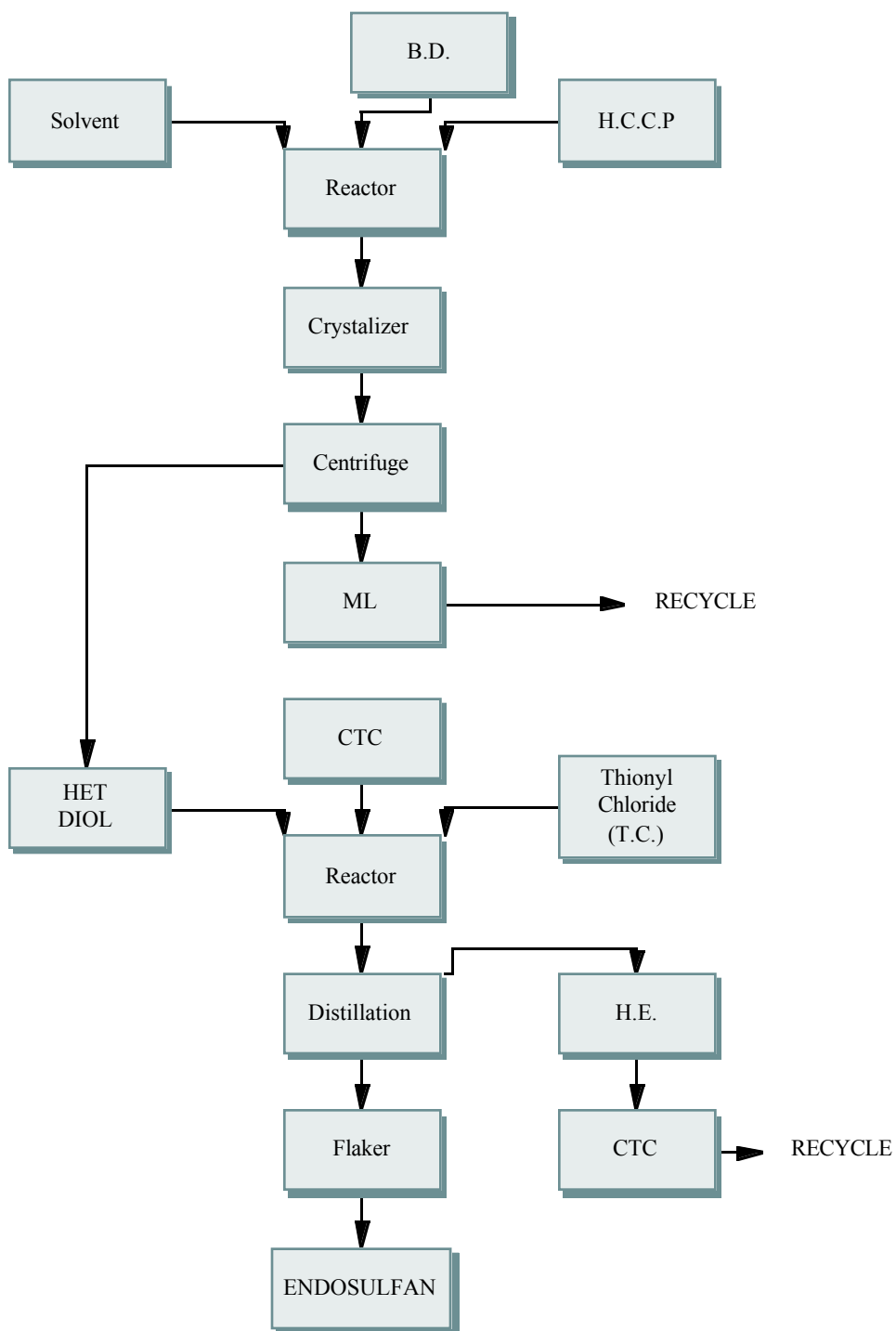
Total consumption of CTC for Endosulfan manufacture by the two producers in the year 1995 was 636 MT. Their production is expected to remain almost at the current level and CTC consumption in the year 2000 is estimated at 650 MT. The entire quantity of CTC represents consumption, as shown in the attached Table giving break up of annual recycle i.e., use and consumption in the Excel Industries process.

C-4.4 Conversion to Use of Non-ODS Solvent

During the years 1993 and 1994, Excel tried out various solvents for Endosulfan reaction and concluded that Ethylene Dichloride can be used as a substitute solvent to produce Endosulfan up to international quality standards. In order to implement this change, some alterations in their equipment and plant operation are necessary to maintain the required production capacity and fulfil safety standards. The manufacturer claims that with assistance CTC consumption of 386 MT per annum can be phased-out.

The second producer of Endosulfan using CTC as solvent is also formulating plans to switch over to a substitute non-ODS solvent and may decide to choose an aromatic solvent for this purpose. Such a solvent being highly inflammable, the cost of conversion in this second case would be higher than that of Excel.

C-4.5 Endosulfan Production Process



C-4.5.2 Material Balance

Item Description	Units	Endosulfan Process
Annual Endosulphan Production	[t/a]	5,000
Annual CTC Recycle	[t/a]	8,375
CTC Recycled Per Production	[t/t]	1.675
Annual CTC Consumption	[t/a]	340
CTC consumed Per Production	[t/t]	0.068
Annual CTC Transformed/Destroyed	[t/a]	0.00
CTC Transformed/Destroyed	[%]	0.00
Annual CTC used as CPA	[t/a]	8,375
Annual CTC Emission	[t/a]	340
to atmosphere	[t/a]	340
to water	[t/a]	0.00
to product	[t/a]	0.00
Annual CTC Emission	[%]	100
CTC Emission Per Production	[t/t]	0.068
to atmosphere	[t/t]	0.068
to water	[t/t]	0.00
to product	[t/t]	0.00
CTC Emission Per Recycle	[t/t]	0.041

C-5 USE OF CTC IN IBUPROFEN PRODUCTION

C-5.1 Introduction

Isobutyl Acetophenone (Ibuprofen) is a basic drug which is used in the manufacture of analgaesic formulations for use as pain killers.

There are not less than 14 plants in India producing this basic drug; a few of them are of medium size while the rest are small scale producers.

C-5.2 Ibuprofen Manufacturing Process

Iso Butyl Benzene is reacted with acetyl chloride in presence of aluminium chloride catalyst with CTC as an inert solvent. By-product hydrochloric acid gas generated is scrubbed with water. The unreacted components like aluminium chloride are dissolved in water by quenching process and Iso Butyl Acetophenone is separated by difference in specific gravity. Iso Butyl Acetophenone, free of solvent is recovered by vacuum distillation. CTC, thus, recovered is recycled for the process.

C-5.3 CTC Consumption and Emission

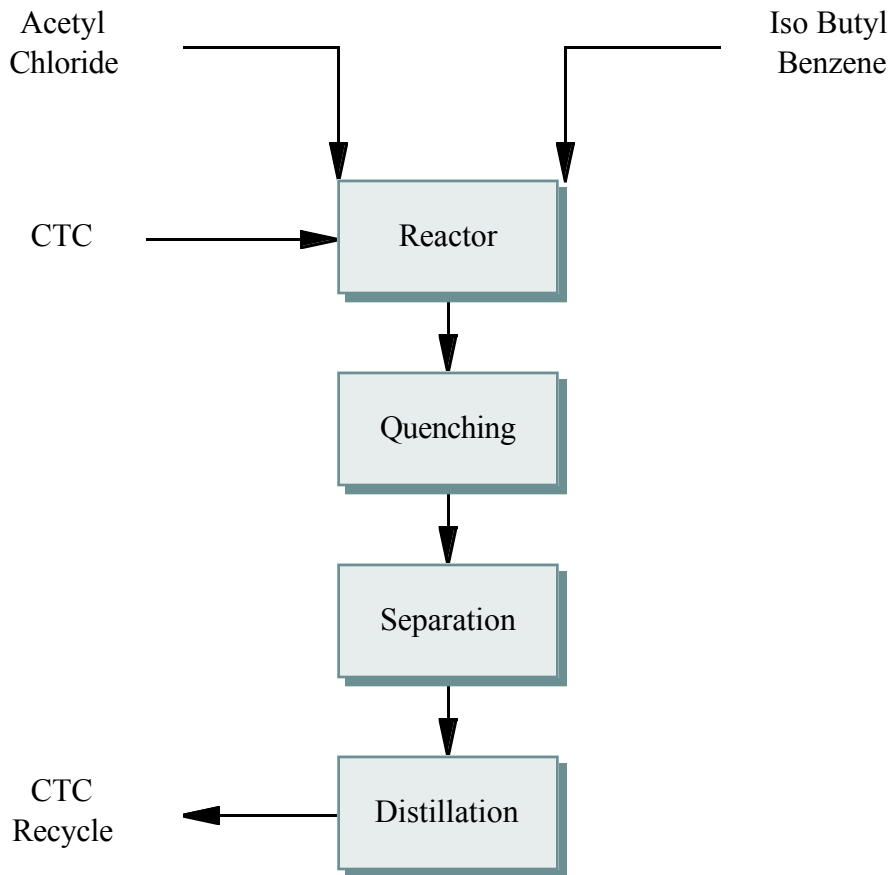
Total consumption of CTC for Ibuprofen manufacture in the year 1991 (base year taken in India country programme) was 1060 MT. Production of Ibuprofen was growing at 15-20 % per annum. The entire quantity represents consumption as shown in the attached Table, giving break up of CTC use and consumption by one of the largest manufacturers of Ibuprofen in India.

C-5.4 Conversion to Use of Non-ODS Solvent

Being conscious of the need for replacing CTC with non-ODS solvent, Ibuprofen manufacturers at their own initiative and considerable expense started converting to the use of Ethylene Dichloride right from the year 1994 onwards. Within about a period of 2 years period 1994-95, CTC consumption for Ibuprofen manufacture has come down sharply and it now stands reduced to a level of around 271 MT. It is expected that assistance will be required to completely eliminate the use of ODS as a process agent in this application.

C-5.5 Flow Chart and Material Balance of Ibuprofen Production Process

C-5.5.1 Shasun Iso-Butyl Aceto Phenone Process



C-5.5.2 CTC consumption and emission in the Shasun Ibuprofen process

Item Description		Ibuprofen Process
Annual Ibuprofen Production	[t/a]	1332
Annual CTC Recycle	[t/a]	2520
CTC Recycled Per Production	[t/t]	1.892
Annual CTC Consumption	[t/a]	810
CTC consumed Per Production	[t/t]	0.608
Annual CTC Transformed/Destroyed	[t/a]	0.00
CTC Transformed/Destroyed	[%]	0.00
Annual CTC used as CPA	[t/a]	2520
Annual CTC Emission	[t/a]	810
to atmosphere	[t/a]	810
to water	[t/a]	0.00
to product	[t/a]	0.00
Annual CTC Emission	[%]	100
CTC Emission Per Production	[t/t]	0.608
to atmosphere	[t/t]	0.608
to water	[t/t]	0.00
to product	[t/t]	0.00
CTC Emission Per Recycle	[t/t]	0.32

Note: The above enterprise has already converted to a non-ODS process

C-6 USE OF CTC IN DICOFOL PRODUCTION

C-6.1 Introduction

Dicofol is an organo chlorine broad spectrum non systemic acaricide with little insecticidal activity. It is currently being used on many fruits, vegetable, ornamental and field crops for the control of various species of mites. In India it is mainly used for tea crop and kitchen gardens. The recommended applications on wide range of crops varies between 0.56 - 4.5 kaI/ha. Acute oral LD for rats is 668-842 mg/kg and 1870 mg/kg for rabbits.

1-1,Bis (4-chlorophenyl) 2,2,2-trichloroethanol is the chemical name for Dicofol. Pure Dicofol is a colourless solid with a melting point 78.5 - 79.5 C.

The technical grade is brown viscous liquid (82% pure) and has density 1.45. It is primarily a mixture of 1-1, Bis (4-chlorophenyl) - 2,2,2 - trichloro ethanol and 1-1 (4-chlorophenyl, 2-chlorophenyl) - 2,2,2 - trichloro ethanol in the ratio of 4 : 1

Technical Dicofol is practically insoluble in water but soluble in most aliphatic and aromatic solvents. The product is compatible with all but highly alkaline pesticides. Its wettable powder (wp) formulations are sensitive to solvents and surfactants and these may affect acaricidal activity and phytotoxicity.

The various formulations of Dicofol are:

- a) 35% wettable powder (wp)
- b) 18.5% and 42% emulsifiable concentrates (EC)
- c) and as 41% flowable

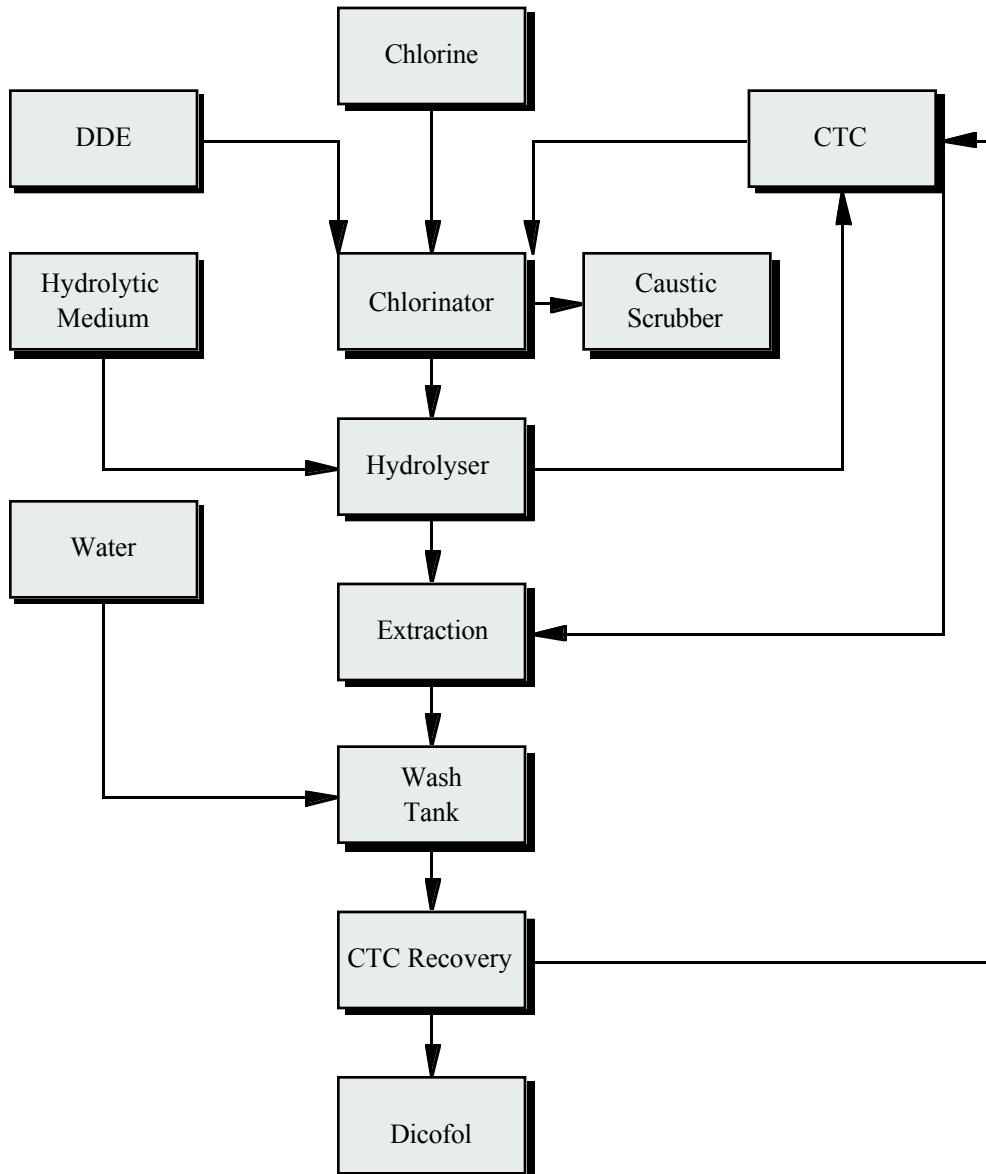
Of the above formulations, generally 18.5% (EC) is widely used in India

C-6.2 Manufacturing Process

The current capacity of the plant in India is 150 tonnes/annum. The product is manufactured by converting tech-DDT, which is mainly a mixture of 1,1 Bis (4-chlorophenyl) - 2,2,2 trichloro ethane and 1,1 (4-chlorophenyl, 2 chlorophenyl), 2,2,2 trichloro ethane to tech-DDE which is also a mixture of 1,1 Bis (4-chlorophenyl) 2,2 - dichloro ethene and 1,1 - (4-chlorophenyl; 2 - chlorophenyl) 2,2 dichloro ethene.

After the conversion of tech-DDT to tech-DDE, carbon tetrachloride (CTC) (4.5 kg for 1 kgh of DDE) is added. The CTC solution containing DDE is then taken to special chlorinators and then chlorinated with chlorine till the intermediate tetrachloro, 1-chloro, 1,1 Bis (4-chlorophenyl), 2,2,2 trichloro ethane and 1-chloro, 1,1 (4-chlorophenyl, 2-chlorophenyl) - 2,2,2-trichloro ethane are formed. The chlorinating solvent CTC is then removed and is recycled.

The product is then hydrolysed by an acidic hydrolytic medium. After the complete conversion of tetrachloro to tech Dicofol, CTC is added to the reaction mixture to extract tech Dicofol from the reaction mixture. The CTC layer which contains Dicofol is separated and then taken to wash tank and washed till product is neutral. CTC is then removed from the product by simple distillation, followed by vacuum distillation to get tech Dicofol.



C-6.3 Conversion to a Non-ODS Process Agent

This process presently produces 150 tonnes/year of Dicofol and uses 960 tonnes of CTC in the production cycle. Due to increasing demands and good potential of the product the company envisages a 20% annual production increase. Although most of the CTC used during chlorination and as a Dicofol extractor after tetrachloro DDT hydrolysis is recycled, 48 tonnes is emitted annually, including residual trace amounts in the product. These emissions will likely increase as production increases.

There is a limited choice of solvents, as only Chlorinated aliphatic solvents can be used as a replacement process agent. Work at the laboratory level has already been initiated to replace CTC using 1,2 dichloro ethane (DCE). The initial results are quite optimistic and it is hoped that this process agent will be a suitable replacement for CTC in this process. However, laboratory experiments so far indicate that if dichloro ethane (DCE) is used as a replacement for CTC, some process modifications will be required to meet the needs of the present and future production schedules, which would have a bearing upon productivity and cost economics of the product. In order to carry out this change from CTC to DCE more studies in pilot plant at 5 kg level are to be undertaken. Moreover, before marketing technical Dicofol, as per C.I.B. guidelines, phytotoxicity studies of the product must be carried out on the alternatively produced product.

Although there is not much change in the solvent ratio in the change from CTC to DCE at the chlorination stage, it has been observed that the chlorination time is 15 to 20% longer, as chlorine has more residence time in CTC compared to DCE. Hence to maintain the present production schedule a complete chlorination unit consisting of a 3 Kl, all glass lined, jacketed vessel, along with two scavengers of the same capacity and kind having proper condenser and other requisite accessories will have to be installed.

The extraction of technical Dicofol after hydrolysis of tetra chloro DDT with CTC is easier as CTC is heavier (density 1.6), compared to DCE (density 1.24) and thus CTC containing the Dicofol remains in the lower layer. However when DCE is used there is no separation of the layer for DCE, either at the top or at the bottom, and much more DCE and water is required to get DCE containing technical Dicofol in the lower layer. Due to the larger volume of DCE and water, the size of the vessel has to be increased substantially. Simultaneously, the present wash tank for washing technical Dicofol in DCE also has to be replaced with a larger one. Therefore to maintain the present production level of technical Dicofol, a 5 Kl MSGL hydrolyser and another 5 Kl MSGL wash tank with necessary accessories must be installed.

C-6.4 Material Balance

Item Description	Quantity	Tonnes
Annual Dicofol (tech) production	t/a	150
Annual CTC recycle	t/a	960
CTC recycle per production	t/t	3.2
Annual CTC make-up	t/t	48
CTC consumed per production	t/t	0.16
Annual CTC transformed or destroyed	t/a	0.00
CTC transformed or destroyed	%	0.00
Annual CTC used as CPA	t/a	960
Annual CTC emission	t/a	48
to atmosphere	t/a	47.52
to water	t/a	0.00
to product	t/a	0.48
CTC emission per production	t/t	0.16
to atmosphere	t/t	0.1584
to water	t/t	0.00
to product	t/t	0.0016
CTC emission per recycle	t/t	0.05

C-7a USE OF CTC IN CHLOROSULPHONATED POLYOLEFIN (CSM) PRODUCTION IN A NON-ARTICLE 5(1) COUNTRY

C-7a.1 Introduction to CSM

Following invention of CSM and introduction in 1952, this product has developed a small, but very important, niche in the global synthetic elastomers market. CSM is a specialty elastomer with properties far superior to general purpose elastomers such as styrene-butadiene rubber, polyisoprene, polychloroprene, and nitrile rubber. The properties of CSM may be summarised as:

- Ability to be brightly or permanently coloured,
- Superb ozone and weather resistance,
- Heat resistance to 125-135 degrees Celsius,
- Low temperature flexibility down to -18 to -23 degrees Celsius,
- Resistance to a wide range of oxidising agents and chemicals,
- Oil, grease, and solvent resistance,
- Good electrical insulating properties, and
- Excellent resistance to abrasion and wear.

In many instances, such as automotive, appliance, military and recreational applications (i.e., white water rafting), general purpose elastomers cannot adequately replace CSM elastomer. The following applications have specifications where CSM is the preferred product:

C-7a.1.1 Coatings

Coatings of CSM are used to provide resistance to gas or moisture vapour permeability, weather, chemicals, oils and solvents while maintaining an attractive colour. Applications include coatings for inflated fabric structures, inflatable boats, diaphragms, tarpaulins, rain wear and protective garments, roof coatings for chemical tanks and liners for secondary containment.

C-7a.1.2 Automotive

Specialty grades are used for vital automotive components because of its proven resistance to heat, oil, grease and ozone. Applications include power steering pressure hoses, fuel hose covers, brake hose and filler neck hose (connected to the gas tank). New grades of this elastomer are being used in the manufacture of high performance timing belts and accessory drive belts which will operate for the life of the vehicle without replacement.

C-7a.1.3 Wire and cable

CSM is widely used as a sheathing material for cable constructions. Its higher thermal rating combined with its low water absorption rate, and resistance to weathering, sunlight, ozone, corona and radiation make it a valuable jacketing material for control cable, nuclear power station cable, and mine trailing cable.

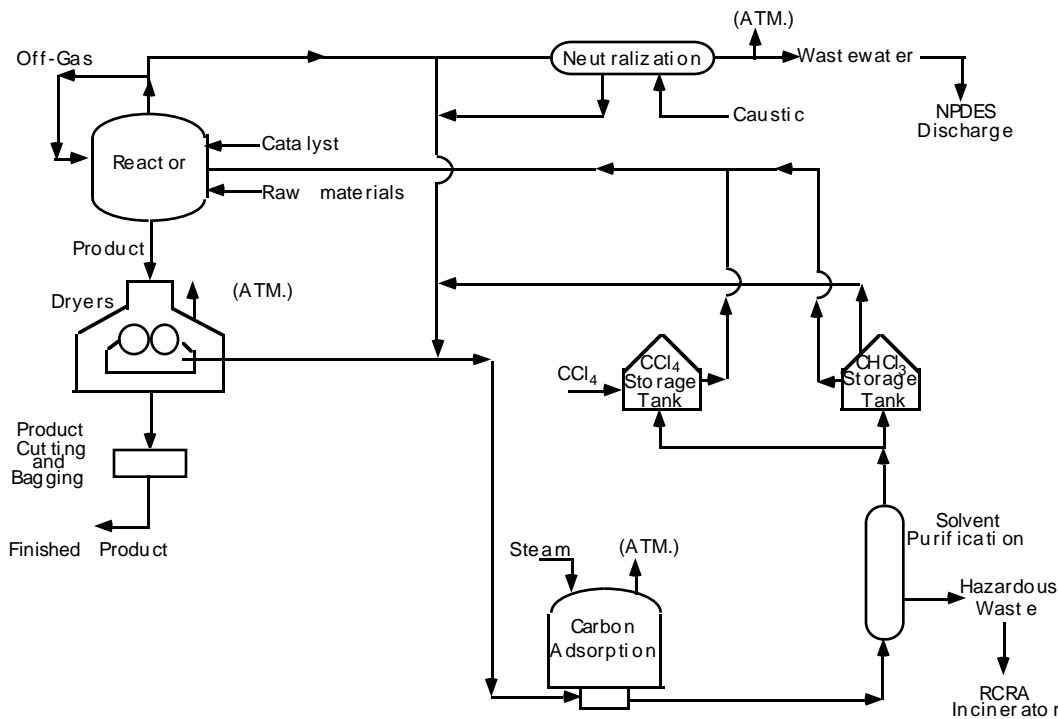
C-7a.1.4 Industrial

CSM has wide spread application in roll covers and acid hoses because of its resistance to a large variety of chemicals and solvents over a wide range of temperatures. Unique binder properties make it the preferred elastomer for magnetic applications which include refrigerator and microwave door enclosures.

C-7a.1.5 Construction

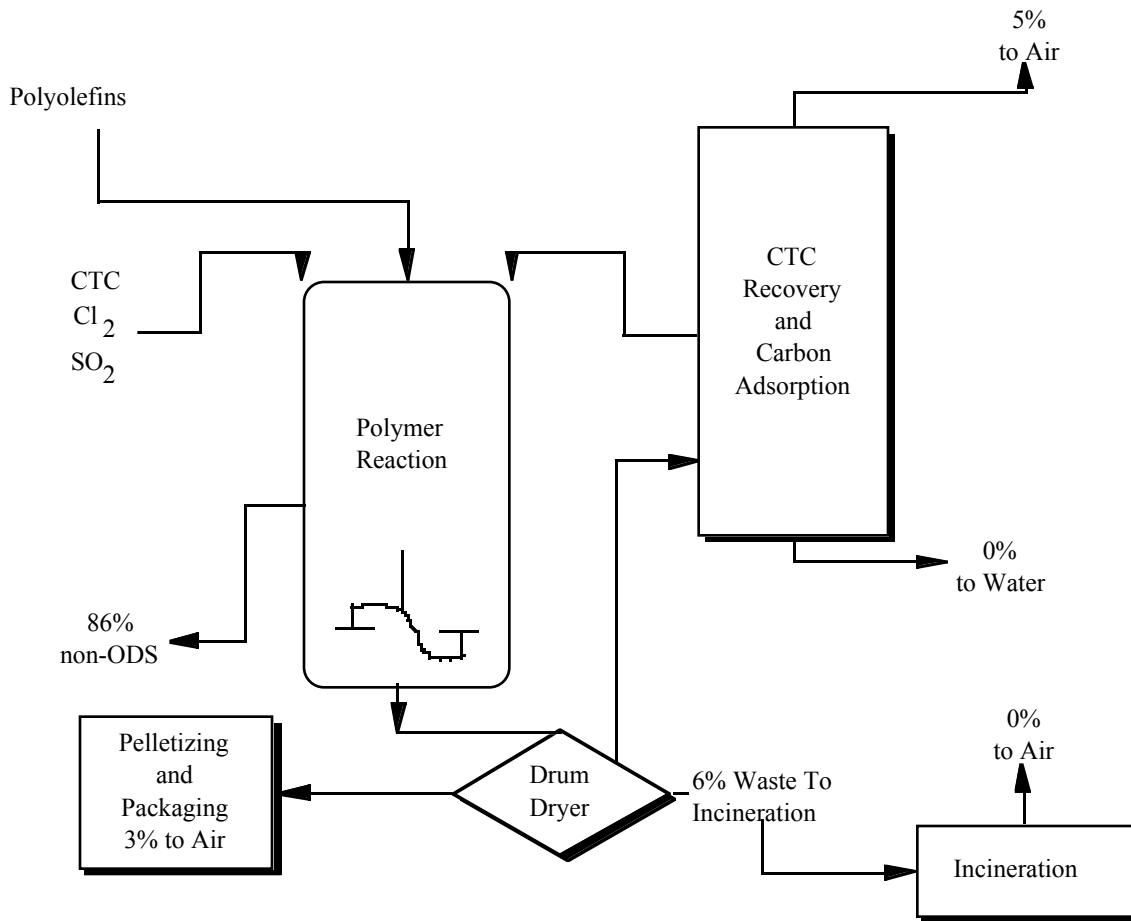
A particular type of CSM is used to produce single ply roofing membranes. The roofing membrane is white in colour for heat reflectance and remains thermoplastic during installation on the roof, enabling heat welding of the seams. The roofing then slowly vulcanises during use. No other elastomer possesses this combination of properties. This type of CSM is used to produce fabric reinforced sheets which are heat welded into liners for reservoirs and effluent ponds.

C-7a.2 Description of the North American CSM Process



The polyolefin “base resin” (typically polyethylene or ethylene copolymer) is first dissolved in hot carbon tetrachloride (CTC) in batch reactors. Chlorine and sulfur dioxide are introduced into the reactor which, in combination with CTC and polyolefin, yield the chlorosulphonated product. Unreacted chlorine and CTC are removed through the off-gas condenser system which condenses and cools CTC prior to recycle to the reactor. Any remaining off-gases from the reactor are either combined and recycled to the reactor or neutralised. The reactor solution is blended, continuously filtered, and dried on enclosed drum dryers. CTC emissions from these enclosed operations are condensed and recovered for reuse in the process. Dilute emissions that are not recovered by condensation are collected in a carbon adsorption system. After steam regeneration of the carbon beds, the remaining CTC is purified and recycled to the process. The finished product is packaged in the form of chips and stored in bags.

CTC Balance for the North American CSM Process



Annual Make-up	Converted to non-ODS	Incinerated	Emitted to Air (direct)	Emitted to Air (from Product)
100%	86%	6%	5%	3%

C-7a.3 Why CTC is Used In the North American CSM Process

The ideal solvent for the CSM Process must have the following characteristics:

- Non-flammable
- Inert to Chlorine
- Proper Vapour Pressure
- Low Solubility in Water

CTC is used in the CSM Process for the following reasons:

1. CTC is a non-flammable solvent that allows safe operation and meets the stringent process safety concerns for large chemical production facilities. The North American CSM Process has been designed for use of non-flammable solvents and cannot use flammable solvents without major changes to the process design and equipment.
2. CTC is fully-chlorinated and, therefore, inert to further chlorination. The reaction step in the CSM Process involves chlorination and sulphonation of polyolefins that have been dissolved in CTC. Side reactions with the solvent during this process step must be minimised to prevent unwanted by-products.
3. CTC has the proper vapour pressure to allow for stripping and condensation to recover and recycle solvent. The CTC vapour pressure is also in the right range for the CSM reaction and storage equipment.
4. CTC is practically immiscible with water which allows for unreacted solvent to be washed and neutralised along with other reactants with minimum solvent losses to the neutralisation systems. CTC is compatible with the CSM caustic system and minimises side reactions in this process step.

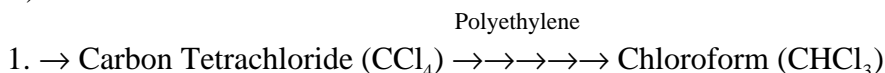
Given the numerous unit operations needed to effectively contain and recover CTC and the large capital investment required, it is necessary to use a solvent that will meet the above criteria.

In addition to the impact on process operations, the properties of specific CSM grades are significantly improved when the reaction is carried out with CTC. Several studies in 1993 demonstrated the impact of CTC versus other solvents on the properties of specific CSM products. Property improvements included oil resistance, low temperature flexibility, dielectric constant and dissipation factor, optimum sulfur levels, heat resistance, water swell, and compression set.

These differences were attributed to the evenly spaced distribution of chlorine atoms along the polymer chain when using CTC. The reason for the more even distribution of chlorine and sulfur atoms was that CTC surrounds each polymer segment in the chain with an envelope of solvating molecules, preventing contact with other segments and chains. This allows the individual chain to remain elongated allowing better exposure to chlorine and sulfur reaction of all polymer segments, and thus more even spacing. Other solvents allow the polymer chains to be irregularly folded into tight coils reducing exposure of the entangled segments to chlorine and sulfur atoms.

C-7a.4 How CTC is Used in the North American CSM Process

In addition to the recycle and reuse of CTC in the North American CSM process, 86% of the CTC is transformed into chloroform during the chlorination reaction. As shown below, CTC gives up a chlorine radical in the reaction, ultimately forming chloroform (a non-ozone depleting chemical).



The chloroform is then consumed in the neutralisation step of the process to form carbon monoxide and sodium formate.



This consumption of chloroform occurs in many locations within the CSM Process. Testing of the North American CSM Process has confirmed that this reaction occurs at high rates.

All the CTC in the North American CSM process is recycled, transformed to chloroform and consumed, or incinerated. All waste streams containing CTC are shipped off-site for incineration. The incinerators operate with a destruction efficiency of 99.99 percent which meets the control requirements of the Montreal Protocol (Decision IV/12). Based on an overall CTC balance for this CSM process, 99.95 percent of the CTC used in the process is recycled, converted (transformed), or incinerated (destroyed). The remaining losses (trace emissions) to the environment (0.05 percent) are largely from product handling.

Table 1 provides the chronology showing how CTC use per tonne of CSM declined from 142 kilograms (kg) to 2.9 kg. of CTC per tonne of CSM. Table 2 is a comparison of the emissions from the CSM Process in North America versus the CSM Process in China (see Case Study C-7b). Emissions of CTC are two orders of magnitude lower in the CSM Process in North America, per tonne of product, versus the CSM Process in China.

Table 1 - Chronology of CSM process emissions North American CSM process

Time Period	Process Changes/ Improvements	Emissions (kg CTC/ tonne CSM)
1957 to 1963	Start-up facility; Reactor upgrade; Solvent Recovery improvements	No emission data.
1964 to 1970	Expansion of capacity; Blend Tank for product uniformity; Off-gas system for recycle of SO ₂ ; Caustic Scrubber for emergency releases; Solvent Recovery improvements; Storage Tank condensers	142
1971 to 1977	Expansion of capacity; Reactor improvements; Solvent Recovery improvements; Carbon Adsorption System and Solvent Purification System installed (1977)	129
1978 to 1983	Expansion of capacity; Process Computer controls; Carbon Adsorption System improvements	8.3
1984 to 1988	Carbon Adsorption System improvements; Chlorine Stripper improvements; Wastewater Effluent Stripper to Carbon Adsorption System (1988)	4.3
1989 to 1994	Carbon Adsorption System improvements (Storage Tanks and Drying Column vents)	4.1
1995	Process control improvements; Continuous Emission Monitoring System improvements; Leak Detection and Repair programme for fugitive emissions	2.9

Notes:

CSM process emissions from the North American facility are for carbon tetrachloride (CTC) only. These estimates include CTC emissions from process vents, storage tanks, wastewater, equipment leaks, building ventilation and products.

Table 2 - Comparison of CSM process emissions 1995 emission estimates

Comparison of CSM Process Emissions	CSM Process China (1)	CSM Process North America (2)
Production (tonnes/ year)	3,000	23,000
CTC recovered, recycled (tonnes/ year)	28,906	135,049
CTC recycled per usage (%)	97	99.4
CTC annual requirement (tonnes/ year)	894	781
CTC transformed/ destroyed (tonnes/ year)	0	717
CTC recycled/ transformed/ destroyed (%)	97	99.95
CTC used in process (tonnes/ year)	29,800	135,830
CTC emissions (tonnes/ year)	894	64
CTC emissions (kg CTC/ tonne CSM)	298	2.9
CTC emission (%)	3	0.05

Notes:

- (1) Information based on the Case Study entitled "Use of CTC in Chlorosulphinated Polyolefin (CSM) Production in China" prepared by Professor Zhang Zhiqun of Beijing University of Chemical Technology for the Report of the UNEP Process Agents Task Force (see C-7b).
- (2) Information based on a paper presented by Mr. Tony Vogelsberg to the UNEP Process Agents Task Force on October 21, 1996.

C-7a.5 Pollution Abatement in the North American CSM Process

The North American CSM Process employs several systems to recover and recycle CTC. These operations include the Reactor, Off-gas, Isolation, Neutralisation, Spent Caustic, Solvent Recovery, Carbon Adsorption, and Wastewater Treatment systems. Although all these systems contribute to the recovery and recycle of CTC, only the Carbon Adsorption and Wastewater Treatment systems are considered pollution abatement operations. Other operations such as a leak detection and repair programme and the waste management programme also contribute to the reduction and recovery of CTC emissions.

CTC emissions that are too dilute for recovery by condensation in one of the other systems are collected in a single header and sent through a bank of carbon adsorber beds. Normally, all but one bed are adsorbing at any given time; the one being regenerated by steam or on stand-by. Each bed contains 40,000 pounds of carbon and can treat 140,000 scfm of air during normal operations. Based on performance data, the carbon adsorption system has a recovery efficiency of greater than 99 percent.

During regeneration of the carbon beds, steam is passed through each bed (effectively removing the CTC from the carbon) and condensed with the recovered solvent in a water-cooled condenser. The recovered solvent is decanted from the water and sent to the Solvent Purification Column which separates the CTC from the solvent by batch distillation. The CTC is recycled to the Neutralisation system and then to the process. Trace compounds and miscellaneous catalyst fragments are left as residual from the column reboiler. This residual waste material is removed

and shipped to an off-site incinerator for destruction of the CTC. The incinerator is required to operate at a destruction efficiency of 99.99 percent.

Monitoring systems in the North American CSM process continuously sample all CTC emissions from process vents to the atmosphere. These systems monitor CTC concentrations at various points throughout the process. The monitoring system data is reported quarterly as a condition of a state air permit and must meet the permit emission limitations. In addition to the continuous emissions monitoring systems, fugitive emissions from valves, pump seals, connectors, etc. are monitored monthly, quarterly and annually. Leaks are repaired within 5 to 15 days of detection.

The results of this program are reported to the federal and state agencies semi-annually under the National Emission Standards for Hazardous Air Pollutants (NESHAP) regulations. New NESHAP regulations issued on September 4, 1996 (specifically for the North American CSM processes) will also require record keeping and reporting of emissions from storage tanks, process vents, wastewater and equipment leaks.

Water from the Solvent Purification Column is stripped with air to recover and recycle CTC prior to being pumped to the Wastewater Treatment system. Other wastewater streams including any process spills and rainwater are collected in a series of sumps and sent to a holding tank prior to being pumped through filters and a coalescer separator and then air stripped for CTC removal. The stripping air is routed to the Carbon Adsorption system for CTC recovery. The water from the process ditch stripper is discharged to a diversion sump which also collects any overflow from the process ditch sumps. This water is pumped through a residence tank which overflows to an outfall which is permitted by the state and federal environmental agencies under the National Pollutant Discharge Elimination System (NPDES).

A continuous sample is taken from the diversion sump and analysed for CTC, as well as, other hydrocarbons, pH, temperature, and total suspended solids. A high signal automatically starts the diversion pump and sends the water stream to the diversion tank for treatment in the process ditch stripper or the pH control systems. Periodic sampling of wastewater discharges for various pollutants (including CTC) is conducted at the NPDES outfall and reported monthly to the state and federal environmental agencies.

Solid wastes (including hazardous wastes) from the reboiler of the Solvent Purification column and drummed wastes are sent off-site for incineration. The shipments are manifested and sent to government-approved facilities for proper handling and treatment. These facilities are required to meet an incinerator destruction efficiency of 99.99 percent. Monthly and quarterly reports of all shipments must be made by the generator, shipper, and incinerator of the wastes to state and federal agencies under the Resource Conservation and Recovery Act (RCRA) regulations.

All monitoring systems and environmental programmes are audited annually by representatives of the state agencies compliance with state and federal regulations. In addition, several internal audits are conducted by corporate and business unit teams annually to ensure all systems and programmes are in place and functioning properly.

C-7b USE OF CTC IN CHLOROSULPHONATED POLYOLEFIN (CSM) PRODUCTION IN AN ARTICLE 5(1) COUNTRY

C-7b.1 Introduction

Chlorosulphonated Polyethylene (CSM) is a specialty elastomer with superior properties in resistance to weather, heat, oil, chemicals and abrasion, combined with excellent flexibility and colour stability. China began to produce this product in the late 1970's and currently production capacity and output has reached over 3,000 tonnes per year.

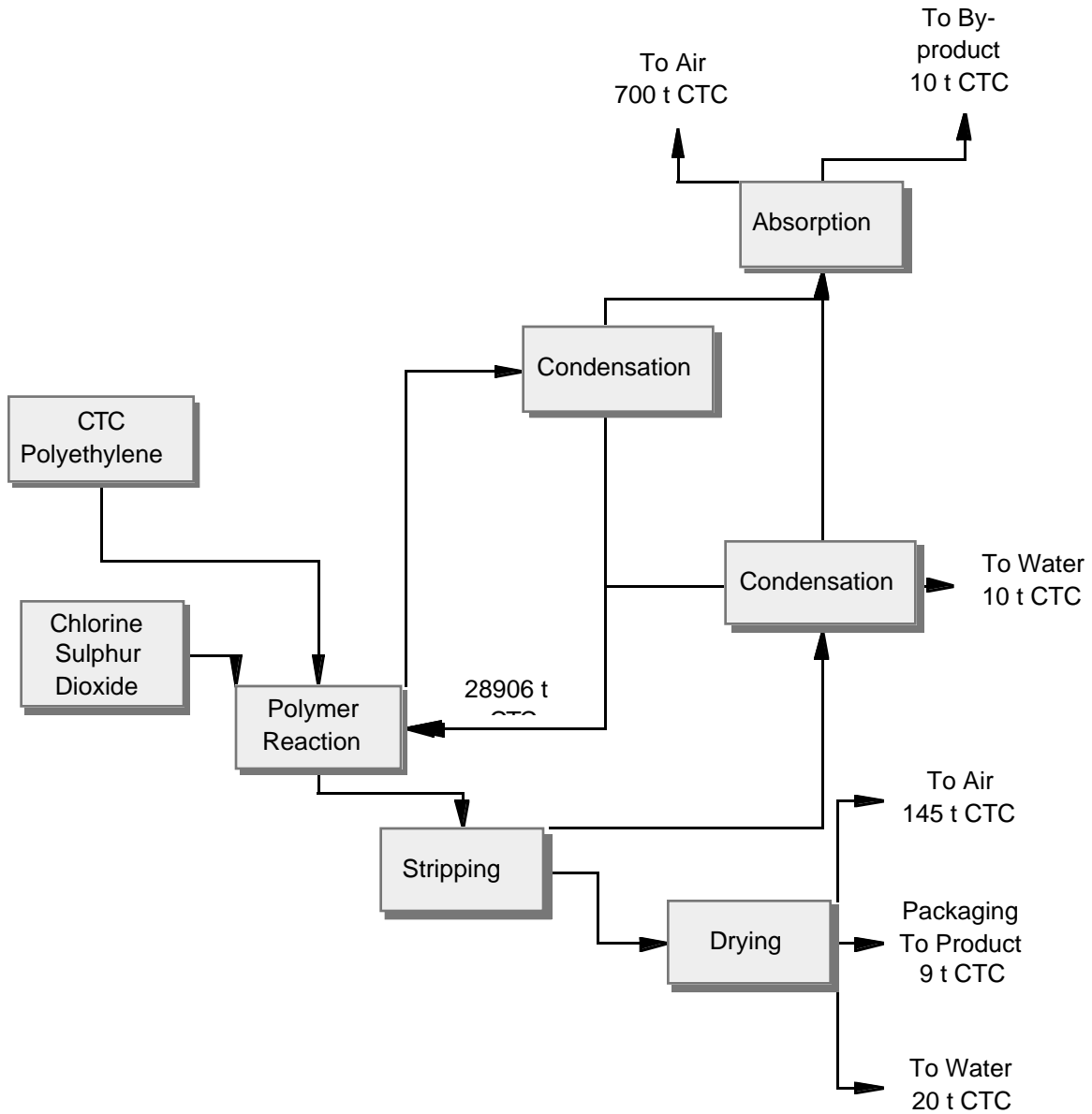
Jilin Chemical Industrial Company Limited (JCICL) is the largest producer of CSM in China. Other CSM producers in China are comparatively small producers and their statistical data are not available as yet. Therefore, only the elaborated JCICL CSM process and its update CTC balance are presented in this case study.

C-7b.2 Description of the Process

The JCICL CSM process was a CTC based process, which was developed and improved by JCICL.

Polyethylene is first dissolved in hot CTC and then, together with chlorine and sulphur dioxide, introduced into the reactor, in which the chlorosulphonated product is yielded. The finished product is further isolated by stripping and drying operations and then packaged in the form of chips. The released CTC from the reactor and rear operations is recovered, purified and recycled by condensation and absorption.

CTC Balance for JCICL Process



C-7b.3 CTC Consumption and Emissions in the JCICL Process

Item Description	JCICL CSM Process
Annual CSM production (t/a)	3,000
Annual CTC recycle (t/a)	28,906
CTC recycled per production (t/t)	9.635
Annual CTC consumption (t/a)	894
CTC consumption per production (t/t)	0.298
Annual CTC transformed/destroyed	0
CTC transformed/destroyed (%)	0
Annual CTC used as PA (t/a)	894
Annual CTC emissions (t/a)	894
to air (t/a)	845 (94.52%)
to water (t/a)	40 (4.47%)
to product (t/a)	9 (1.01%)
Annual CTC emissions (%)	100
CTC emissions per production (t/t)	0.298
to air (t/t)	0.282
to water (t/t)	0.013
to product (t/t)	0.003
CTC emissions per recycle (t/t)	0.03

C-7b.4 CTC Alternative Process

In the 1970's JCICL had explored the feasibility of using chlorobenzene instead of CTC as a process agent for CSM production. After years of research, this option was abandoned for the following reasons:

1. Energy consumption is much higher than that of using CTC due to higher boiling point of chlorobenzene.
2. Chemical stability to chlorine and sulphur dioxide is not as good as use of CTC in the process
3. In-plant safety is not as good as that of using CTC due to flammability, explosivity and toxicity of chlorobenzene.

C-8 PRODUCTION OF POLY-PHENYLENE-TEREPHTAL-AMIDE WITH THE AID OF CTC IN AN INTERMEDIATE RAW PRODUCT

C-8.1 Introduction

The aromatic polymer PPTA (Poly-Phenylene-Terephtal-Amide), is produced in the Netherlands. Carbon tetrachloride (CTC) is used as a process agent in the production of an intermediate raw material.

C-8.1.1 Products

The main products are fibres with a wide field of high tech application based on the extreme strength (5 times as strong as steel) combined with a series of other outstanding properties including: high tensile modulus, good chemical stability, very low creep rate, good dielectric properties, flame resistant, self extinguishing and others.

C-8.1.2 Application

The perfect manufacture of complex products which exceed design specifications are enabled. The applications are in composites with rubber and synthetic materials and in composed textures. Composites are often combined with existing materials to improve properties.

In combination with steel, the fibre is used for impact shields to give protection for equipment and vehicles. This means that police and civilian vehicles can be armoured and yet be light and manoeuvrable. Similarly tanks and military vehicles become lighter and safer. Weight savings amount between 30 and 60%. The material is also used to provide light weight body protection in the manufacture of helmets for motor cycling, police and military (a 100% better ballistic performance than a steel helmet) as well as flexible, bullet and fragment resistant vests which are easy to wear. As an impact resistant composite material, it is used as an anti piercing shield for the protection of railway and road tank cars transporting dangerous goods.

Reinforced refrigerator trailers are some 25% less in weight, are better insulated and less sensitive to damage. Savings result from a lighter weight, smaller refrigerator with greater payload.

Optical fibre cables can be made lighter in weight and rodent resistant.

In the field of rubber goods better performance is achieved for transmission belts, hydraulic hoses, automotive hoses, conveyor belts and ultra light weight automobile tires, the latter also leading to savings in fuel consumption. Wood laminates can replace hardwood applications without loss of strength (for instance large warehouses).

The PPTA fibre plays an important role in replacement of asbestos for brake linings, brake blocs and disk brake pads; for chemical resistant gaskets; for heat resistant workwear and fire blankets.

There is a growing market for these applications.

C-8.2 The Manufacturing Process

The polymer is produced from the raw materials PPD (para-phenylenediamine) and TDC (terephthaloyldichloride). The raw materials PPD and TDC are produced at the same facility. The plant has a permitted capacity of 18,000 tons of polymer.

The only use of CTC is in the production of TDC. TDC is produced by side chain chlorination of p-Xylene in CTC followed by fusion with terephthalic acid. Purification is by distillation; hydrochloric acid (muriatic acid) is produced as a by-product. CTC is separated from product streams and recycled constantly in the process. It is regenerated for reuse by distillation. The CTC distiller waste is incinerated. All waste streams (gas and liquid) are purified. Wastewater and vent gases are purified in an integrated system by air stripping and active carbon adsorption. Active carbon is regenerated with steam; the condensed CTC is recycled. The Hydrochloric acid (HCl) is purified by steam stripping and the recovered CTC is recycled, see flow chart. The entire process is contained.

C-8.3 Why CTC is Used

CTC is used for the following reasons:

1. Quality by avoiding side reactions during chlorination. The quality is crucial for the polymerisation.
2. Safety by avoiding explosion risks during chlorination.
3. A carrier for recycling of incomplete chlorination products which results in less waste and a high yield.
4. A cleaning agent for the HCl emerging from the reactors. The cleaning solution is recycled.

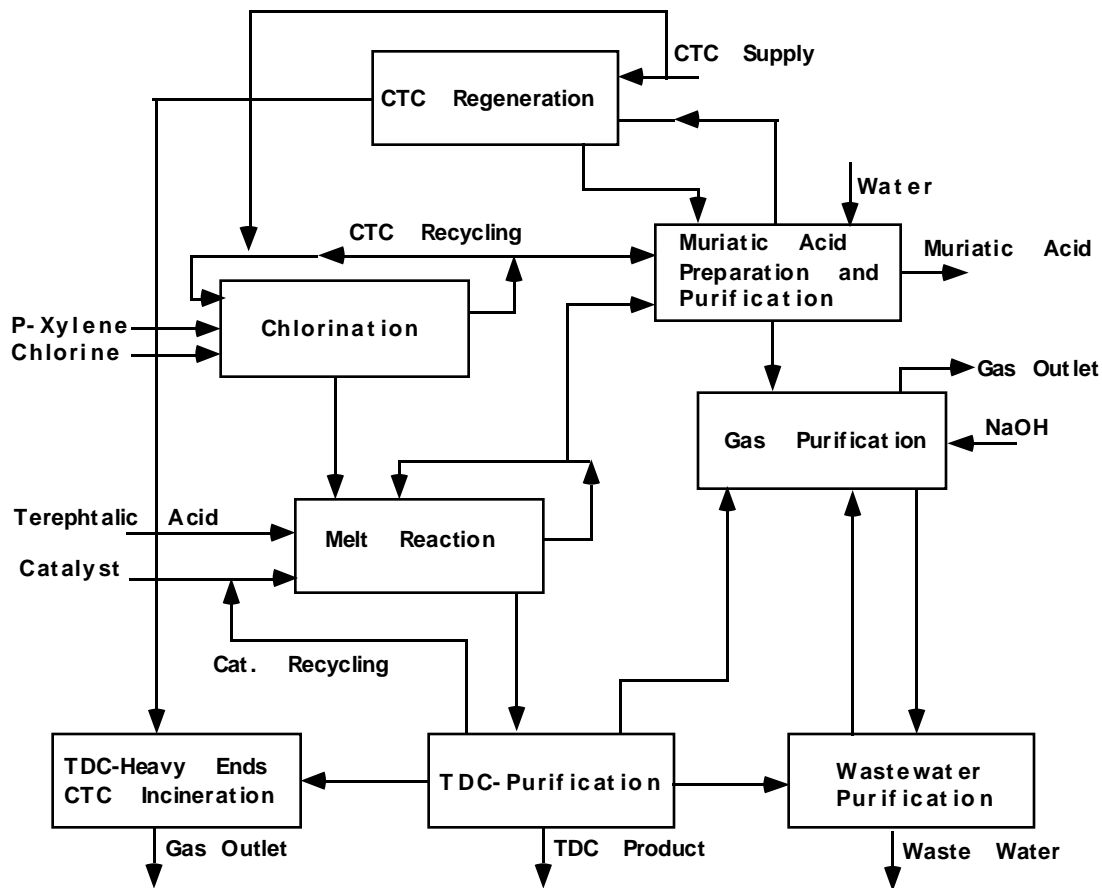
Combination of all these purposes, under the various conditions of the process, can, according to current knowledge and practical experience, only be fulfilled with CTC. There is no single chemical that can replace CTC in this process.

It is unique:

- 1 it is inert in all process steps;
- 2 prevents side reactions to take place in the reactor;
- 3 has the right vapour pressure to prevent explosive reactions in the gas cap of the reactor;
- 4 is easy to recover;
- 5 has a low solubility in HCl.

As a consequence the use of CTC from the start of the TDC-plant has been fully integrated in the process.

TDC Process for Aramid polymer Production



C-8.4 How CTC is Used

The “make-up” quantity (1995) is 72.5 tons per year, mainly arising from the destruction of CTC distillers waste (the unusable bottom fraction that remains in distilling the recycled CTC).

Source	Name	Discharge of CTC ton/year	Remarks
Product	TDC	0	
Product	30% HCl	max. 0.240	
Wastewater	after treatment	max. 0.060	
Vent gas	after treatment	ca. 2	improvement foreseen
Diffuse	losses in collecting system	pm	project for total containment in execution
Leakage	losses	0.030	measured and calc. EPA
Incidental	losses	0.200	fixed entry for maintenance
Waste	incineration	70	
Required	Make-up	72.5	year 1995

C-8.5 Pollution Abatement

In August 1989 at Nairobi carbon tetrachloride (CTC) was placed on the list of ozone depleting chemicals. From that time efforts have continued to replace CTC. These efforts have been made up in 2 areas:

- Reducing emissions in the existing TDC-plant;
- Research for substitutes for CTC or other processes.

C-8.5.1 The emission reduction has led to the following results:

- The CTC discharge in wastewater was reduced by 99% by redesign and installing more separators for CTC.
- The CTC discharge in waste gas was reduced over 90% by investigation and redesign.
- Liquid and gas flow systems were simplified to facilitate recycling.
- All waste streams are monitored.
- Wastes containing CTC are incinerated by an UNEP accepted technique.
- The CTC content of HCl was reduced with the aid of monitoring.
- Diffuse losses were measured and reduced to some 30 kg/year (according to correlated emission factors).
- The inadvertent losses relative to the total circulation rate amounts ca. 0.01%.
- The environmental management system has been certified under British Standard 7750.

Emissions for 1990 and 1995 in tons of CTC/year:

Source	Name	1990	1995
Product	30% HCl	0.45	0.12
Wastewater	after treatment	1.680	0.06
Vent gas	after treatment	35	1.62
Diffuse	losses	0.54	0.03
Incidental	losses	0.20	0.20
Total emission		37.87	2.03

C-8.5.2 Research activities have led to:

- Substitution of CTC in a coolant system for reactor lamps.
- The understanding that there is no single substitute for CTC for all the purposes to be served. Every other substitute for a single purpose suffers from degradation or contamination by chlorination and possible origination of CTC thereby complicating the process to an unknown degree in relation to the desired quality of the product.

- A commercial alternative process for the production of TDC is known, however this process belongs to the only competitor. In addition the cost of buying and building a complete new TDC plant next to the operating one is prohibitive. A rough cost estimate is US \$150 million (reducing the CTC emission by 2 tonnes per year).

C-8.5.3 Regulatory

The environmental regulations together with the decisions of the Montreal Protocol have had their influence on the restrictions of emissions in a direct and indirect way as the following table shows.

Legislative aspects versus measures and results:

#	Type of law ¹⁾	Conditions	Applied technique	Results ²⁾
1	Restriction of water pollution	Reduce existing pollution 50 -90%	Separators followed by air stripper	99% reduction
2	Restriction on air pollution	Reduce existing pollution to standard	Active carbon adsorbers, containment	1995: 90% reduction; ongoing programme
3	Unpolluted products	max. 10 mg/kg	steam stripper	Well below 10 mg/kg
4	Waste destruction to standard	According to Dec IV/11	Incinerator	Destruction more than 99,9%
5	Unpolluted soil	No polluted soil	impenetrable slabs with water collecting provisions	No pollution

- 1 There is a voluntary convention between government and the chemical industry to restrict emissions as low as is feasible.
- 2 Monitoring has added a lot to good and reliable results.

C-8.6 Future Aspects

In the near future:

- The vent gas purification will be improved on the basis of the data of the monitoring.
- A project for a fully closed CTC wastewater collecting system will be carried out to achieve complete containment of the plant.

After these improvements which will give a further reduction of emissions the best available techniques and the best environmental practice for this production have been applied. This is confirmed in the environmental permits (Dutch Air pollution act and water pollution act) which are based on the figures given in the table. The monitoring of the waste streams have to be reported on a quarterly basis for wastewater and for waste gases on a yearly basis.

Further extensions are expected in the future. Therefore efforts are being made to gather knowledge about modifications in the existing process without the use of CTC. The objective is worth pursuing and the efforts are appreciable but the chance on success can't be predicted. However adoption of this course is seen as the best there is, given the circumstances that growth

of sales and sales potentials must make further extensions possible. As of 1996 this knowledge has not been developed adequately to eliminate use of CTC for future expansion of the production facility.

C-8.7 Substitutes without ODS Application

As already mentioned there is one commercial process to produce PPTA without the use of CTC in producing one of the raw materials: TDC. However the possibility of using this process is limited while licensing meets considerable constraints in terms of competitiveness and introduction of other environmental problems. The process is based on a different chemical reaction and it is carried out with phosgene as a raw material. Such use is only technical and commercial viable when phosgene is already present or is used for more than one product (which is not the case). Moreover the cost of adopting this process is estimated 150 million US dollars which is not feasible. Research is done to find a better corresponding ODS free alternative. The progress of this programme looks promising.

The possibility of using alternate products is more or less contradicted by the market that consumes the product on the base of exploiting the outstanding properties of the polymer as there are:

- replacement of asbestos in brake applications, heat resistant workwear and fire blankets,
- impact protection properties of hitherto unknown quality,
- composites of hitherto unknown strength.

In these fields there are only alternatives if one abandons the progress in quality of the products or safety.

C-9 USE OF CFC-113 FOR MANUFACTURING A FAMILY OF FLUOROPOLYMER RESINS

C-9.1 Introduction

Fluoropolymer resins that have traditionally used an ODS processing agent are manufactured by a small number of multinationals in Europe, North America, and Japan. One North American-based multinational chemical, plastics, and fibre company manufactures three basic product lines of fluoropolymers that have traditionally used CFC-113 as a process agent. Its manufacturing facilities are located only in non-Article 5(1) countries. The generic types of fluoroproducts are typically:

- Ethylenetetrafluoroethylene or ETFE
- Ethylenechlorotrifluoroethylene or ECTFE
- Perfluoroalkoxy, fully fluorinated resins or PFA
- Perfluorovinylethers

C-9.1.1 Process description

These products are typically produced in batch operations where resins, process agents (solvents), and other reactants are batch charged into reaction vessels followed by product isolation, product purification, and solvent recovery.

The operations described in this case study are unique to the industry due to their much higher volume and use of some continuous instead of batch technology for much of the production.

C-9.2 Unique Product Properties

The products are all high value resins used primarily in industrial applications where lower cost resins are unable to meet demanding performance criteria typically characterised by:

- Ultra-high purity and chemical inertness for chemical processing operations.
- Mechanical toughness and chemical inertness for containers dedicated to handling hazardous or toxic materials in a safe, environmentally sound manner.
- Predetermined electrical conductivity for extended use high temperature components.

Specific uses for these fluoropolymer resins include:

- Electrical and control wiring for commercial and military aircraft because of excellent electrical insulation properties, inertness to atmospheric pollutants, and retention of properties over very extreme temperatures.
- Non-stick coatings on high value cookware.
- Computer wiring.

C-9.3 Why and How is CFC-113 used as a Process Agent?

	Purpose
Quality of final product	XX
Safety	X
Necessary for reaction	
Yield	X
Cost	X
Other	

Notes to Table: X signifies the main purpose, XX signifies a secondary purpose

CFC-113 was originally selected as a process agent for this family of fluorinated resins because it exhibited several key properties:

- Low toxicity.
- Provides excellent dispersions.
- Suitable solvency for several polymer structures that are insoluble and a wide range of solvents.
- Inhibits explosion of tetrafluoroethylene (TFE) (backbone of these products).
- Chemical stability to temperatures and pressure.
- Non-flammable.

Since the four world scale manufacturing facilities exist and represent a combined investment of several tens of millions of dollars, it is economically impractical to convert to a flammable solvent without complete redesign of all process equipment and building to a flammable hazard classification.

The unique properties for several critical customer applications are very dependent upon the specific solvent and process conditions. Hence, finding a suitable solvent replacement requires not only that it provide similar process operability, safety, and cost, but its specific products must be rigorously proven in every unique customer application.

Another process safety concern is to suppress the explosion tendency of the main feedstock, TFE. Experience has demonstrated that hydrocarbon solvents that may exhibit suitable solvent properties will not suppress TFE explosions. The only practical solvents have proven to be fully halogenated materials like CFCs, perfluorocarbons (PFCs), hydrofluorocarbons (HFCs), and marginal hydrofluorocarbons (HCFCs).

Documented CFC-113 use for the global fluoropolymer plants are not accurate prior to the late 1980s since CFCs were not recognised as harmful to the environment and their use and emissions were not under any special control. Undocumented memory indicates that just one of four sites used about 400/tonnes/yr. of CFC-113. Documented use by 1988 was in the range of 250 metric tonnes per year for the four plants. By taking steps described in the following text, emissions have been cut by more than two-thirds of the 1988 documented experience; while product output has risen.

C-9.3.1 Efficiency of ODS recovery

Emphasis has been placed on developing technology to displace CFC-113 as opposed to expenditure of large R&D plus capital to achieve 99.9+% recovery. The short term process improvements and handling practices have generally resulted in a 90+% efficiency in CFC-113 use. See Section C-8.4. for details.

C-9.4 ODS Abatement and Containment

Overall process agent emissions are one-third of what they were in the late 1980s due to several capital and procedure steps taken at all four plant sites globally. It is important to note that one plant anticipated shutting down rather than spend the large amount of capital to convert to a non-ODS process agent; however sharply increased global demand necessitated continued operation of this facility. It is now planned to convert this facility to a non-ODS process agent if global market conditions support this activity.

All sites use similar technology to minimise ODS loss or to abate emissions. Vent collection and recovery systems capture and recycle 99% of CFC-113 in the primary vents. Losses previously experienced during plant maintenance are now recovered in a maintenance vent recovery system. Product dryer modifications reduce CFC-113 emission by greater than 90% of prior experience during dryer regeneration. A fugitive emission programme aimed at leak detection and repair has been instituted. Special emphasis has been devoted to mechanical seal designs, maintenance techniques, and use of a non-ODS seal flush. CFC-113 detectors have been installed on equipment pressure relief vents to ensure rapid correction of a relief device failure or activation. Finally, a rigorous solvent record keeping and emission tracking programme pinpoints sources for future CFC-113 reductions as well as focusing attention on current emissions.

Since the ultimate objective is to convert all plants and their respective products to non-ODS process agents, there has been a balance of scarce development resources and capital between minimising current CFC-113 losses and completion of the transition to non-ODS process agents.

Since the total makeup for the four plants is a rather modest amount, inventory at each site was established prior to the end of 1995 with the expectation that future ODS purchases would be unnecessary, assuming successful conversion to non-ODS process techniques.

C-9.4.1 Regulatory requirements

All four plant sites are in countries where chemical production facilities are permitted by national, state, or local authorities. CFC-113 is regulated in some states as a ground water pollutant, so any non-volatile waste is disposed of in environmentally secure landfills.

C-9.5 Non-ODS Technology Options

Efforts to identify potential alternate process agents that would work in the four different global plants and for the full range of fluoropolymer products got underway in 1987, following U.S. CFC industry recognition and support for an international regime to stabilise or reduce CFC emissions globally.

Any suitable replacement solvent(s) (process agent(s)) would have to deal with a host of process and product issues that were all cost effectively managed with a single solvent, CFC-113. Safety was of foremost concern since tetrafluoroethylene (TFE), the backbone of much of the product line has a tendency towards severe deflagration (explosion). A key property of the process agent of choice suppresses the deflagration tendency of TFE. Hydrocarbons will not suppress TFE deflagration but fully halogenated solvents will. With CFCs, carbon tetrachloride, and halons already set for phaseout, and HCFCs scheduled for near term phaseout, the options were significantly limited; primarily PFCs and HFCs.

Close to fifty potential process agents have been explored over the past eight years as part of a multimillion dollar research and development programme.

It is expected that much of the product line will be converted away from CFC-113 during 1997 and 1998. However, there are still specific critical customer applications that have not yet been able to accept the non-ODS products. Effort is continuing to find an acceptable process agent or suitable processing conditions for these products.

After eight years of extensive research and development, there are still unresolved challenges to a 100% ODS use phaseout and some continued use could occur past 1998.

A Japanese, manufacture of fluoropolymer resins has converted to a non-ODS process utilising a proprietary technology, however the facility does not produce the full range of fluoropolymer products.

C-10 USE OF CFC-11 IN MANUFACTURING A FINE SYNTHETIC FIBRE SHEET STRUCTURE

C-10.1 Introduction of Process

C-10.1.1 Products made, use of the products:

Fine synthetic fibres are formed into strong sheet structures used for a variety of important applications including:

- Air infiltration barriers in buildings to reduce heating and air conditioning costs and to extend the useful economic life of wooden building material (by excluding water rot)
- Medical device packaging that allows sterilisation after packaging and providing long, safe, shelf life
- Protective clothing for workers handling toxic or dangerous chemicals (i.e. asbestos removal)
- Packaging for important products and information in tear resistant light-weight envelopes that save shipping costs and assure intact long distance delivery
- graphic applications that ensure long life of maps, banners, tags, under severe climate or service conditions
- special purpose clothing, packaging, padding, and insulating applications

C-10.2 Description of Overall Manufacturing Process:

Fine synthetic polyolefin fibres are manufactured using CFC-11 as a process agent. CFC-11 is contacted with high density polyethylene pellets in a slurry mix tank, pumped with high pressure pumps through a heat exchanger and stirred tank mixers to form a spinnable polymer solution.

Using a manifold, the polymer solution is fed to spin packs mounted on top of a 'spincell'. Filaments are flash spun inside the spincell onto a belt to form a sheet structure which is consolidated, extracted from the spincell through seals rolls, devolatilised inside an air enclosure before being wound-up. The process agent, in vapour form inside the spincell, is entirely recovered, neutralised and returned to storage.

C-10.3 Why is the ODS used as Process Agent ?

QUALITY OF FINAL PRODUCT	PURPOSE XX
SAFETY	X
NECESSARY FOR CHEM. REACTION	
YIELD	X
COST	X
OTHER	

Notes to Table: X signifies the main purpose, XX signifies a secondary purpose

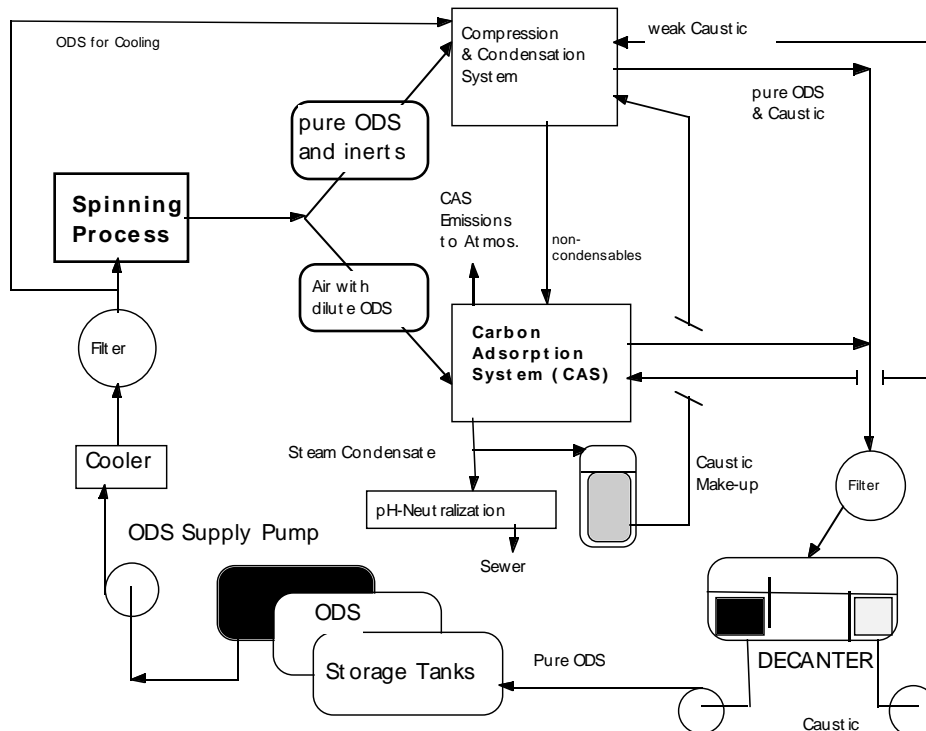
C-10.3.1 Unique process agent properties:

- low toxicity
- non flammable
- physico-chemical properties: boiling point, critical temp. / pressure
- solvency power (capability to enter polymer matrix)
- controls solution viscosity and process operating pressures
- chemical stability to high temperature and pressure
- non corrosive

C-10.4 How the ODS is used as process agent

Fine Synthetic Fiber Sheet Structure: Process Agent Recovery Flow

C.Metzdorf 10/96



C-10.4.1 Efficiency of ODS recovery after use

Typical ODS recovery efficiencies are 99.96 - 99.99 %, recognising a circulation of 19-24 tonnes/h in each production line.

C-10.4.2 Disposal of the ODS

The goal of the ODS containment process is the total recovery within the direct manufacturing boundaries. Disposal is not applicable to the type of ODS used.

The recovery process has a blowdown collection tank able to collect 'contaminated' ODS from the process and boil-off the pure ODS to be recovered.

C-10.4.3 Quantity required for make-up, past and future changes

Total process agent make-up quantity is in the 130 to 160 tonnes per year range reflecting different equipment utilisation rates.

C-10.4.4 Process Agent Losses: past and future changes for total global capacity:

Year	Locations/Lines	Losses [Tonnes]	Losses as % of '86 base
1986	U.S./2	2323	100
1987	U.S./2	1626	70
1988	U.S./2	1211	52
1989	U.S./EU/3	813	35
*			
1995	U.S./EU/3	131	< 6

It must be noted that approximately 10 % of the process agent losses are the result of ODS transformation or destruction, not from a diffuse or point source emission. In fact chloride salts measured in the active carbon adsorption system steam condensate neutralisation station confirm the ODS transformation and destruction mechanism.

C-10.5 Pollution Abatement

General description of control technology (EU plant data presented for case study consistency). The CFC-11 Recovery process essentially distinguishes between:

C-10.5.1 Primary Recovery (CCS)

The main process agent flow (approx. 24,000 kg/h) from the spincell (volume \approx 1000 m³) is recovered in a 'compression and condensation system' (CCS) utilising a spraycooler, compressor, condenser and vent condenser.

Recovered liquid is neutralised with caustic water injection, decanted before being pumped back to storage.

Non-condensables are vented to CAS.

C-10.5.2 Carbon Adsorption System (CAS)

Process agent vapours from the sheet devolatilisation process inside the air enclosure and other small quantities or dilute sources of process agent from process equipments are conveyed to the Carbon Adsorption System. Roughly 3 % of the main process agent flow is recovered in CAS.

Steam condensate from CAS containing trace amounts of process agent is recovered using an air stripper. The Carbon Adsorption System presents two 'point' emission sources: process agent from the continuous air exhaust and drying cycles.

Recovery Systems in place during upset conditions:

Following devices recover the process agent during process upset conditions:

a) all vessels presenting a vapour space with potential vapour pressure build-up are protected with a rupture disc connected to a containment tank. In case of spincell over-pressurisation due to recovery compressor failure, process agent vapours are also collected in this containment tank. Recovery of containment tank vapours takes place via CCS and CAS.

b) cold liquid process agent from rupture disk discharge lines are collected in a blowdown collection tank. Cold pellet/process agent slurry rupture disk discharge lines first pass a pellet collection tank before the liquid process agent is recovered in the blowdown collection tank.

c) hot process agent and polymer solution rupture disk discharge lines are connected to a flash tank. Flashing of polymer solution in the flash tank produces a fluffy polymer material that requires separation in a cyclone before the process agent vapours can be collected in the containment tank.

Diffuse emissions from valves, gaskets, etc. inside the building, including the pack change sequence which involves the opening of the spincell to exchange a spin position, are reported as H&V exhaust point source emission to the authorities.

C-10.5.3.a Recovery System Design Considerations:

Measures to collect routine losses previously not controlled:

- enclosure of sheet handling section of spinning machine
- tightening of spincell windows, new gaskets and local CAS vapour evacuation capability in case window has to be opened to remove polymer from inside machine spinning packs to maintain continuity
- additional partition wall in secondary enclosure to avoid dilution and provide second counter current air stripping slot
- installation of containment tanks to capture ODS from over-pressurisation of spincell and blowdown cell

- Venting of spin deck pack change 'bathtub' arrangement and pack cavity to Carbon Adsorption System (CAS)
- CAS air capacity increased to capture more air from different areas
- enclosure and air sweep to CAS around most centrifugal pumps in recovery and ODS supply system
- slurry pump packings vented to CAS
- all rotating penetrations into spincell vented to CAS
- impulse lines reduced to minimum essential length to avoid fittings at elbows which eventually leak due to associated equipment vibrations
- additional headers with connections to CAS to all areas requiring maintenance work and quick containment of small leaks

Carbon Adsorption System Upgrade:

- Titanium Vessels to fight corrosion from HCl gas, a result of ODS destruction
- CAS Steam-out manifold modified to avoid carbon blow-out and steam channeling
- high pressure steam supply for CAS steam-out; HP/LP steam ratio allows higher steam-out pressure to desorb more ODS
- CAS air capacity increased to capture more air from different areas
- added heater into main air duct to control relative air humidity and reduce competitive adsorption water vs. ODS on active carbon
- Insulation of CAS feed air piping
- additional heating coil in the drying air heater to reach max. 80° C drying air temperature

1995/1996

- close monitoring of all CAS valves (corrosion of valves has impaired proper functionality)
- exchange of active carbon after 7 years of service (9 tons of active carbon per bed)

- Control of Losses with Steam Condensate Discharge to Sewer:
- CAS steam condensate is decanted before discharge
- Steam condensate leaving the beds during heat-up is collected in separate tank for ODS vapour recovery before discharge
- CAS and Compression & Condensation System (CCS) combined to minimise caustic turn-around and ODS lost with aqueous discharge
- low temperature discharge and manual draining eliminated
- Steam Condensate multi-stage stripper prior to discharge to plant process sewer
- CAS steam condensate/caustic flows redesigned to scale-down discharge to plant process sewer
- water skimming equipment installed in all three ODS storage tanks for removal of decanted water (water being entrained into the tanks from the caustic neutralisation process during recovery)

Pressure Relief Containment:

ODS / Slurry System

- process pressure rating designed to shut down slurry pump rather than have polymer/ODS release to atmosphere
- containment and auto shutdown of slurry pump in the event of cold slurry rupture disc failure
- additional protection of all relief valves with rupture discs
- all cold/slurry relief lines connect to a pellet collection tank tied to the blowdown collection tank for evaporation of the cold ODS

ODS Vapour

Concept: Containment Tanks

- all vessels presenting a vapour space with potential vapour pressure build-up are protected with a rupture disc connected to the containment tanks..
- both the spincell and the blowdown tank are connected to the corresponding containment tank. In case of spincell over-pressurisation due to recovery equipment (compressor) failure, process agent vapours are also collected in this containment tank.

- Recovery of containment tank vapours takes place via CCS and CAS.
- the spincell containment tank has capacity for 10 minutes of major equipment failure prior to procedural shutdown of the process once the tank level alarms at 75 %
- Polymer Solution and Flush System
- all (17) rupture discs located in the high pressure polymer solution or flush system are connected to a flash tank. Flashing of polymer solution in the flash tank produces a fluffy polymer material that requires separation in a cyclone before the process agent vapours are collected in the containment tank.

C-10.53.b Process Control Strategies: Monitoring

C-10.5.3.b.1 Maximise Process Control

Redundant Distributed Control System (DCS)

- > 300 control loops
- 5000 monitored data points
- Flexible multivariable central control functions
- Computer assisted Carbon Adsorption System Troubleshooting Process Equipment: Spare and Protection
- Spare ODS Compressor; changed start-up from field to DCS
- Spare Carbon Adsorption System Blower
- Design done with Power-dip consideration allowing ride-through in case of minor interruption (< 0.7 sec.) and safely shutdown with contained ODS situation in case of major power loss

Misoperation and Equipment Failure Protection:

- Power dip ride-through ability up to 15 seconds with main drives of process, automatic shutdown of spinning and solutioning systems in the event of a major power dip in order to maximise ODS containment
- On-line spare ODS compressor available, remote S/U from DCS
- On-line spare CAS blower
- Laminar sparging of spincell with ODS installed to prevent recovery upsets due to excess air
- ODS flushed from Solutioning process and solution filters via additional heat exchanger to Blowdown Cell: ODS is superheated to eliminate liquid accumulation in Blowdown Cell
- Blowdown Cell walls heated to prevent condensation during Start-up and ODS accumulation in polymer mass after shutdown

Focus on Human Control Aspect

Provide adequate Control Tools

- 20 point building air monitoring system for quick detection of local losses
- 3 portable IR analysers for spot measurements
- H&V exhaust analyser for area loss detection (baseline between 1-2 ppm, pack changes cause a 4 ppm peak, baseline above 3 ppm triggers an area search using the portable analysers and the monitoring indications from the multipoint analyser)

C-10.5.3.c The 'HUMAN' Factor

C-10.5.3.c.1 Training and Failure Prevention

- Operator training; emphasis on process understanding and attention to detail
- Operators utilise all available tools (computerised troubleshooting, portable analysers) to localise and contain area ODS leaks
- Operator Acceptance Test for process control responsibilities
- Total commitment to control losses from all plant personnel
- Leak incident reporting system with corrective actions
- Computer-based equipment to continuously monitor ODS inventories in tanks, piping systems, vessels, automatically providing alarms as well as day-to-day loss rates to operators and managers
- An operator suggestion system rewarding those suggestions implemented in the field
- Equipment lock-out procedure not only aimed at safety but also at environmental control
- During maintenance activities, ODS drained out of piping, vapours evacuated to CAS, and liquid collected in central drum before being pumped into central process "evaporator"
- Preventive Maintenance program me to check mechanical integrity of all rotating equipment in contact with ODS
- Failure Mode and Effect Analysis (FMEA) performed for all routine practices, i.e. filter change, with the purpose of determining potential failures causes and work out procedures and or equipment modifications to avoid occurrence

- 'Zero Leak Team' Effort; cross section of organisation analysed all potential small leak sources and worked out solution to increase containment
- Strong analytical understanding of loss sources & material balances
- True technical team work with US plant & Engineering. counterparts
- Building multi-point analyser for continuous monitoring
- Wide spread attack with priority for large sources first

C-10.5.3.d Public Opinion:

- Open relationship with local government officials via timely technical information meetings about containment status and programmes
- Community Awareness and Emergency Response (CAER) as part of the 'Responsible Care' programme to inform local communities of plant activities
- Plant visits by customers, government officials and interest groups are conducted to demonstrate efficient production & recovery facilities and discuss containment strategy

C-10.5.4 Specific regulations affecting operations: (EU plant)

- Plant Permit modified from 10 kg/h in 1991 to 6 kg/h (50 to) since 1992
- Emissions to atmosphere from any point source to be < 27 ppm according to the German TA-Luft
- Diffuse emissions from valves, gaskets, etc. inside the building, including the pack change sequence which involves the opening of the spincell to exchange a spin position, are reported as H&V exhaust point source emissions to the authorities on a monthly basis
- CAS emissions are reported on 30 minute average basis to the authorities on a monthly basis
- Total Investment for Recovery Unit Equipment: 25 million \$

C-9.5.4.1 Reporting Requirements

Emission data from the commercial line are transmitted on a monthly basis to the local administration of the Environment. The data show the year-to-date and monthly loss rate and recovery efficiency of CFC-11, in addition the point source emissions of the H&V exhaust and carbon absorption system (CAS) are reported with indication of the 50 % and 98 % percentile.

C-9.5.4.2 Enforcement:

The plant management and employees are committed to strictly operate the facility according to local and/or international legislation.

C-10.6 Substitutes without CFC-11

C-10.6.1 Description

The fibre manufacturing area, including the solutioning, spinning and process agent recovery equipment, is the source of ODS losses.

No simple, safe, drop-in candidate has been identified to replace CFC-11 in the existing spinning facilities, despite a continuing (more than four years) programme that has examined over one hundred possible process agents. In contrast, our technical efforts in the past four years working with our central and corporate R&D lab facilities have successfully focused on developing a zero ozone-depleting process agent, but it requires completely new spinning and recovery facilities to use it.

C-10.6.2 Limitations

A pilot plant in the USA was authorised in January 1991, and was completed in May of 1992 to develop these new spinning processes. Significant learning's from the pilot plant have been incorporated in the new facilities being in a product prove-out mode now.

- THE NEW PROCESS AGENT was one of the compounds in the original patents but, in the late 1960's, non-flammability made CFC's a better choice for development.
- THE NEW PROCESS AGENT has since been demonstrated to yield different sheet properties in commercial plant prototype testing
- This new spinning process includes about 70 % new technology, most of it being associated with the spincell, spin pack hardware and for the commercial operation, the pack change technology used (and patented)
- The pilot plant continues to demonstrate new spinning hardware and procedures that are needed to safely manage the new process agent, combine it with the polymer, manage its recovery and recycling after flash spinning, devolatilise the sheet product, and provide the proper seals and ventilation. Pilot plant tests are refining optimum process conditions and developing the basic data for the major process elements.
- Process safety management is the key to maintain a safe operating environment.

C-10.6.3 Recent replacement

Two commercial lines were started up in mid 1995 but have not reached nameplate capacity mainly due to product property shifts that have required extensive technical work to find new operating conditions that will meet key sheet properties needs.

Delays of 15 months in commercialisation were caused by unexpected equipment failures, process safety and training issues.

Different sheet properties and visual appearance slowed customer acceptance.

To date, only 20 % of the complete product offering are considered as being commercial. All other products still require substantial technical development work to match the properties of the CFC-11 product offering.

C-11* USE OF TRICHLOROETHANE IN THE PRODUCTION OF SEMICONDUCTORS

*Note: This case study was prepared from information supplied by the supplier of the ODS for this application.

C-11.1 Description of How and Why the ODS are Used as a Process Agent

C-11.1.1 Introduction of the Process

The chemical 1,1,1-TCA (Trichloroethane) is used for oxidation purposes in the semiconductor industry. The products are DRAM, Microprocessors and discrete semiconductors.

C-11.2 Reason for the Use

1,1,1-TCA is used as a liquid chlorine source in order to generate ultra high purity HCL in a diffusion furnace. It is used to reduce heavy metals and mobile ions from furnace tube walls and as a source of HCL for thermal oxidation.

TCA has been used to shrink the size of staking faults and as a gettering source during the oxidation to reduce the effect of mobile ions.

C-11.3 Quality of the Product and Material Specifications

1,1,1-TCA is used only in the semiconductor industry for production of very sensitive devices. The oxide thickness could meet a range of 100 Angstrom, therefore the purity of the chemical should be in the ppb level for metallic elements and for the assay in order to avoid contamination of the silicon device.

C-11.4 Safety Aspects in the Production

TCA is not corrosive and easy to use. The delivery is made in very pure quartz bubbler with hermetic seals for protecting the chemical from environment influences.

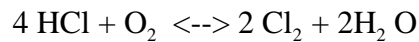
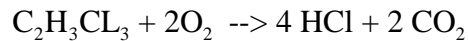
Compared with HCL, the TLV value is very high and is in the range of 200 ppm compared to 5 ppm for HCl. An HCL leak is one of the most destructive occurrences in the operation of a wafer plant. HCL will react with water to form chlorine, a very corrosive chemical which will damage the SS tubing and is dangerous for the humans in the plant.

C-11.5 Consumption

The total consumption for this application in Germany are as follows:

	1996	1992
1,1,1-TCA	100 litres per year	700 l/year
1,2 trans-DCE	600 litres per year	-
Methylene chloride	-	-

In the production, this chemical is used in the high temperature application. The temperature is always in the range of 800 °C to 1150°C. The reaction takes place as follows:



The amount of emitted 1,1,1-TCA is very low, because under normal circumstances a 100% transformation reaction will take place.

C11.6 Opportunities for Substitutes for ODS Use and Limitations

Prior to 1992, 1,1,1-TCA was the preferred source chemical for in-situ generation of HCL. The producer has developed new application for 1,2 -trans DCE and will now substitute the use of 1,1,1-TCA in the semiconductor production. This substitute is now the world wide standard for tube cleaning and oxidation application.

The second alternative is Methylene chloride. This chemical is used partly but the disadvantage is that it could be carcinogenic.

C-11.6.1 Comparison between all three chemicals

Material Identification	Trans-LC	TCA	Methylene Chloride
Flash Point	2 °C	no	no
Auto-ignition temp.	460 °C	540 °C	555 °C
Flammable limits in air	9.7 - 12.9%	7.5 - 14.5 %	12 - 66.4%
Usage compared with TCA	10% more	-	same

C-11.6.2 Cost for retrofit TCA plant to Trans-LC or Methylene Chloride

Trans-LC

Customer must modify the current temperature control system and requalify the process for all kind of semiconductor.

Time required is about 6 months and cost for average plant for equipment modification (30 tubes) is (US) \$30,000. The producer has spent approximately (US) \$5,000,000 for development and change of production.

C-11.7 Pollution Abatement

The production plant uses a wet scrubber to reduce the amount of 1,1,1-TCA emitted to the atmosphere.

Under normal conditions, there are no emissions of TCA to the atmosphere. Emissions would only occur as the result of an accident. In Germany where are national regulations for production. The production plant is located in US (Ca) and must comply with applicable national and international regulations.

PATF Comment:

Noting that feedstock is defined as “A controlled substance that undergoes transformation in a process in which it is converted from its original composition except for insignificant trace emissions as allowed by Decision IV/12” it would appear that this is a feedstock application rather than a process agent application.

C-12 USE OF CFC-12 IN THE PURIFICATION OF GRAPHITE

C-12.1 Introduction

Graphitisation is a method for the thermal treatment of carbon in which the disordered C atom structure is transformed into a parallel-layered grid-like-crystalline system. The transformation of the atomic structure takes place at temperatures of between 2,500 and 3,000 °C.

Thermal treatment takes place in electric furnaces. The material to be graphitised serves as the electric conductor. By supplying electric energy, the material to be graphitised is heated to approximately 2,500 °C, using direct resistance heating.

To obtain high quality special graphite, CFC-12 and nitrogen, serving as reaction gas and purge gas, respectively are fed into the furnace. This takes place during heating and cooling of the furnace at temperatures greater than 1,400 °C.

C-12.2 Why ODS is Used

	Purpose
Quality of final product	X
Safety of plant production	
Necessary for the chemical reaction	XX
Yield	
Cost	
Other	

Notes to table: X signifies the main purpose, XX signifies the secondary purpose

Graphite produced using the conventional graphitisation technique contains, among others, the elements Al, B, Cu, Fe, Mg, Si, Ti and V as impurities and has a total ash content of more than 1,000 ppm.

Special kinds of graphite with a total ash content of less than 100 ppm are needed for special industrial uses, e.g. X-ray tubes, heating elements and heating systems and for products for the semiconductor industry.

C-12.3 How ODS is Used

All of the CFC-12 is decomposed in the process. The halogens from the decomposition of CFC-12 react with the above mentioned impurities to form volatile metal halides.

C-12.4 Pollution Abatement

The halogens not transformed in the cleaning process following thermal decomposition of CFC-12 react with water in the air to form hydrochloric acid (HCl) and hydrofluoric acid (HF). The HCl and HF containing waste gas is collected by means of a closed hood situated above the furnace (encapsulated furnace) and fed to a scrubbing system. In scrubbing, concentrations in the waste gas are reduced to the permissible levels and the waste gas is subsequently vented to the outside.

C-12.5 Substitutes without ODS

Since 1991 the German facility has sought alternatives to the use of CFC-12. The results of tests in which R-134a and R-22 were used at various concentrations have shown that their cleaning effect was insufficient.

A direct change of CFC-12 with another substance does not seem possible at present. The facility is now attempting to modify the process conditions to achieve the same graphite quality using other non-ODS substances.

PATF Comment:

Noting that feedstock is defined as “A controlled substance that undergoes transformation in a process in which it is converted from its original composition except for insignificant trace emissions as allowed by Decision IV/12” it would appear that this is a feedstock application rather than a process agent application.

D

GLOSSARY

ATM	Atmospheric pressure
BAP	Best available technology
BEP	Best environmental practices
CAER	Community awareness and emergency response
CAS	Carbon adsorption system or carbon adsorption stripper
CCS	Compression and condensation system
CFC-11	Trichloromonofluoromethane
CFC-113	Trichlorotrifluoroethane
CR	Chlorinated rubber
CSM	Chlorosulphonated polyolefins
CTC	Carbon tetrachloride
DCS	Distributed control system
DCE	Dichloroethane
DRAM	Digital random access memory
ECO	Ecological
ECTFE	Ethylenechlorotrifluoroethylene
EDC	Ethylenedichloride
eop	End of pipe
ETFE	Ethylenetetrafluoroethylene
EU	European Union
FMEA	Failure mode and effect analysis
H&V	Heating and ventilation
HCFC	Hydrochlorofluorocarbon
HF	Hydrofluoric acid
HFC	Hydrofluorocarbon
HP	High pressure
IR	Infrared
LEL	Lower explosive limit
LP	Low pressure
MACT	Maximum achievable control technology
MT	Metric tonne
NPDES	Non-point discharge elimination system
ODS	Ozone depleting substance
PA	Process agent
PATF	Process Agents Task Force
PAWG	Process Agents Working Group
PFA	Perfluoroalkoxy, fully fluorinated resins
PFC	Perfluorocarbon
ppb	Parts per billion
ppm	Parts per million
PPD	Para-phenylenediamine

PPTA	Polyparaphenyleneterephtalamide
R&D	Research and development
SBR	Styrene butadien rubber
SS	Stainless steel
TEAP	Technology and Economic Assessment Panel
TCA	Trichloroethane
TDC	Terephtaloyldichloride
TFE	Tetrafluoroetheylene
TLV	Threshold limit value
UV	Ultraviolet

**MONTREAL PROTOCOL
ON SUBSTANCES THAT DEplete
THE OZONE LAYER**



Technology and Economic Assessment Panel

**PART III: ASSESSMENT OF THE USE OF FLAMMABLE
REFRIGERANTS**

**April 1997 Report
Volume II**

**Montreal Protocol
On Substances that Deplete the Ozone Layer**

UNEP Technology and Economic Assessment Panel

PART III: ASSESSMENT ON THE USE OF FLAMMABLE REFRIGERANTS

April 1997 Report, Volume II

The text of this report is composed in Times Roman.

Co-ordination: **TEAP and the Sub-committee of the TOC
Refrigeration, AC and Heat Pumps**

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EXECUTIVE SUMMARY

This report presents a preliminary assessment of flammable refrigerant options such as hydrocarbons and their mixtures, as well as certain HFCs. It will be followed by a complete assessment in 1998 which will present a broader picture including all refrigerant options for all refrigeration, air-conditioning and heat pump sub-sectors.

The search for CFC and HCFC substitutes has, in parallel with the evaluation of non-flammable chemicals, resulted in the identification of flammable refrigerants as replacements. It has now led to a renewed evaluation of the possible use of these flammable refrigerants. They had previously not been widely considered because they could not meet the safety standards in force at that time for certain uses. This assessment presents a brief overview of the current national and international standards and compares the various approaches to safety. The report also shortly discusses risk assessment and other tools to make a given use safe and describes the present-day available status of purity requirements applicable to flammable refrigerants such as hydrocarbons.

Currently, the use of flammable refrigerants is primarily limited to the field of domestic refrigeration in Northern and Central European countries where it has captured about 35% of the market. This represents about 8% of the world refrigerator market. Although several flammable refrigerants could be used either as pure fluids or as blends, the most prominent flammable refrigerant option is isobutane (HC-600a), which is being applied in virtually all new domestic products that use a flammable refrigerant. Products, including compressors, have undergone life-testing with good results and a great deal of experience has been built up by appliance manufacturers in Europe. When applied in small refrigeration equipment such as domestic refrigerators, the energy efficiency of HC-600a is comparable to, or often better than, the energy efficiency of CFC-12 or HFC-134a.

The emphasis to date has been on newly designed units, but there has also been "retrofit activity". Changing to a flammable refrigerant when the refrigeration circuit needs to be repaired is an option in countries where repair is an attractive option because of the low cost of manpower and the relatively high cost of new appliances. This option is already used in some Article 5(1) countries. Training for safety measures should be emphasised for all technicians, in both the formal and informal sector, which would include instruction on product modifications. Questions still exist about technical maturity and reliability of several types of hydrocarbon mixtures since the results of proper life testing are not generally available.

Hydrocarbon refrigerants are also beginning to be used in other refrigeration sub-sectors, such as commercial refrigeration, and in some air-conditioning systems. This report also summarises the current status of the market for hydrocarbons in commercial refrigeration, chillers, heat pumps, as well as portable air-conditioning units.

For uses other than domestic refrigeration, the application of flammable refrigerants in new products has been rather limited to date since there has been no mass production. The following trends may influence near-future market developments:

- manufacturers of commercial stand-alone equipment may benefit from the work which has been carried out on domestic appliances, particularly on compressors;
- a limited number of commercial refrigeration equipment has been installed in Germany, Sweden, the United Kingdom, in which options such as propane and propylene are being applied;
- compared to other European countries, the use of HCs in products other than domestic is most proliferated in the United Kingdom, where many pieces of stand-alone equipment are operated on hydrocarbons in the commercial sector;
- the market for heat pumps for heating only is restricted to Europe and the number of units using hydrocarbons is still rather limited (the number of outdoor units sold in Germany was about 800 in 1995);
- the air-conditioning market is dominated by American and Japanese companies which do not use hydrocarbons in this type of equipment. However, one Italian manufacturer of portable domestic AC systems uses propane for products sold on the German market (where the volume has been stated to be about 60,000 units in 1996).

With increasing experience in the Article 5(1) countries, flammable refrigerant technology is being and will increasingly be exported to the Article 5(1) countries, particularly in the field of domestic refrigeration. On the one hand, financial assistance from international mechanisms for conversions will certainly be contingent on studies of the differences between the operating costs for hydrocarbons and for other options. On the other hand, export of the technology will, for a larger part, be determined by the technology partnerships that exist or will be established between Non-Article 5(1) and Article 5(1) country manufacturers.

Information on the application of flammable refrigerants will continue to improve as more experience is gained from applications outside the domestic refrigeration sector. It particularly applies to cost comparisons and possibilities for and barriers to wider application. These aspects, amongst others, will be reflected in the 1998 Refrigeration, AC and Heat Pumps TOC Assessment Report.

Foreword

Historically, flammable refrigerants were only used in large refrigeration systems located in petrochemical facilities where large quantities of flammable products could be appropriately handled. The search for CFC and HCFC substitutes has, in parallel with the evaluation of non-flammable chemicals, resulted in the identification of flammable refrigerants as replacements. This has now led to a renewed evaluation of the possible use of these flammable refrigerants which had previously not been considered because, due to flammability, they could not meet the safety standards in force at that time for certain uses. Flammable refrigerants have currently found wide application in refrigerators sold in Northern and Central Europe; the option is also increasingly being applied in Southern Europe as well as in several other countries outside Europe, e.g. Australia, New Zealand and China. Flammable refrigerants are also being introduced in a growing number of commercial refrigeration applications and domestic heat pumps, mainly in Northern and Central Europe.

Amongst others, some ENGOs (Environmental Non Governmental Organisations) are promoting the use of hydrocarbon refrigerants for many types of new refrigeration and air-conditioning products, and the use of hydrocarbon mixtures as retrofit candidates, especially for refrigerators. This raises the question whether this is the beginning of a world-wide trend, and also the question for which use the flammable options are mature and can be handled and applied in a safe manner. Particularly in new small applications the use of flammable refrigerants is reported to yield comparable to better performance than CFC-12. Good results have also been reported in the case of larger capacity demonstration projects. On the other hand, for certain refrigeration sub-sectors the application of flammable refrigerants is less probable, since other substitute options, including HFCs, are already applied or under development.

As flammable refrigerants have recently become popular in some sectors, the UNEP Technology and Economic Assessment Panel requested its TOC Refrigeration, Air-Conditioning and Heat Pumps to undertake a preliminary assessment in early 1997, to be followed by a more complete assessment report which will be published in 1998. This assessment will be limited to only describe issues involved in the application of flammable refrigerants such as hydrocarbons and their mixtures, as well as certain HFCs.

In September 1996, the TOC established a Subcommittee to draft a comprehensive report on the use of flammable refrigerants. After discussions with several TOC members, the TOC co-chairs created a small Task Force (consisting of TOC members and experts from outside), to report on the use of flammable refrigerants in domestic appliances. The Subcommittee co-chairs also agreed to merge the Subcommittee and the Task Force reports into one assessment report on flammable refrigerants. Membership of the Subcommittee and the Task Force is annexed to this assessment report.

1 SCOPE

This report identifies the present considerations given to the use of flammable refrigerants in domestic and commercial refrigeration and air-conditioning products. It also provides elements judged critical in the assessment of social and technological knowledge or experience in relation to the potential uses of flammable refrigerants in new and existing refrigerating systems. Within this framework, the present report (i) provides a general overview of flammable refrigerants, (ii) carries out an assessment of the safety codes used, (iii) describes the application of flammable refrigerants in new domestic and commercial products, and (iv) discusses retrofits to flammable refrigerants. The emphasis is on the currently available technical knowledge related to both reliable and safe application. The report also tries to identify those areas where more experience is needed and where a more thorough evaluation could lead to a reliable and safe application of flammable refrigerants.

A more comprehensive picture on all refrigerant options will be presented in the 1998 assessment report.

2 GENERAL ASPECTS OF FLAMMABLE REFRIGERANTS

Flammable refrigerants are classified as moderately or highly flammable, depending upon the concentration at which they become flammable in air and upon the heat of combustion. The less flammable group is defined as group 'A2' in the ASHRAE Standard 34, and the more flammable one is defined as group 'A3', respectively '2a/2b' and '3' in the Pr-EN 378 Standard which has, for the larger part, been copied from the ASHRAE standards. In this report, the principal focus will be on the group 'A3' refrigerants (which excludes ammonia). For a more elaborate discussion, one should refer to sections 2.3 and 3.2.

2.1 Definition of Flammability

All definitions of flammability depend on the concept of flammability limits. The concentration of a gas in air below which the mixture will not ignite is the lower flammability limit (LFL), while the concentration in air above which the mixture will not ignite is the upper flammability limit (UFL). These limits are frequently defined as lower and upper explosive limits (LEL and UEL). Those gases which have a LFL and a UFL in air at atmospheric pressure and temperature are generally considered to be flammable. For many well known gases, there are already published limits of flammability using a variety of test methods. Since these gases are distinctively flammable, these methods result in only small differences in the LFL's or UFL's.

For new refrigerants for which there is little or no published data (which does not apply to most HCs) or for which flammability characteristics have not been previously studied, some standard-setting bodies rely on ASTM Standard E681, written by the American Society of Testing and Materials (ASTM). E681 defines a test method for determining flammability limits. Over a series of trials in which the concentration in air at atmospheric pressure increases by a set amount, a refrigerant sample is vaporised and exposed to an ignition source. The test method specifies the volume and shape of the flask, the ignition sources, and the increments of concentration. The flammability limits are the lowest and highest concentrations at which flame propagation occurs. Flammability testing is relatively simple for pure refrigerants. In contrast, blends pose new challenges because they change composition as they vaporise.

Historically, the goal of flammability testing was to find non-flammable refrigerants, not to define the precise boundary between flammability and non-flammability. Test protocols were designed to provide adequate safety margins within the bounds of non-flammability. Because of the CFC phaseout, however, the situation has changed as several flammable refrigerants have found application; certain blends that contain flammable components have also emerged. New standards have been written and are still being further developed to better define and limit test conditions. Specific test procedures may be obtained from the appropriate bodies.

The relationship between flammability of a refrigerant and safety of refrigeration systems is described below, in sections 3.1 and 3.2.

2.2 Environmental Factors

Flammable refrigerants belong to various chemical families including hydrocarbons (HCs), ethers and hydrofluorocarbons (HFCs). The interest in these chemicals is increasing because they generally have a rather low Global Warming Potential (GWP), a zero Ozone Depletion Potential (ODP), and acceptable properties for use as a refrigerant. Of these chemicals, only HCs are currently applied (mainly in domestic refrigeration) and show a recent history of successful operation. Whether other types of flammable refrigerants will be developed depends on needs, on the possibilities for experimental optimisation and lifetime testing, provided that adequate transport and property data exist or can be developed.

Table 2.1 summarises some key environmental indices of several flammable refrigerants. All HC refrigerants considered in table 2.1 are Volatile Organic Compounds (VOCs) and could be subject to local regulations when handled in large quantities. The small amount of hydrocarbons used in refrigeration (or aerosols), compared to the very large quantity used for combustion (more than 99%), leads to the conclusion that the VOC aspect of HC refrigerants will remain small. If one takes into account the fact that they are normally applied in hermetic or tight systems, it implies that concerns should only be directed at VOC emissions during manufacturing or disposal.

Table 2.1 - Environmental data for selected flammable refrigerants which could be applied as pure fluids /UNE94/.

Refrigerant	Name	Ozone Depletion Potential	Global Warming Potential	Volatile Organic Compound
R-50	Methane	0	24.5	Yes
R-170	Ethane	0	<15	Yes
R-270	Cyclopropane	0	<15	Yes
R-290	Propane	0	<15	Yes
R-600	Butane	0	<15	Yes
R-600a	Isobutane	0	<15	Yes
R-1270	Propylene	0	<15	Yes
E-170	Dimethylether (DME)	0	<1	Yes
HFC-32	CH ₂ F ₂	0	650	No
HFC-152a	CH ₃ CHF ₂	0	140	No

Note: the GWP values given for the different hydrocarbons are one to three orders of magnitude lower than the GWP values of the refrigerants they replace (e.g., GWP (CFC-12) = 8500, GWP (HCFC-22) = 1700). The GWP of these HC refrigerants could change as has the GWP for methane. Methane had a value of 11 for a 100 year time horizon (integration period) in the 1992 IPCC report. However, in the 1994 IPCC report, the value was revised to 24.5, because the estimate of its atmospheric lifetime was modified due to the fact that its indirect effect, i.e., the creation of another greenhouse gas (tropospheric ozone), was taken into account /IPC94/.

GWP data alone of a particular refrigerant are not sufficient to assess the full global warming contribution of its use because the GWP of the CO₂ associated with the energy consumption of the refrigeration system has to be taken into account. The Total Equivalent Warming Impact (TEWI) concept allows comparison of the impact of energy consumption and the impact of refrigerant emissions during the system's lifetime. A number of calculations have been published /DOE94/ which show that, in the case of HFCs, the energy consumption represents between 90 and 95 % of the total warming impact for a domestic refrigerator.

In the case of e.g. hydrocarbons, virtually 100% of the total warming impact stems from emissions related to energy consumption. Depending on the emissions, the direct effect of the refrigerant release can be much larger, e.g. for larger systems and also for mobile air-conditioning. However, many assumptions are made in the calculation of the TEWI factor (power generation mix, leakage rates, recycling at disposal etc.) which will result in a wide range of TEWI factors which are then difficult to use in an absolute sense. Clear and consistent definitions are needed when comparisons are made; the TEWI is very useful for comparison between products.

2.3 Manufacturing Considerations

As with any chemical, many issues have to be analysed to assess the feasibility of application in an industrial setting, and the associated servicing cost. Several factors that have been identified are (i) purity, (ii) availability, and (iii) price.

2.3.1 Purity

A wide range of technical opinions exist concerning the required level of purity of HC refrigerants. There is no mention of flammable refrigerants in any of the refrigerant standards, such as ARI 700, as most flammables were not used in domestic or commercial refrigeration systems at the time the standard was written. Therefore, there was no need to develop specific flammable refrigerant purity specifications at that time.

Commercial grades of HCs used for combustion vary in quality throughout the world and often permit up to 10% of gases other than the nominal composition. These other gases include other HCs, nitrogen, CO₂, air, moisture etc. The effects on the performance and reliability of a refrigeration system over the life of the product have - at least so far - not been adequately assessed.

The application of HCs in domestic refrigeration led to the draft of the German standard DIN 8960 that requires a comparatively high purity (99.5%) for HC refrigerants. More than a question of thermodynamics, the 99.5% purity level ensures that levels of undesirable impurities like unsaturated chemicals and sulphur compounds are kept down to trace amounts. Another reason for tight purity specifications is the known toxicology of probable impurities (e.g., benzene, a carcinogen; n-hexane, a neurotoxin) in these products /OOR95/. The level of purity required today for HC refrigerants in domestic refrigeration is high; it corresponds to the grade 2.5 for the petroleum gas industry. The presence of other HC compounds in the refrigerant may have negligible effect on system operation, but the standard practice should be to follow the compressor manufacturer's or OEM's recommendations. The level of purity required affects availability and price of the product.

2.3.2 Availability and Price

Availability and price of flammable products vary primarily in relation to their purity. Although technical grades are cheap, refrigerants of the purity recommended at present by refrigerator manufacturers (and by the draft DIN 8960), for new products and servicing are relatively expensive.

The price list of a refrigerant wholesaler shows that isobutane -with a purity that is lower than that of the grade 2.5 - can be twice as expensive as HFC-134a for comparable packaging /HRP95/. In the case of domestic appliances, the quantity of charge required by systems using HC refrigerants is approximately half of that required for the equivalent HFCs, therefore this difference is offset.

The high cost of the currently applied HC refrigerants is only partly due to higher transport and filling costs required for safety. The principal factor is the purity required, and the limited number of companies that can supply this quality, even in the developed countries. If lower levels of purity could be applied, the cost of HC refrigerants could be significantly reduced. It is important that at least 97% of such a mixture be the nominal refrigerant, and at least 99.5% of such a mixture be saturated alkanes. This specific level and definition of purity will, in turn, affect cost. The market for aerosol propellants of high grade purity may also be of influence.

Of course, one can anticipate that a larger market will motivate petrochemical companies to invest in purification plants, leading to lower prices. However, quantities may remain too low for a dramatic change, since the volumes required as CFC substitutes are very small compared with the world trade in the relevant HC compounds for other applications /OOR95/. It is difficult to elaborate on future price development because it is difficult to estimate the extent to which HC based systems will penetrate the market.

If HC refrigerants are to become prevalent world-wide, then Article 5(1) countries will have to choose between developing an indigenous supply of purified HC refrigerants and importing them /OOR95/.

3 SAFETY OF SYSTEMS USING FLAMMABLES

The opinions of experts involved with standards related to safety of products, product repair, product manufacturing, transport of refrigerants, and other important considerations, have been expressed in various forms.

The following attempts to synthesise these views into a single cohesive picture in order to aid in refrigerant selection.

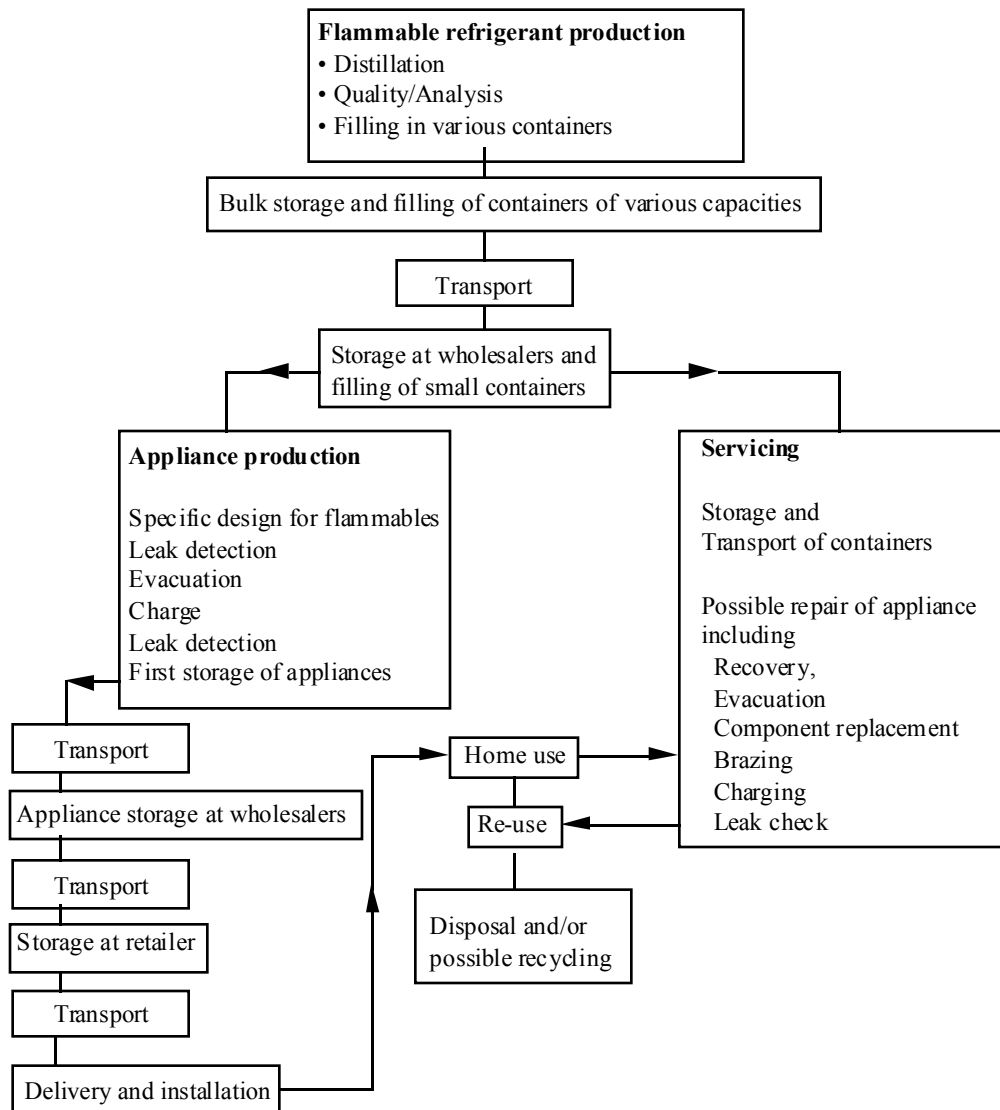


Figure 3.1 - Major life cycle steps used in domestic refrigerators safety analysis.

3.1 What is to be Considered for Safety

Handling and use of refrigerants, particularly flammable refrigerants, requires an analysis of various phases of the life cycle for each refrigerant and each application. Figure 3.1 summarises these major phases.

The analysis is peculiar to each type of refrigeration or air-conditioning system. The refrigerant production is independent of the application, but major differences exist between plant-assembled systems and those assembled in the field. The example shown in Figure 3.1 corresponds to mass production of an appliance which does not require field assembly.

Existing standards or regulations do not cover all phases of the life cycle of the refrigerant in detail. Rigorous procedures are required for all companies and individuals handling flammables. The three following aspects have to be addressed.

(1) Manufacturing, Transport and Storage

The following aspects need to be particularly mentioned:

- Storage areas for flammable refrigerant containers and systems containing flammables require special design and control;
- Areas where flammables are handled must be specially designed and must be in compliance with safety regulations;
- In Europe, transport regulations apply only to flammable refrigerant in containers, and do not apply to final products containing a flammable refrigerant.

(2) Consumer Safety

Consumer safety is covered by the principle of responsibility of the system's manufacturer who is legally responsible of the risks incurred by the end-user for a "normal" use of the system or appliance.

Discussions are still ongoing in standards' groups on the principle of the compulsory labelling and the use of standardised marking to inform the consumer that the system or appliance contains a flammable refrigerant. To date, only the compressor of the appliance shows the standardised warning for flammable materials. In many cases it is not at all easy to see. None of the domestic appliances (refrigerators, air-conditioners or dehumidifiers) sold in Europe and containing flammables are marked with such a standard label.

Servicing

- Special training of operators is required for safe handling of flammable refrigerants and all operations related to system servicing. In Germany, where many refrigerators are running with isobutane, the servicing teams are employed by the companies which produce the refrigerators. This is a departure from normal practice in which refrigeration technicians, wholesaler's and retailer's staff or individual entrepreneurs generally deal with refrigeration servicing.

- Equipment designed especially for flammable refrigerants must be available, particularly for leak detectors, vacuum pumps and recovery equipment. Brazing or welding must be performed under special safety conditions or simply prohibited. A large producer of HC refrigerants recommends that suitable fire extinguishers should be sited adjacent to the work area /Cal/.
- End-of-life disposal of systems/appliances has to be considered carefully since policies for recycling of domestic appliances and their refrigerants have been initiated or have already been implemented in many countries. Refrigerant disposal or recycling is part of these policies.

3.2 Content of Safety Standards

Safety of refrigeration systems concerns two aspects: (i) mechanical and (ii) electrical. International safety standards are promulgated by IEC for electrical aspects and by ISO for mechanical aspects. Even though ISO and IEC tend to be in harmony, it appears that there is no formal co-ordination of both types of standards, and some recommendations can be different -if not conflicting- between the two standard types.

3.2.1 Mechanical Standards

For mechanical safety standards, at least 3 references have to be considered (i.e. ISO 5149, Pr-EN378⁵, ASHRAE 15). In Annex 1 a more detailed comparison is presented. Those standards intend to assure safety of persons and goods as far as the characteristics of design, installation and operation of refrigeration and air-conditioning systems are concerned.

They cover classification of :

(1)refrigerants

Safety classification of refrigerants takes into account toxicity and flammability. ASHRAE 34 defines the flammability categories based on the results of testing in accordance with ASTM E681 plus the heat of combustion.

(2)refrigerating systems

This classification aims at characterising the potential for direct emission of the refrigerant into occupied spaces.

(3) room occupancy

This is based on their use and their occupancy density.

Limitation of use

Based on these 3 classifications, a specific chapter in each standard defines refrigerant restrictions tailored to the room, occupancy type, and the refrigeration system characteristics. ISO 5149 and ASHRAE 15 ban the use of A3 “ flammable refrigerants ” , except in laboratories and industries.

⁵ The Pr-EN378 standard has not been finalised. Discussions are still ongoing in which way the requirement for installation, restrictions in room occupancy, type and training should be dealt with. It implies that some changes may still be made. Data presented in this document stem from the most recent Pr-EN378 version.

Related to the application, the guidelines of Pr-EN 378 are more complex:

- A3 “ flammable refrigerants ” can be used up to 1.5 kg for any type of occupancy as long as the refrigerant charge is lower than the practical limit of 8 g/m³ at room volume
- in a machinery room, maximum quantities can be 5 kg, 10 kg, or unlimited depending on the type of occupancy. When machinery rooms are located in basements, the limit is 1 kg in all cases.

Many references are made to the updated British Standard BS 4434 which was revised in 1995 in order to deal with flammable refrigerants ; it must be clear that this standard will be superseded when EN-378 will be enforced.

3.2.2 IEC Standards

Annex 2 synthesises the content of the two amendments ⁶ of IEC electrical standards which address the subject of flammable refrigerants in domestic appliances.

Concerning the use of “group A3” flammable refrigerants:

- IEC 335-2-24 defines safety rules for appliances using up to 150 g of flammable refrigerants ; and
- IEC 335-2-40 defines safety rules for air-conditioning systems that use up to 5 kg of flammable refrigerants.

In the case of flammable refrigerants, installation requirements of IEC 335-2-40 draft are as follows :

- for outdoor or indoor installations which contain less than 5 kg, the construction requirements of Annex 2 apply;
- for indoor installations the additional provisions of Table 3.1 apply;
- for indoor or outdoor installations which contain more than 5 kg, national standards apply.

	m < 0.15 kg	0.15 kg < m < 1.0 kg	1.0 kg < m < 5 kg
Unventilated	N.T.	X	X
Natural ventilation	N.T.	N.T.	X
Forced ventilation	N.T.	N.T.	N.T.

Table 3.1 - Installation requirements as contained in the IEC 335-2-40 draft, e.g. for R-290 (X: test required; N.T. : no test required)

⁶ The draft of amendment IEC 335-2-24 (domestic refrigeration) is being circulated for vote and the draft of amendment IEC 335-2-40 (air-conditioning) has just been submitted to the secretariat. Thus contents of these amendments are still subject to change.

The current versions of the IEC standards do not take into account flammable refrigerants and the updating process has not yet been finished.

3.3 Risk Assessment

Risk is the likelihood of an adverse outcome. The risk analysis covers two parts :

- the description of the event's consequences;
- estimation of likelihood.

For refrigeration systems, the causes of potentially hazardous events are:

- over-pressure and explosion of pressurised enclosures;
- leaks of toxic, flammable or suffocating chemicals;
- large emissions of refrigerant when opening the system or transferring the refrigerant.

Several factors affect flammability risk. First, risk is extremely sensitive to the specific refrigerant and the charge size. Both flammability limits and the energy produced when refrigerants burn (heat of combustion) can vary substantially.

The key measure of risk posed by flammable refrigerants is a scientifically valid, comprehensive risk assessment. Such an assessment must reflect potential leak scenarios, potential ignition sources, the likelihood of ignition, the consequences (injuries, deaths, and property damage) of ignition or explosion, and potential measures to mitigate against risk.

A valid assessment combines testing to identify relevant leak scenarios and ignition sources, review of existing data, reasonable assumptions and extrapolation, and analysis.

After appropriate testing, it is important that statistical data be found that accurately describe the particular refrigerant/system combination being investigated. This information will generally take the form of service histories, types and frequencies of system failure modes, etc.

For a domestic refrigerator, useful statistics would include the percentage of refrigerators that leak into the interior of the cabinet vs. the exterior, the percentage of systems that need servicing, and the frequency of compressor failure that could cause sparking or excessive temperatures.

Finally, a risk assessment combines testing and statistical data with a set of assumptions intended to represent the real world. Typically, a great deal of data are either unavailable or prohibitively difficult to obtain, so it is important to identify any assumptions and to explain in detail why they are valid.

Flammable refrigerants may pose risk at every step in the system's life; it is important that the discussion not focus solely on consumer safety. Worker safety must be considered, including assembly line, transportation, installation and servicing personnel. In addition, disposal of systems taken out of service must be taken into account.

The end product of a risk assessment is typically an estimate of the increase in the occurrence of fires, personal injury, and property damage as a consequence of a particular course of action or the use of a particular product. The assessment does not assign an “acceptable” level of risk; that decision must be made by the appropriate authorities within a given jurisdiction.

4 EXISTING FLAMMABLE REFRIGERANT OPTIONS

4.1 General Remarks

A number of pure fluid flammable refrigerant options could be considered for use in refrigeration and air-conditioning; these have been listed in Table 2.1 above. Properties of most of these fluids are given in Annex 3.

None of the pure flammable refrigerant fluids has the same boiling point at atmospheric pressure as CFC-12. Ethane and butane may be considered for specific applications which are not dealt with in this report. On the basis of its pressures and performances, propane (HC-290) is normally considered as a substitute for HCFC-22. The boiling points of both E-170 (dimethylether) and HFC-152a are almost the same, and are comparable to that of HFC-134a. This is why HFC-152a is sometimes considered as a 'low GWP alternative' for the non-flammable HFC-134a.

In Table A3.1 of Annex 3, the properties of the single fluid flammable refrigerants are given, along with the properties of CFC-12 and HFC-134a. Tables A3.2 and A3.3 in Annex 3 give the properties of the flammable mixtures. All properties have been calculated using the "REFPROP 5" programme distributed by the US National Institute of Standards and Technology /NIS96/. Technical feasibility and engineering options for domestic refrigeration in particular will be dealt with in more detail in Annex 5. Some preliminary observations can be found in this section.

4.2 Specific Observations

For the pure flammable refrigerants as well as for their mixtures, a number of observations apply. In this report, they are derived in part from the properties described in the three tables in Annex 3 (here a reference compression cycle between -25°C and $+55^{\circ}\text{C}$ is used, related to domestic appliances, but used for other purposes as well). Some observations come from other sources, such as material compatibility studies and lifetime testing.

(1) In the case of pure fluids, the following observations are relatively important:

- pressure ratios vary widely, from 20% lower than that of CFC-12 (in the case of HC-290) to 40% higher (for HC-600, butane). The pressure ratios for most hydrocarbons are higher than the one for CFC-12. Particularly in the case of isobutane, propane and butane one can observe significantly lower discharge temperatures. This characteristic may increase the efficiency of some compressors (which also depends on the compressor design);
- the discharge temperatures for cyclopropane HC-270, dimethylether E-170 and HFC-152a are rather high, compared to CFC-12, which might cause difficulties unless design changes are made, particularly if these refrigerants would be used at high ambient temperatures;
- theoretical considerations show that, in order to maintain refrigeration capacities similar to that of CFC-12, an increase or decrease of the compressor displacement will be required. As shown in Table 3.1, the v values are (i) +90% for HC-600a, (ii) -33% for HC-290, (iii) +13-15% for both DME and HFC-152a and (iv) +140% for HC-600. In practice, due to somewhat different temperature and pressure influences, compressor displacement changes will be slightly different than the values given in Table 3.1, e.g. for HC-600a: 75-80%, instead of 90%.

- compared to CFC-12, the pressure differences across the piston are about 40% higher for propane and 40% lower for isobutane, which may require either higher or lower viscosity lubricants, respectively. In contrast, cyclopropane (HC-270), dimethylether (E-170) or HFC-152a exhibit pressures similar to CFC-12;
- the COP values calculated for a cycle (-25° C evaporation and 55°C condensation with sub-cooling) are almost identical for CFC-12, HC-290, E-170, HFC-134a and HFC-152a;
- the COP values calculated for isobutane and butane are 6-8% higher than those calculated for other pure (flammable and non-flammable) fluids (this includes two-temperature level refrigerator-freezer combinations).

(2) For propane/isobutane mixtures:

- the necessary compressor displacement for different percentages of the HC-290/HC-600a mixture varies from -10% to +5% of the CFC-12 displacement. COP values calculated for different percentages are not much different than those for CFC-12. For certain percentages of propane (50-60%) in the propane/isobutane mixture, the mixture is, thermodynamically spoken, good replacement;
- a mixture with 60% propane and 40% isobutane could be considered as a direct replacement for CFC-12. If higher percentages of isobutane are applied in a CFC compressor, the necessary motor torque will be reduced (0-30%), leading to lower motor efficiency;
- the temperature glide for the propane/isobutane mixtures is considerable, which is in fact prohibitive for application in multi-temperature level refrigerators, unless significant design changes are made.

(3) For propane/butane mixtures:

- for high percentages of propane in a propane/butane mixture (in the order of 70 weight percent of propane), the CFC-12 compressor displacement would be sufficient for capacity reasons, the pressure levels would be comparable to CFC-12, and the discharge temperatures would be low. Based upon these facts, the mixture could, in principle, be a replacement, at a slightly reduced efficiency;
- for butane percentages in the range between 40 and 70%, the refrigeration capacity reduction is substantial, which will lead to a decrease in efficiency. Unless the compressor displacement is adjusted, these mixtures cannot be considered as replacements for CFC-12;
- the temperature glide of propane-butane mixtures is even higher than that of the propane-isobutane mixtures. E.g., for mixtures containing more than 60% butane, the increase in the temperature glide in the evaporator is substantial (10-14 K), which makes it highly unlikely that this mixture can be applied without significant design changes, at least in multi-temperature level refrigerators. Questions can even be raised regarding an adequate application in simple refrigerators.

In the case of hydrocarbon mixtures, it is possible to select mixture ratios in such a way that the refrigerant mixture can be considered as a direct replacement for CFC-12 on the basis of capacity. In principle, this applies to mixture of propane and isobutane, as well as to a mixture of propane and butane.

It is not clear whether one can directly transfer the properties of mixtures containing highly purified propane and butane to those (commercially) available mixtures, called "Liquefied Petroleum Gas", or "LPG". LPG is a mixture of propane and butane (butane weight percentage in the order of 30-70% , average 50%); it also contains small (not well defined) percentages of other saturated alkanes, and contaminants, including moisture at an unknown percentage. Together with the high boiling point of butane, this implies that this mixture cannot be considered as a reliable (over the lifetime of the product) replacement for CFC-12, even not on the basis of equal capacity. It will even be difficult to give some adequate guidelines regarding its application at present. Further considerations can be found in Annex 5.

Commercially available "LPG" is promoted by some environmental groups as a retrofit refrigerant for domestic refrigeration in Article 5(1) countries. It is unclear what composition of LPG would be available in the "typical" Article 5(1) country, because reliable data are lacking. Some sources mention that it can contain isobutane in addition to propane and butane, and an unknown percentage of impurities. This raises serious questions about whether a recommendation for application should be made at all at this stage, since, in addition to technical aspects, the reliability and performance of the retrofitted product may be seriously affected. More results from technical evaluations and case studies are needed to make a more valid recommendation. Nevertheless, it is claimed by Cuba that 60,000 refrigerators have been converted to mixtures of hydrocarbons including LPG in their country. No scientific data on performance and reliability have so far been published.

The azeotropic mixture of HFC-134a and HC-600a shows a very high refrigeration capacity (22% larger than that of CFC-12), which implies that it cannot be considered as a direct replacement. From a thermodynamic viewpoint, the azeotropic mixture of HFC-152a and HC-600a seems to be a more appropriate replacement for CFC-12. It has been developed and is being promoted by GYPH St Petersburg; no performance or reliability measurements have so far been presented in the open literature. The efficiency of the mixture (in a -25/55 °C refrigeration cycle) is calculated to be 10% higher than that of CFC-12; however, there is only a small difference compared to pure HC-600a. For both mixtures, a polyolester lubricant should be used. The application of mineral oil leads to high equilibrium pressures which may complicate reliable application of certain products (high suction and discharge pressure at start-up).

5 USE OF FLAMMABLES IN DOMESTIC REFRIGERATION

5.1 General Remarks

This section gives a number of observations that are related to the application of hydrocarbons in small systems.

Refrigerant Charge

The charge of hydrocarbons in refrigeration systems is considerably lower than the charge of fluorochemicals (CFCs, HCFCs, HFCs) in equivalent systems. This is often considered to be a cost advantage, however, this can only be related to cost price level differences (per kg) and not to thermodynamics. In liquid and gas volume, the amounts are more or less identical; this is due to the difference in liquid density. Flammability limits are expressed in % volume in air, therefore the gas volume is the only relevant parameter. Furthermore, the refrigeration cycle is designed around volumes and not on the mass of refrigerant applied.

A small charge may imply that charging is more difficult, since small differences in charge lead to considerable differences in energy consumption. Overcharging could lead to a small liquid refrigerant flow to the compressor (if not evaporated in the suction line heat exchanger) which might have an effect on oil viscosity, and could even damage the compressor. This does not apply so much to new production with automated equipment but very much to servicing, where very accurate equipment will be necessary. Ways would need to be developed to determine the correct amount of charge for retrofit of a CFC-12 appliance.

The application of hydrocarbon mixtures may, from a compressor design standpoint, not be much different from the application of pure fluids. However, as far as charging is concerned, this will be the same as other refrigerants, liquid charging will be required when zeotropic mixtures are used which is far most difficult for small charges.

Lubricant

In several cases, no change of the hermetic compressor lubricant (mineral oil) will be required. However, in the case of low pressure refrigerants a reduction of the lubricant viscosity may be possible (sometimes requiring additives), which will have a favourable effect on the energy efficiency (efficiency increases up to 6% have been measured by at least one European compressor manufacturer). In contrast, using high pressure refrigerants, one may need a higher viscosity lubricant due to viscosity reduction by dilution or due to higher forces on the bearings requiring higher viscosity, particularly at start-up (this applies to propane and to several propane-based mixtures, if the compressor is not totally redesigned). Information on hydrocarbon solubility in mineral oil can be found in several publications /Hes93/.

Contaminants

Hydrocarbons for refrigeration purposes (particularly in small, capillary tube systems) must be as free as possible of impurities such as sulphur compounds, unsaturated hydrocarbons (olefins), n-hexane, aromatics, non-condensables and water. Most manufacturers have experience that indicate that hydrocarbon systems are less sensitive to moisture than CFC-12 systems, however, some state the opposite. Nevertheless, it raises serious questions about the applicability of commercially available LPG (see above).

Some suppliers have offered , or are offering , hydrocarbons with a certain (relatively low) impurity level of other stable hydrocarbons (on the order of 3%). This raises concerns related to efficiency deterioration caused by changes in the boiling point and by the temperature glide of the refrigerant mixture. Tests performed by Wenning /Wen95/ indicate that mixing a pure hydrocarbon with 3% of other, stable hydrocarbons should not significantly affect the system performance (shown on isobutane applications). Nevertheless, virtually all manufacturers of domestic refrigeration products which use hydrocarbons (isobutane) require the highest purity level of 99.5% (2.5 grade).

5.2 New Appliances

5.2.1 Brief history

Hydrocarbon refrigerant s were introduced in the beginning of the 20th century (i.e., Linde in Germany, 1916). In the 1920's and 30's, refrigerators were developed that used isobutane (an HC), sulphur-dioxide and some methyl-chloride. Due to the fact that several accidents occurred (particularly with sulphur-dioxide), CFCs were developed in the early 1930's as non-toxic and non-flammable refrigerants. They gradually replaced all other refrigerants. Nevertheless, in the early 1950's one could still find some new products using isobutane on the European market . Soon thereafter, a world-wide change to CFC-12 as the preferred refrigerant took place.

The use of flammable refrigerants in mixture s received some attention after 1987. Comparable to the use of HFC-152a in refrigerant R-500, a company promoted a mixture of CFC-12 and the flammable dimethylether (DME, E-170) which gave a 30% saving of CFC-12. More or less at the same time, the use of pure flammable refrigerants, such as isobutane, R-152a, dimethylether and others, was considered in a publication by Kuijpers et al. /Kui88/. As a result, the use of HFC-152a received attention as a possible alternative to HFC-134a . Some applications are still being considered, mainly in China (pure HFC-152a and a mixture of HCFC-22 and HFC-152a).

The flammable hydrocarbon options received considerable attention in Germany in 1990/91. This increased in 1993 when one company started marketing appliances using a mixture of propane and isobutane as refrigerant. Since the foam applied consisted of EPS (extruded polystyrene) these were the first "CFC/HCFC/HFC"-free appliances. However, their energy consumption levels were substantially higher than comparable appliances on the market, mainly due to the low insulating quality of the EPS. Nevertheless, as a result of actions by Greenpeace, an increasing environmental awareness, and competitive market forces in Germany, the hydrocarbon option became reality.

The result ing publicity led all major German appliance manufacturers to investigate how hydrocarbons could best be used in a refrigeration cycle. After many investigations, virtually all large German appliance manufacturers selected isobutane as the preferred flammable refrigerant. Mainly due to problems in the control of multi-temperature appliances, and also due to higher noise levels compared to HFC-134a, mixtures of hydrocarbons (propane and isobutane) were not considered further.

In 1993, cyclopentane became widely available as a blowing agent, and all German companies converted an increasing proportion of their production to isobutane refrigerant. The rate of conversion was largely determined by market forces, by the availability of isobutane compressors and by the capacities of development departments.

5.2.2 Present situation in Europe

If a flammable refrigerant is considered, isobutane (HC-600a) is strongly preferred in new refrigerator production, due to:

- its superior efficiency compared to HFC-134a (which partially offsets a possible energy efficiency penalty due to the use of cyclopentane insulation);
- the low isobutane compressor noise level (due to low pressures);
- the possibility of using mineral oil;
- the low discharge temperatures so that high loads can be adequately met;
- the longevity of components (e.g. compressor) is very good;
- the high critical temperature so that relatively high refrigeration capacities are available at high ambient (condensing) temperatures.

Currently, approximately 90% of German refrigerator/freezer production uses isobutane as the refrigerant. Manufacturers in Germany have produced on the order of 8- 10 million appliances using isobutane from 1993 through 1996. They were sold in Germany and other European countries.

Appliances using isobutane are also marketed by companies elsewhere in Europe. Manufacturers can be found in Italy, the Nordic countries, the UK, Spain etc.; marketing is mainly limited to Northern and Central Europe. The number of appliances using isobutane produced in these countries is lower than the number produced in Germany up to 1997; it is estimated that, through 1996, three to four million units have been produced in these countries. The market share of isobutane appliances in Europe is currently estimated to be in the range 33-38%. During 1996, no significant market change occurred. However, the market is expected to grow further in the long-term.

The momentum isobutane has gained cannot be denied. Since the "European" eco-label now requires a very low GWP for substances to be applied (which, in fact, favours hydrocarbons), many manufacturers in Europe currently consider hydrocarbons to be the "final choice" in the conversion from halogen containing chemicals. Use of hydrocarbons in foams may be subject to future modifications (pure cyclopentane, n-pentane/iso-pentane or cyclopentane/ isobutane mixtures), but isobutane is the only flammable refrigerant expected to be used in new appliances in the foreseeable future in several parts in Europe (along with the non-flammable HFC-134a, which is still preferred by several manufacturers in Europe).

5.2.3 The market situation outside Western Europe

An increasing number of companies outside Western Europe are considering the use of isobutane, or are already importing and marketing appliances using isobutane. First are countries that export to Western Europe (e.g. Slovenia). In this case the current production volume is relatively small (due to limited availability of isobutane compressors). Although there have been many investigations into the use of isobutane by manufacturers in the USA and Japan, these manufacturers are hesitant to convert to isobutane. However, Japanese compressor manufacturers produce isobutane compressors for export.

Several companies in Article 5(1) countries have developed project proposals for conversion from CFC-12 to isobutane; in several cases, these projects are technically supported by European companies. As far as the current global appliance production volume is concerned, this is still very small compared to the numbers produced in Europe. No general tendency is seen in the Article 5(1) countries even though products or components for use with isobutane are manufactured here (e.g., Brazilian compressor manufacturers produce large quantities of isobutane compressors for export).

5.2.4 Product design for flammable refrigerants

Safety of products containing flammable refrigerants requires that one addresses:

- risk assessment to define hazards
- conversion of refrigerators dependent on the type of refrigerator
- product redesign in case safety requirements are not met.

The risk assessments carried out by German manufacturers /e.g. Lot94/ for “suitable” products showed that the probability for explosions is very low, and no ignition of other substances is likely (furniture, substances used in kitchens and living rooms).

Common recommendations for use of flammable refrigerants include :

- Refrigerant charge. The refrigerant charge should be kept small . A maximum of 150 g is normally used, which accommodates virtually all domestic refrigerators/freezers. This is also part of the DIN7003 standard;
- Evaporator. In the case of a hidden -foamed in- evaporator, common in Europe, the chance that there will be refrigerant leaking into the refrigerator is very small. (To assess safety, a leak is normally simulated at the capillary-evaporator connection, and concentrations are measured inside the appliance) . In the case of a cooling system with the evaporator inside the cabinet , switches should be placed outside, (electrical components should comply with standards such as EC 79/15), the evaporator should have a smooth surface, and connections between copper tubes and the aluminium evaporator should be protected against corrosion). Thicker heat exchanger wall materials should also be considered;
- Condenser. The condenser should be mounted such that the risk of damage during transport and use is minimised;
- Compressor. Sparking should be avoided, which implies use of sealed switches only; electrical connections should be shielded from the ambient air. Furthermore, sufficient air flow should be allowed around the compressor, if possible (this cannot always be the case, as e.g. for built-in appliances).

A number of other requirements apply:

- The refrigerator or freezer should be labelled or marked “risk of fire”, as a warning to the service technician;
- The refrigerator should have a clear information package dealing with cleaning, handling and transport;
- The pressure test should be more stringent than in the case of CFCs, e.g. the high pressure side should be tested with a pressure equal to 3.5 times the saturation pressure at 70° C (38 bar), the low pressure side should be tested with a pressure equal to 5 times the saturation pressure at 20° C (15 bar). This minimises the application of heat exchangers which are too thin;
- special electrical components and switches have to be used to prevent arcing.

For a number of products, the redesign will be minimal, especially for foamed-in evaporators in small refrigeration-only products. For freezers with tube evaporators inside the cabinet, special designs or redesigns may be necessary. This also applies to no-frost (“frost-free”) products with electrical defrosting of the evaporator. The application of special fans, switches and defrost controls is necessary and the use of double-wall evaporators may be desirable to minimise risks. German manufacturers were hesitant to convert no-frost products to hydrocarbons, but have done so (compared to products manufactured in the USA, conversion is easier for European products which employ a foamed-in evaporator in the refrigerator compartment, implying low risk; it is complicated to make the common US design of a no-frost appliance suitable for flammable refrigerants).

In developing country designs, more attention has to be paid to both the evaporator and compressor.

As a result of product redesign, product costs have increased, but it is difficult to find many references. Only one citation /Jür95/ is found in the literature. In this publication, a range of US\$ 15-30 is presented. Yet, the value will be very dependent on the type of appliance and the market conditions.

5.2.5 Manufacturing operations for flammable refrigerants

It should be assured that products charged with flammable refrigerants do not degrade the production environment, i.e., a risk assessment should result in acceptability of the operations: the manufacturing equipment should comply with local or national safety regulations. Before the conversion is made, the production technicians and service technicians should complete an adequate training programme.

In the manufacturing department :

- new storage tanks and piping distribution systems must be installed. In the case of small production volumes, the refrigerant can be taken from containers which are exchanged regularly,
- new charging stations must be installed. These stations must have very tight tolerances due to the small charges involved;
- appropriate designs for exhaust systems must be applied, together with the adequate monitors and alarm systems;
- although it is not directly related to flammability, extensive and rigorous leak detection and correction is necessary (e.g. using helium systems) due to the small charge involved.

All these investments will impact the cost of the product. This applies to all manufacturers where it concerns charging. It is very difficult, however, to generalise about distribution and exhaust systems since they will be very dependent on the lay-out and environment control system in the existing plant. It may not be practical to convert some manufacturing sites to the use of flammable refrigerants.

The same considerations apply to both Non-Article 5(1) and Article 5(1) countries.

5.3 Servicing and retrofits

5.3.1 General remarks

For the purpose of this report, servicing is normally defined as repair of a refrigerating appliance without changing the refrigerant or lubricant. Retrofit is defined as a change from one refrigerant (mostly CFC-12) to another. A retrofit may require a lubricant change and certain product modifications to accommodate the new refrigerant.

Since servicing of products with flammable gases is relatively new, procedures have been developed to avoid fires or explosions. These relate to:

- the evacuation procedure
- the assembly of pipes (use of expensive Lokring construction instead of welding; however, all operations before charging could include brazing or welding)
- refrigerant charging (with high precision balances)
- precautions to assure that leaked refrigerant does not accumulate and form an explosive mixture.

For retrofits from CFC-12 to hydrocarbons, special attention needs to be paid to the refrigeration capacity of the retrofit refrigerant. Most pure fluids would not give adequate capacity or energy efficiency. Hydrocarbon mixtures may result in comparable performance or capacity but may lead to difficult behaviour (control). Hydrocarbons are often reported to have better heat transfer characteristics than CFC-12, which would increase energy efficiency; however, in domestic refrigeration products the air-side heat transfer, which is significantly smaller, dominates. This implies that the total heat transfer is not significantly different between hydrocarbons and other refrigerants.

Retrofits to flammable refrigerants should not be made in products that have not been designed to use them, or where the risk of using flammables cannot be easily mitigated, e.g. a retrofit should not be done on second-hand products that have a high probability of leakage due to corrosion. It implies that products should be retrofitted only where safety can be assured, possibly via product modifications.

5.3.2 Servicing

In Europe, and particularly Northern Europe, HFC-134a is used for servicing those appliances designed for HFC-134a or CFC-12 (if the CFC-12 appliance is not discarded, which is common practice). In servicing, isobutane is used only for those appliances that have been designed for isobutane.

In principle, one could apply isobutane to CFC-12 appliances (“retrofitting”) if the compressor were exchanged. This is not carried out under normal circumstances, since it would require other product modifications for safety. In servicing operations by refrigerator manufacturer service organisations in the Non-Article 5(1) countries, retrofitting to hydrocarbon mixtures is never considered (however, hydrocarbon mixtures are used by certain environmental firms that promote “green servicing” of small equipment in some Non-Article 5(1) countries).

In the developed countries, service technicians must normally complete a training programme before they start using flammable refrigerants. This training programme should cover (i) the character of leaks and the behaviour of leaked refrigerant, (ii) evaluation of where leaks are most likely to occur and procedures for connecting pipes, (iii) the charging of refrigerant, (iv) the proper use of the flammable refrigerant, and (v) what type of leak tests to apply, and how to interpret the results.

In the Article 5(1) countries, the same should apply concerning training programmes. However, this may be difficult due to the presence of a large unorganised sector. Since production of appliances using flammable refrigerants has only recently started in these countries, this is not perceived as urgent yet. However, one will certainly have to deal with the servicing of flammable refrigerants in the future here as well.

5.3.3 Retrofits

As stated above, domestic appliances are not retrofitted to flammable refrigerants in the developed countries. It is reported that it is different in Article 5(1) countries (in the context of this report, HFC-134a appliances and possible retrofits are not considered). In principle, one could retrofit from CFC-12 to isobutane if the refrigerant and the isobutane compressor were available.

In the Article 5(1) countries, hydrocarbon mixtures are often represented as the “appropriate” refrigerant for servicing of CFC-12-based domestic refrigerators. Due to the ability to use mineral oil and due to the ‘drop-in nature’ of HCs (as far as capacity is concerned, and not taking into account the flammability/ safety aspects), several sources state that these are “easy conversions”.

Some references give arguments such as (i) the hydrocarbon mixture is a simple solution, (ii) its purity is not so “important” (iii) it may extend the life of the equipment, (iv) it has better heat transfer, and (v) it yields higher efficiencies. As evidence for the retrofits with hydrocarbon mixtures, the Cuban experience is often mentioned, where it is claimed that many thousands of appliances function in a reliable and efficient way with the use of commercial LPG.

However, one can also find references which mention that (i) it is difficult to extend the life of CFC-12 equipment, (ii) the better hydrocarbon heat transfer is not important, (iii) the efficiencies are at the most equal to CFC-12, (iv) the HC based systems are more sensitive to moisture than CFC-12 systems, (v) it is difficult to charge the hydrocarbon mixture in a liquid form, (vi) much greater precision is needed in charging a much lower weight, (vii) a high purity is needed regarding non-condensables and moisture, (viii) the hydrocarbons may affect the lubricant viscosity and, (ix) in case of a drop-in, the electric motor loading is different which may result in reduced performance or higher risk of burn-out than with CFC-12, (x) the mixture has never been tested to appropriate standards and, of course, (xi) hydrocarbons are flammable.

It should be stated that, in retrofits to flammables, all possible measures should be taken to assure the highest possible safety. Certain equipment cannot and should not be retrofitted. However, criteria are difficult to define and stringent guidelines are lacking. It is usually the service technician who determines whether or not to retrofit. Safety issues are particularly involved in the design of the evaporator, the possibility of corrosion, the type of compressor and the type and location of electrical switches as mentioned under 5.2.4.

The first issue that should be underscored is training, particularly for small workshops in the unorganised sector. Training is an essential part of the introduction of flammable refrigerants but the ability to reach the majority of the service technicians may vary from country to country. Training should deal with safety, handling, leak testing, and particularly with charging of hydrocarbon mixtures. It should also concern decision-making on whether certain appliances can be retrofit or not. In the literature it is proposed /e.g., Dev96/ that charging be done by the use of small (pre-mixed) cans containing a certain weight of hydrocarbons. However, this can only be useful if the number of different types of appliances to be serviced is limited (as e.g. in India with its 165 litre refrigerator). In other cases, the charge has to be determined experimentally, which can easily lead to overcharging.

Taking training into account, and the technical arguments given above, it must be stated that the “servicing with hydrocarbon mixtures” issue still needs the adequate attention, related to both product reliability and safety issues.

5.4 Improving the Knowledge Level on Retrofits

From the preceding, it is clear that a number of investigations still have to be made before it can be concluded that hydrocarbons or hydrocarbon mixtures are reliable retrofit refrigerant options for appliances, particularly in the Article 5(1) countries (the investigations recommended below fall outside the Terms of Reference for Multilateral Fund financial support). Such investigations would be motivated by assertions in the literature that application of hydrocarbons might result in better energy efficiency, longer life and higher reliability, despite the necessity for safety training.

1. The mixture of HC-290/HC-600a should be investigated in single temperature appliances designed for CFC-12, to investigate the influence of the capillary tube capacity and the sensitivity to over- or undercharging, and to quantify the influence on performance and reliability of a small overcharge (separation of the mixture in accumulators, oil etc.);
2. The performance of several compositions of HC-290/HC-600 (possibly even LPG quality) should be investigated in single temperature appliances to determine their feasibility and any associated problems. Long-term testing of appliances will show whether impurities and moisture content of LPG would adversely affect performance or endurance. This might be combined with more data on the “Cuba case study” where LPG is reported to be widely applied;

3. DME should be investigated in HFC-134a appliances with mineral oil, and life testing of compressors using conventional lubricants should be performed;
4. Theoretical considerations of the mixture HFC-152a/HC-600a predict high efficiency. Since it is an azeotrope, it could be used for retrofits of various types of domestic refrigerators. The azeotrope should be investigated in different types of appliances, using CFC-12 designs with mineral and with polyolester oil.
5. Normally propane is stated to yield inferior results in retrofits; however, several studies and practical data suggest the opposite. Tests should be performed using propane in a conventional (CFC-12) refrigerator to investigate the effect on energy consumption at different ambient temperatures ; this should accompany accelerated endurance testing with conventional mineral oil, of the viscosity used for CFC-12, to verify lubrication for higher pressures on the mechanical parts. This should yield clear recommendations whether propane can be used at all.

The above investigations should result in clear recommendations whether certain flammable pure fluids and/or mixtures are viable retrofit refrigerants. The field should be narrowed to just one or two. In this context, one should strive to determine whether a single candidate can be recommended for both single temperature and multi-temperature appliances (the latter are also gaining market share in the developing countries). It is also probable that further investigations on the behaviour of pure DME will permit its use as a low GWP refrigerant with suction pressures comparable to HFC-134a.

Basic considerations of the condition of the product to be serviced, as well as the feasibility of charging procedures in small service shops in the Article 5(1) countries should be an integral part of the proposed investigations.

It is recommended that similar investigations be performed as joint ventures between two laboratories in Non-Article 5(1) countries and two or more laboratories in Article 5(1) countries. In this way the programme can be considered as a 'multilateral' programme between Non-Article 5(1) and Article 5(1) countries ("round-robin testing").

6 USE OF FLAMMABLE REFRIGERANTS IN SYSTEMS OTHER THAN DOMESTIC REFRIGERATION

Mass production of refrigerators using isobutane has led to some European companies considering the advantages of using flammable refrigerants in other applications.

The application of flammable refrigerants has begun in commercial applications, particularly in stand-alone equipment, and also in air-conditioning applications (small chillers or heat pumps). Many of these units undergo field-testing, particularly in those countries where R-22 will be phased out at short notice (or where the phaseout schedule is being accelerated).

More detailed information on all options for the replacement of ODSs, including flammable refrigerants, will be given in the 1998 TOC assessment report.

6.1 New Systems

The following table 4.1 is taken from the Status Report of Heat Pump Programme Annex 22 of IEA, revised in May 1996 /TRO/96. Data are gathered from the 8 countries which are members of the IEA Annex.

Applications (category)		Number of installations							
		CD N	DK	JP	NL	NO	CH	UK	US
Residential and commercial heat pumps	Space/water heating (resid.)	-	1	-	-	-	25	3	-
	Space/water heating (com.)	-	-	-	-	1	-	-	-
Industrial heat pumps	Distillation	3	-	-	-	-	-	1	-
	Evaporative concentration	-	-	-	-	-	-	1	-
	Heat recovery	-	1	-	-	-	-	1	-
Air conditioning	Air cooled systems	-	-	-	-	-	-	5	-
	Water chillers (commercial)	-	-	-	-	-	-	1	-
	Automotive/transport	-	-	-	-	-	-	200	-
Refrigeration	Commercial applications	-	-	-	-	-	-	600	-
	Process cooling	-	-	-	-	-	-	5	-
	Transport	-	-	-	-	-	-	1	-

Table 6.1 - Number of non-conventional heat pumping installations with hydrocarbons (1995) /Tro96/

Additional data show that in the United Kingdom a number of packaged air-conditioners and split systems using either propane or a propane/ethane blend have been installed /Tro96/. The cooling/heating capacity is in the range of 5 to 10 kW and the refrigerant charge is between 1 and 3 kg.

In fact, from the numbers given above, it seems that the application of hydrocarbons in non-domestic systems is currently the most proliferated in the United Kingdom

6.1.1 Refrigeration

Commercial refrigeration

Hydrocarbons are used in some new commercial systems, especially in Germany, Sweden and the United Kingdom. Two options are known: a small central system in a machinery room, using heat transfer fluid which circulates to the vending area of a supermarket, or direct expansion systems in display cases.

- One major German supermarket refrigeration equipment supplier has built several indirect systems using propylene as the refrigerant. Good system COPs were reported /Haa96/. Another major supplier has built several indirect systems running with propane.
- In several supermarkets in the United Kingdom, equipment has been installed which is operated using hydrocarbons; it is reported that in 5 cold rooms hydrocarbon-based equipment has also been installed /Pow96/.
- More than 10 ,000 wine bar coolers, each containing 0.8 kg of flammable refrigerant, are reported to have been sold in the United Kingdom; this also applies to 100 pieces of stand-alone equipment containing up to 1.5 kg /Bla 97/.
- Two supermarket installations have been built in Sweden using a hydrocarbon blend of propane-ethane (90%/10%) /Pow96/. Both installations are working with indirect systems using mono-propylene-glycol for the cooling range and using the evaporation of carbon dioxide for the freezing range. The cooling capacities reported for the two supermarkets are 200 kW and 130 kW , respectively; 50 kW and 25 kW are reported as freezing capacities. Refrigerant charges are 4 to 5 kg per system. A number of compressors are working in parallel in order to provide the total cooling capacity /Kau97/.

Laboratory freezers

In the United Kingdom, 600 two-stage laboratory freezers are operated at -85°C with a refrigerating capacity of 150W; they use a mixture of ethane and propane in the lower stage. The total charge of HCs is about 0.3 kg per freezer /Tro96/.

6.1.2 Air-conditioning

Portable air conditioning systems

Propane is used by one major manufacturer of portable domestic air-conditioning systems in Europe. The amount of propane in the largest model (2.5 kW) is 0.24 kg. The units are normally sold on the German market; the manufacturer reports to have sold about 60,000 units in 1996 .

Water chillers

Two air-conditioning applications with water chillers using a hydrocarbon-blend of propane-ethane (90%/10%) are reported to be used in Sweden /Kau97/. One installation has a 19 kW cooling capacity using 1 kg of the hydrocarbon-blend. The second installation has a 260 kW capacity, consisting of several individual units each charged with 5 kg of the hydrocarbon-blend. The market for chillers in Sweden is reported to be growing / Bla97/. It is stated that there are about 100 water chillers installed in United Kingdom containing up to 10 kg of pure HCs or blends / Bla97/.

Heat pumps

Propane is used by heat pump manufacturers in outdoor units in Germany and Austria. The number of units sold in Germany was about 800 units in 1995 /Tro96/. It is reported that also heat pumps using propane are installed for indoor use here. One manufacturer claims that the heating COP of the heat pumps charged with propane is 10 to 20% better than the COP of the same unit using R22 /Sta96/. German electric utility companies give financial support for individual households when installing a heat pump. Lately, these supports have been limited to hydrocarbon based heat pumps /Kau97/.

6.2 Existing systems

The use of flammable refrigerants in existing systems (i.e., retrofits) other than domestic has been primarily limited to demonstration units. One HC manufacturer advocates the use of blends to retrofit existing refrigeration systems, with the requirement that safety standards be followed and that one should attend dedicated training on the use of HCs. Some governments require approval by the equipment manufacturer before they allow retrofitting to a flammable refrigerant.

It is reported that several milk-coolers have been retrofitted to hydrocarbon mixtures in the Netherlands /GTZ96/.

Air-conditioning

A number of low-charge heat pumps have been retrofitted from R-22 to propane in Germany /Tro96/.

A number of reversible split units and glycol chillers have been retrofitted in the United Kingdom using hydrocarbon charges varying from 1 to 8 kg. The blend of propane and ethane (as mentioned above under "water chillers") is considered to be a direct replacement for R-22.

MAC

It is reported that a number of car air-conditioners have been retrofitted to flammable blends in Australia /Kau97/.

6.3 Concluding Remarks

The amount of equipment using flammable refrigerants in applications other than domestic appliances is rather small since there is no mass production of such applications.

Tendencies which can be identified are :

- Commercial stand-alone equipment manufacturers may benefit from the work which has been carried out on components for domestic appliances, especially on compressors.
- The heat pump market in Europe is limited and the number of units using HCs is also limited.
- Market leaders in air conditioning systems are American and Japanese companies. Their own market does not call for a quick phaseout of R-22. It implies that there is so far no incentive for those companies to develop new products using flammable refrigerants for the domestic market. However, they may produce products containing flammable refrigerants in order to maintain a certain European market share.

The increase in the use of flammable refrigerants is dependent upon several factors:

- fast development of technical solutions using HFCs as replacement refrigerant for R-22;
- possible restrictions on the HFC emissions;
- costs of safe design of systems using flammable refrigerants for quantities between 150g and 10 kg;
- acceptance of flammables by contractors despite the additional risk for installation and maintenance;
- special training for safe handling of flammable refrigerants;
- reform of liability laws to shield manufacturers from unreasonable claims.

7 ENERGY EFFICIENCY OF SYSTEMS USING FLAMMABLES

7.1 Domestic Appliances

7.1.1 New appliances

In an early publication by Jürgensen in 1992 /Jür92/ for a DKV meeting in Germany, measurements on refrigerators using both pure flammable fluids and mixtures were presented. In these investigations the compressor displacement was adjusted, but only one displacement per refrigerant was studied (-20% for propane, and +60% for isobutane at 50 Hz). Results reported on energy consumption were: a slight increase for isobutane, a 25% increase for propane, and a 6% increase for a 50/50% HC-290/HC-600 mixture (application in a refrigerator, with an increase of 30-40% in a multi-temperature appliance). In some of the measurements, the capillary tube length was increased. These results were presented at a rather early stage in the development, and no real optimisation can be assumed here.

Wiest /Wie94/ reported results of investigations involving the application of isobutane, propane and mixtures of these two refrigerants in a single-temperature refrigerator. These measurements were much more detailed than those of Jürgensen, employing a large series of compressor displacements and different refrigerant charges. The table given by Wiest has been reproduced in Annex 4.

Wiest concluded that:

- isobutane as a pure fluid yields the best efficiency and an energy saving of about 8% (a confirmation of calculations, see Table A3.1 in Annex 3);
- application of the R-290/600a mixture results in 0-10% higher energy consumption than CFC-12 if refrigerant charge and displacement are adjusted but not fully optimised;
- at the appropriate compressor displacement, for high isobutane percentages in a mixture, energy consumption reduction varies between 0 and 6% (the latter value for a mixture with 60% isobutane);
- the amount of refrigerant charge used influences the results substantially.

The above conclusions are only valid for a single- temperature refrigerator. In the case of two-temperature appliances, the separation of the two fluids is stated to result in unacceptably high refrigerator temperatures and functional defects /Wie94/.

Comparison of the energy efficiency of different refrigerants without detailed information on the level of optimisation of the hermetic compressor for the specific refrigerant has very limited value. The larger part of the energy efficiency increase or decrease when changing from one refrigerant to another (i.e., 60-80%) may be attributed to influences caused by compressor parameters. In fact, the results measured by Wiest, which show a number of influences in the energy efficiency, may be largely due to the different compressors used. This underscores the important influence of the compressor, which cannot be easily determined and separated from the influence of the refrigerant.

In 1995, Jürgensen /Jür95/ mentioned that the performance of HC-600a is 4 to 7% better than HFC-134a in refrigerators, and slightly worse than HFC-134a in freezers. This was stated earlier by Lotz /Lot94/ who reported small energy reductions for refrigerators and small increases for freezers (up to 2%). This was confirmed by Wenning /Wen96/ who stated that, on average, European refrigerators using HC-600a show a 4-5% lower energy consumption than HFC-134a, while the consumption of freezers is comparable to that with HFC-134a. Jürgensen /Jür95/ emphasised that HC-600a shows much better performance than CFC-12 and HFC-134a at high condensing temperatures, due to its high critical temperature.

In many cases, TEWI analyses have been applied to refrigeration systems to investigate the impact of direct and indirect (energy production related) greenhouse gas emissions. Under most conditions, HC-600a is at least as efficient as most other refrigerants. This, combined with its low GWP, favours the use of isobutane. TEWI values of 0.92-0.96 times the HFC-134a value have been quoted in several references /DOE94/. If a comparison were made on an equal cost basis, it might yield different results. Less expensive HFC equipment could be made more efficient by investment in more efficient components and thus become equally or more efficient. However, this has not been thoroughly studied and it will also depend on extra investments required for HC applications where figures are difficult to generalise.

7.1.2 Retrofitted systems

Agarwal reports on investigations of 165 litre Indian refrigerators, with one evaporator, using different propane/isobutane mixture compositions and different capillary tube lengths /Aga95, Aga96/. He reports results comparable to those obtained with CFC-12 (only for one charge of 60/40% propane/isobutane mixture and a significantly longer capillary tube, there was a decrease of some percent).

Dijkstra reports in 1995 that "experiments in the Netherlands indicate that propane, propane-isobutane and propane-butane mixtures can be used as drop-in substitutes" /Dijk95/. He mentions similar cooling performance and equivalent to better energy consumption compared to CFC-12.

In fact, there is no consensus on the comparative performance of hydrocarbon mixtures. In small domestic appliances in particular, many parameters influence the overall performance of the product. This relates to the behaviour of components, particularly the compressor, whose influence is probably much larger than the effect caused by the differences in thermodynamic properties of a refrigerant.

7.2 Systems other than Domestic Appliances

Reports on the performance of flammable refrigerants in existing systems other than domestic appliances are rather scarce. The main difficulty is how to compare performance levels. For some types of equipment, direct expansion can be used and performances can be directly compared. In the case of systems which use a large refrigerant charge, the comparison is made between HFC-based direct system and propane-based indirect system (which is normally applied for safety reasons).

Case	Configuration	Conditions	TEWI	% of R-22
1	R-22 / Direct	NIST "D" Input Power 0.63 kW	3698	Base Case 100
2	R-410 / Direct	NIST "D" Input Power 0.66 kW	3890	105
3	R-410 / Direct	same Input Power as R-22 0.63 kW	3729	101
4	R-290 / Direct	NIST "D" Input Power 0.66 kW	3584	97
5	R-290 / Direct	same Input Power as R-22 0.63 kW	3423	93
6	R-290 / 2nd loop	NIST "D" + 2nd loop Input Power 0.82 kW	4234	114
7	R-290 / 2nd loop	R-22 COP + 2nd loop Input Power 0.78 kW	4027	109

Table 7.1 - TEWI calculation of various propane options for R-22 replacement in air-conditioners /Mor97/.

Many computer design simulations and performance calculations have been performed by different companies. Calculations gathered by Morikawa give the results as presented in Table 7.1 /Mor97/.

In Table 7.1 it can be observed that the energy efficiency of the propane option strongly depends on whether direct expansion or a secondary loop is employed. This is, in fact, one of the key issues when secondary loops are applied.

One should understand that normally proper design of new systems using propane will show a rather good energy efficiency compared to R-22. The discharge temperatures in the case of propane will also be lower than in the case of R22.

8 CONCLUDING REMARKS

This report presents a preliminary assessment of flammable refrigerant options only; it will be followed by a complete assessment report to be published in 1998. The full 1998 TOC report will present a broader picture including all refrigerant options for all refrigeration, air-conditioning and heat pump sub-sectors.

The use of flammable refrigerants has reached maturity in the domestic appliance sector where markets are still further developing. In the commercial refrigeration and air-conditioning sectors, most of the emphasis has been on demonstration projects and "niche" products; further developments are reported. Geographical differences can be concluded, namely the market for new products and equipment using flammable refrigerants can be found specifically in Northern and Central Europe, but also in Australia and New-Zealand. The conversion to the use of flammable refrigerants is also taking place for factories producing new domestic appliances in the Article 5(1) countries, which is supported by the Montreal Protocol Multilateral Fund.

The option to use flammable refrigerants in retrofits of domestic appliances has recently been explored in a few developing countries (there is one exception, i.e., Cuba, where retrofits are reported to have been carried out over a longer period). It is currently a subject of discussion in other developing countries.

8.1 Global Overview

At the beginning of 1997, the use of flammable refrigerants is primarily limited to the field of domestic refrigeration in Northern and Central European countries, where it has reached maturity; it has captured a significant portion of the market here. Due to the market share of about 35% in Europe, appliances using flammable refrigerants represent about 8% of the world refrigerator market. Although several flammable refrigerants could be used either as pure fluids or as blends, the most important flammable refrigerant option is HC-600a, which is applied in virtually all new products that use a flammable refrigerant. Products -including compressors- have undergone life-testing with good results and a great deal of experience has been built up by appliance manufacturers in Europe. When applied in small refrigeration equipment such as domestic refrigerators, the energy efficiency of HC-600a is comparable to, or often better than, the energy efficiency of CFC-12 or HFC-134a.

In principle, isobutane is the only flammable option considered for new appliances since the optimisation of the circuit is easiest for a pure fluid, particularly in the case of multi-temperature appliances. There is some use of the flammable HFC-152a, but this appears to be limited to China.

For manufacturers, the main challenges in implementing HC-600a consisted of the following:

- upgrading safety of the manufacturing plant for storage, charging, etc;
- establishment of a limit for the charge (in Germany, 150 g);
- establishment of recommendations to use high purity isobutane;
- change of mineral oil viscosity to a lower level (if necessary and/or possible);
- redesign of refrigerators: general use of foamed-in evaporators for refrigerators, modification of switches, etc;
- training of servicing staff, which is relatively easy in these developed countries where appliance manufacturers have their own servicing agencies.

For new domestic refrigerators, the use of hydrocarbon mixtures has so far not been considered (except the production by one company during a number of years). Considerable design problems are foreseen in the use of mixtures for multi-temperature appliances including an unacceptable significant increase in noise levels.

The use of flammables in appliances which were not designed for their use is not being done in industrialised countries. To do so, it would require product modifications to preserve safety. However, servicing of the refrigerating circuit, during which an appliance could be retrofitted, is the exception rather than the rule.

Changing to a flammable refrigerant when the circuit needs to be repaired is an option in countries where repair is an attractive option because of the low cost of manpower and the relatively high cost of new appliances. This option is already used in some Article 5(1) countries where hydrocarbon mixtures and even commercial grades of hydrocarbon mixtures such as LPG have been, or are still used. Training for safety measures should be underlined for all technicians, including those in the informal sector including how to perform product modifications necessary to preserve safety. Questions still exist about technical maturity and reliability of several types of hydrocarbon mixtures since the results of proper life testing are not generally available.

Nevertheless, apart from the concerns addressed above, retrofits of domestic appliances from CFC-12 to HC290/HC-600a mixtures are possible without changing the compressor provided that:

- the usual safety standards are applied (e.g. no thermostat and evaporator in the same space);
- it is limited to one-evaporator refrigerators if good temperature control is to be achieved;
- the condition of the refrigerator is such that leakage is not likely to occur (no old refrigerators with corrosion problems should be retrofit, with any flammable refrigerants);
- accurate refrigerant charging can be done;
- technicians are trained.

For uses other than in domestic refrigeration, the application of flammable refrigerants in new products has been rather limited to date since there has been no mass production so far.

Tendencies identified which will influence near-future market developments:

- manufacturers of commercial stand-alone equipment may benefit from the work which has been carried out on domestic appliances, particularly on compressors;
- particularly in the United Kingdom, many pieces of stand-alone equipment are operated on hydrocarbons in the commercial sector; in fact in the United Kingdom the use of HCs in products other than domestic is the most proliferated;
- the market of heat pumps for heating is restricted to Europe and the number of units using hydrocarbons is still rather limited (the number of outdoor units sold in Germany was about 800 units in 1995);
- the air-conditioning market is dominated by American and Japanese companies which do not use hydrocarbons in this type of equipment. However, one Italian manufacturer of portable domestic AC systems uses propane for products sold on the German market (where the volume has been stated to be about 60,000 units in 1996).

8.2 Existing problems in the application of hydrocarbons

Domestic appliances

For the use of isobutane, the market has reached maturity in a few countries . Should other flammable fluids be needed, it would require a significant amount of development work which is questionable in Europe but may occur elsewhere.

In retrofits to flammable refrigerant mixtures, considered mainly in the developing countries, the precision in refrigerant charging and the influence of the lubricant viscosity should receive adequate attention. This also relates to the level of contaminants in mixtures of hydrocarbons and especially in commercial grade LPG which may be unsuitable for proper functioning during the remaining lifetime of the product. For proper resolution of these questions, a mixture of case studies, monitoring of products after retrofit, investigation of the effect of over-charging, and extensive standardised energy consumption tests, and life testing are required . This will bring to Article 5(1) countries the confidence they need if this option is to be pursued.

Commercial refrigeration and air-conditioning

The problems which have not been resolved in these sectors are mostly related to safety issues and are very product specific. In new products this particularly applies to the development of secondary heat exchanger loops in order to reduce the amount of flammable refrigerants.

Retrofits of existing products to hydrocarbons are even more sensitive to safety concerns . They would require product modifications to adequately satisfy existing safety standards . In many cases, a retrofit will not be possible since acceptable safety can not be reached. Acceptance by contractors to the use of flammable refrigerants has to be verified, because HC servicing implies new procedures and special training.

8.3 The Near Future

The use of flammable refrigerants can be considered as a trend in some European countries but it is difficult to estimate how far this trend will go. This will depend upon further developments of safety codes and measures, the costs of flammable refrigerants and the equipment investments needed to accommodate them, as well as the energy efficiency, which can be achieved.

As an example, flammable refrigerants are so far not used by US and Japanese manufacturers . To a certain degree, this is the consequence of the product concepts in use in these countries; it is also the consequence of the way attention is paid to liability by the manufacturers here. Since a large amount of refrigeration and air-conditioning equipment is being manufactured by multi-national companies with a significant US component, it can be expected that the number of products using flammable refrigerants will not grow in the same way as in other countries. For the foreseeable future, it implies that there will be two options, the non-flammable (HFC) and flammable refrigerants, in addition to products based upon alternative refrigeration methods.

New products could be manufactured with dimethylether (DME) using HFC-134a compressors charged with mineral oil (this is related to the concern about moisture absorption in polyolester oil). However, it would require much more R & D before this option can be reliably applied in practice; nevertheless, it is an interesting option within the framework of flammable refrigerants.

It can be expected that:

- the market share of domestic appliances using isobutane will further grow in Europe (also due to some degree to introduction of the eco-label in Europe); it also applies to stand-alone (small) products in the commercial refrigeration and air-conditioning sector;
- the market of commercial refrigeration equipment operated mainly on propane (or maybe on propylene) may particularly grow in Northern and Central Europe;
- an increasing number of electrical heat pumps for heating may be operated on propane (mainly in Northern/Central Europe);
- in certain European countries, the market may further develop for air conditioning products using flammable refrigerants;
- competition between HFC and flammable refrigerant operated products will increase, mainly due to the fact that HFC products at increased energy efficiency will be offered at price levels comparable to the presently marketed products using flammables (which will also depend on the specific costs for safety measures which may be very product specific).

It is too early to present reliable figures on the future market at this stage where in many application areas, mainly demonstration products have been realised. Market trends will very much depend on the development in the areas of cost price, safety standards, energy consumption levels, environmental awareness, national regulations and, above all, on the international market place.

With increasing experience in the Non-Article 5(1) countries, it is beyond doubt that flammable refrigerant technology will be exported to Article 5(1) countries, particularly in the field of domestic refrigeration. On the one hand, financial assistance from international mechanisms for conversions will certainly be contingent on the differences between the operating costs for hydrocarbons and for other options. On the other hand, export of the technology will, for a large part, be determined by the technology partnerships that exist or will be established between developed and developing country manufacturers.

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ANNEX 1

COMPARATIVE ANALYSIS OF ISO 5149, PR-EN 378 AND ASHRAE 15

IEA (International Energy Agency) performed a comparative analysis of safety standards /Haa96/. An overview is presented below. This overview compares the 1995 version of ASHRAE 15 and the current content of the future European standard Pr-EN 378 which will be circulated for voting, taking ISO 5149 as a reference. Each of these three standards covers classification of :

- refrigerants depending on their risk level,
- refrigeration system configuration based on their potential to discharge refrigerant directly into buildings,
- room occupancy based on their use and their occupancy density.

Based on these three classifications, a specific chapter in each standard defines refrigerant restrictions tailored to the room occupancy type and to the refrigeration system characteristics.

This chapter has a different title for each standard: Restrictions on Refrigerant Use in ASHRAE 15, Prescription for Refrigerant Use in ISO 5149 and Selection of Refrigeration Systems in Pr-EN 378.

A chapter in each standard on the Design and Construction of these systems summarises standard practice in the construction of pressurised systems. This chapter is particularly well documented in the ISO 5149 and includes most of the technical specifications including all those covered by the two other standards.

Scope of the 3 standards

Each of the standards is intended to assure safety of persons and goods as far as the characteristics of design, installation and operation of refrigeration and air-conditioning systems are concerned.

The standards encompass all types of cooling systems in which the refrigerant is evaporated and then condensed in a closed system, including heat-pumps and absorption systems, but excluding systems using water or air as a refrigerant.

The 3 classifications

• Classification of refrigerants

Classification of refrigerants in ASHRAE 15 originates from ASHRAE Standard 34-94; ASHRAE 15 defines practical limits.

Two criteria are considered simultaneously for safety : flammability and toxicity. According to ASHRAE 34, flammability is rated 1/2/3 and toxicity A/B. Only flammability is discussed here. As the refrigerants concerned are classified as non toxic, the rating of flammability will appear as A1/A2/A3.

	Flammability	Definition
Group 1	Non flammable	
Group 2	Moderately flammable	For ISO 5149 and Pr-EN 378: LFL \geq 3.5% in volume when mixed with air For ASHRAE 34, group 2 (moderately flammable refrigerants) is defined by two criteria: LFL $>$ 0.1 kg/m ³ and heat of combustion $<$ 19,000 kJ/kg.
Group 3	Highly flammable	For ISO 5149 and Pr-EN 378: LFL \leq 3.5% in volume when mixed with air. For ASHRAE 34, LFL $<$ 0.1 kg/ m ³ or heat of combustion $>$ 19,000 kJ/kg.

Table A1.1 - Classification of refrigerants.

- **Flammability ratings A2 and A3**

ASHRAE 34 defines the flammability categories based on the results of testing in accordance with ASTM E681 plus the heat of combustion. For blends, ASHRAE 34 assigns a flammability rating to both the worst-case formulation and to the worst-case fractionated composition. A blend that is non-flammable and does not fractionate to become flammable would be rated A1/A1. A blend that is non-flammable but becomes flammable in the worst-case scenario of fractionation will be rated, for example, A1/A2 as for R406A.

Density of saturated vapour	Lower Limit (LFL)		Upper Limit (UFL)		Practical limit ⁷ (defined below)	Safety classification	Lower Heating Values
	kg/m ³	% v/v	kg/m ³	% v/v			
R-152a	0.137	5.1	0.462	17.1	27	A2	17.4
R-600a	0.043	1.8	0.202	8.5	8.2	A3	49.4
R-290	0.038	2.1	0.171	9.5	8.0	A3	46.4
E-170 (DME)	0.064	3.5	0.489	26	11	A3	?

Table A1.2 - Relevant factors for flammability characteristics description. (for the characterisation of flammability)

The LFL and UFL values are not exactly the same from one standard to another, but are practically the same. Accurate values will certainly become more and more widely available due to the renewed interest in these gases.

⁷ Minor numerical discrepancies are carried out from ASHRAE standard 34.

The practical limit is used for all refrigerants, either due to reasons of air breathability (A1 group), or due to toxicity or flammability. The practical limit for A2 and A3 flammable refrigerants, in g/m^3 , corresponds to 20 % of the LFL, the reference volume is the whole volume of the room where the refrigerant is presumed to expand uniformly in case of a leak. Density of these gases (e.g. propane, isobutane, ...) is higher than that of air. So, higher concentrations can be expected near the floor.

For non flammable refrigerants, practical limits of dilution (in g/m^3) are defined depending on the volume so that the air is still breathable in the most worst case leak scenario. All three standards indicate the same values.

- **Classification of systems**

This classification aims at characterising the potential for direct emission of refrigerant into occupied space depending on whether the refrigerant flows through the heat exchangers cooling or heating the rooms.

The number of possible system classifications varies in the three standards: 6, for ISO 5149; 5 for ASHRAE 15; and 4 for Pr-EN 378, fortunately 4 of them are the same for the three standards.

- **Classification of occupancy**

The lack of harmony is most evident in occupancy classification.

- ISO 5149 covers 5 categories (Institutional, public, residential, commercial, industrial)
- ASHRAE 15 covers 7 categories : the same 5 as ISO 5149 plus mixed occupancy and “ large mercantile ”
- Pr-EN 378 presents only 3 distinct categories, the criteria being the status of occupants:
 - A: people are restricted in their movement, a large number of people can be in the building;
 - B: rooms or parts of buildings where a limited number of people can be, some of them knowing general safety precautions;
 - C: rooms or parts of buildings to which only authorised people have access.

- **Limitations of use**

The main chapter that pulls together the consequences of the three classifications (refrigerant, system and occupancy type) results in the definition of prohibitions against the use of refrigerants under circumstances which would not be safe. This is the case for ISO 5149 and ASHRAE 15 which ban the use of A3 “ flammable refrigerants ” except in laboratories and industries under conditions defined in ASHRAE 15 and ISO 5149.

Through the prohibition of flammable refrigerants, except in laboratory and industrial applications, these two standards apply the general safety principle of selecting the least hazardous of two competitive technical options with substantially comparable performance. The consequent traditional prohibition of flammable refrigerants in most applications has given preference to the conventional non-flammable refrigerants.

Regarding Pr-EN 378, the application guidelines are more complex:

- A3 “ flammable refrigerants ” can be used up to 1.5 kg for any type of occupancy as long as the refrigerant charge is lower than the practical limit of 8 g/m^3 (for propane and isobutane) the reference being the volume of the room where the system is located with the additional restriction that there be no ignition source associated with the refrigeration system;
- in a machinery room, maximum quantities can be of 5 kg, 10 kg, or no limit depending on the type of occupancy, A, B, C, respectively, as described above. When machinery rooms are located in basements, the limit is 1 kg in all cases.

ANNEX 2

COMPARISON OF IEC 335-2-24 AND IEC 335-2-40

Standard	IEC 335-2-24 (61C/98/CDV)	IEC 335-2-40 (61D, WG5, OCT.96)
Title	Household appliances for Refrigeration	Electrical Heat-Pumps, Air Conditioners and Dehumidifiers
Current Status	IEC SC61C, committee draft voting, closing date for voting 1996.12.31.	IEC SC 61 D, Working Group 5 draft to be submitted to SC 61 D.
Scope	Safety rules for household refrigeration appliances including those which use up to 150g of flammable refrigerant. It does not cover construction features and operation of refrigerators and freezers which are dealt with in ISO standards.	<p>Safety rules for products with a maximum mass of flammable refrigerants (as defined in ANSI/ASHRAE 34) of up to 5.0 kg. For systems with more than 5.0 kg, reference should be made to the appropriate national standard.</p> <p>Note : the use of a flammable refrigerant introduces some additional risks in the use of refrigeration and air conditioning equipment and dehumidifiers, some of which may not be known because most experience has been developed using non-flammable refrigerants.</p> <p>These requirements only address the risk of a leak with respect to the appliance. Safety considerations beyond the appliance are based on the very low probability of fire or explosion.</p>
Definition	class 2 or class 3 according to ANSI/ASHRAE 34	class 2 or class 3 according to ANSI/ASHRAE 34
Marking and instructions	<ul style="list-style-type: none"> - Shall be marked with the symbol "Caution, risk of fire". - The instruction sheet shall include information for handling, installation, cleaning, servicing and disposal. - The type of gas used for insulation foam blowing, if flammable, shall be marked on the outside of the cabinet. 	<ul style="list-style-type: none"> - Marking with a flame symbol plus the words "Caution, risk of fire" shall be visible. - The installation and operation manual shall include handling, installation, cleaning, servicing and disposal considerations appropriate to flammable refrigerants. - For appliances using more than 150g of propane, the standard specifies the minimum volume of the room or the special requirements for the room in which the appliance can be located.

Standard	IEC 335-2-24 (61C/98/CDV)	IEC 335-2-40 (61D, WG5, OCT.96)
Construction	<ul style="list-style-type: none"> - Cooling system refrigerant circuit shall withstand a pressure of 3.5 times Saturated Vapour Pressure (S.V.P.) at 70°C for the highside, and 5 times S.V.P. at 20°C for the lowside. - Protective, construction for the cooling system is defined in details. - Appliance shall be constructed to avoid any fire or explosion hazard in the event of leakage of the refrigerant. - Safety in the event of leakage is checked by inspection and by the tests defined in details in this standard. - A leak simulation at the most critical point is defined by the standard. - The method for simulating a leak is defined by the standard and the measured value of the concentration shall not exceed 75% of the LFL and shall not exceed 50% of the LFL for a period exceeding 5 minutes. - Temperatures on surfaces that may be exposed to leaked flammable refrigerant shall not exceed the ignition temperature of the refrigerant reduced by 100 °C. 	<ul style="list-style-type: none"> - General requirements including pressure tests for refrigeration safety from ISO 5149 shall be applied. - Shall be constructed so that any leaked refrigerant will not accumulate so as to cause a fire or explosion hazard in areas within the appliance where electrical components, which could be a source of ignition, are located. - Electrical components shall comply with IEC 79-15 section 3 and 4 for group IIA gases, or the refrigerant used, or the compliance shall be checked by test. - A leak is simulated at the most critical point as specified by the manufacturer. - The method for simulating a leak is left to the manufacturer but the measured value of the concentration shall not exceed 75% of the LFL and shall not exceed 50% of the LFL for a period exceeding 5 minutes. - In case of blends, the test shall be carried out at the most unfavourable location and under the most unfavourable conditions. - Temperatures on surfaces that may be exposed to leaked flammable refrigerant shall not exceed the ignition temperature of the refrigerant reduced by 100 °C.
Installation	Not specified	The appliance with flammable refrigerant shall be installed according to the maximum allowable mass of charged refrigerant and ventilation status of the room defined in the standard.

ANNEX 3

**PROPERTIES OF FLAMMABLE PURE REFRIGERANTS
AND FLAMMABLE REFRIGERANT MIXTURES**

ANNEX 3

Properties	CFC-12	HC-600a	HC-270	HC-290	E-170 (DME)	HC-600	HFC-152a	HFC-134a
Molecular formula	CF ₂ Cl ₂	CH ₂ (CH ₃) ₃	C ₃ H ₆	C ₃ H ₈	(CH ₃) ₂ O	C ₄ H ₁₀	CH ₃ CHF ₂	C ₂ H ₂ F ₄
Molecular weight	120.91	58.12	42.08	44.10	46.07	58.12	66.05	102.03
Critical temperature /°C/	111.8	134.7	125.2	96.7	127.0	152.0	113.3	101.2
Critical pressure /bar/	41.8	36.3	55.8	42.5	53.2	38.0	45.2	40.7
Boiling point (1.013 hPa)	-29.8	-11.6	-32.5	-42.1	-24.8	-0.5	-24.0	-26.1
Vapour pressure at 55°C /bar/	13.72	7.72	15.08	19.07	12.95	5.65	13.32	14.91
Vapour pressure at -25°C /bar/	1.24	0.58	1.39	2.03	1.00	0.36	0.97	1.06
Pressure ratio	11.1	13.3	10.9	9.4	12.9	15.7	13.7	14.0
Enthalpy diff. (suct. 32°C - liquid 32°C) (kJ/kg)	142.4	336.1	406.9	355.0	411.2	365.4	290.5	185.9
Suction density at 32 C (-25 evap.) /kg/m ³ /	6.06	1.35	2.35	3.64	1.86	0.83	2.57	4.36
Enthalpy diff. * suction gas density /kJ/m ³ / (and change in order to be equal to CFC-12)	862.6 (1.000)	452.3 (1.907)	958.3 (0.900)	1294.1 (0.667)	763.2 (1.130)	304.0 (2.838)	747.8 (1.154)	811.5 (1.063)
Discharge temperature /side/ at 35°C/35°C/	130.2	104.6	142.9	118.5	139.6	107.5	141.1	121.7
C.O.P.	2.599	2.787	2.521	2.618	2.609	2.806	2.583	2.630
Material compatibility (steel, copper, al.,brass)	Very good	Very good	Very good	Very good	Very good	Very good	Very good	Very good
PTFE (Teflon)/NBR/polysulfide (Nylon)	Good	Good	Good	Good		Good	Good	Good
Silicone	Good	Bad	Bad	Bad		Bad	Good	Good
Fluorinated rubber	Good	Good	Good	Good		Good	Bad	Bad
Lubricant solubility mineral oil/alkylbenzene	Good	Very good	Very good	Very good	Very good	Good	Not miscible	Not miscible
Lubricant solubility polyol ester	-	Good	Good	Good	Good	Good	Good	Good
Toxicity /ppm/	1000	1000	400	S.A.	-	S.A.	1000	1000
Flammability limits /% vol./	None	1.4-8.5	2.4-10.4	2.1-9.5	3.4-27.0	1.4-8.5	3.2-18.0	None
Δh combustion /kJ per kg/	-	49.4		50.3		49.5	17.4	-
Life tests performed (C compr.)(A appliance)	(C) (A)	(C) (A)	(-) (-)	(C) (-)	(-) (-)	(-) (-)	(C) (A)	(C) (A)

Table A3.1: Properties of the pure flammable refrigerants considered

Properties	CFC-12	HC-290/ HC-600a (70/30)	HC-290/ HC-600a (60/40)	HC-290/ HC-600a (50/50)	HC-290/ HC-600a (40/60)	HC-290/ HC-600a (30/70)
(weight percentages)						
Molecular formula	CF ₂ Cl ₂					
Molecular weight	120.91	47.54	48.81	50.15	51.56	53.06
Critical temperature (°C)	111.8	117.1	120.7	124.3	128.1	132.0
Critical pressure (bar)	41.8	47.2	46.5	45.8	45.0	44.2
Boiling point (1.013 MPa)	-29.8	-37.8/-31.2	-36.0/-28.0	-33.8/-25.0	-31.2/-22.2	-28.0/-19.4
Vapour pressure at 55 C (bar)	13.72	15.40	14.22	13.08	11.97	10.89
Vapour pressure at -25 C (bar)	1.24	1.45	1.29	1.15	1.01	0.89
Pressure ratio	11.1	10.6	11.0	11.4	11.8	12.2
Enthalpy diff. (suct. 32 C - liquid 32 C) (kJ/kg)	142.4	346.8	345.1	343.4	341.5	339.4
Suction gas density at 32°C (kg/m ³)	6.06	2.80	2.55	2.32	2.11	1.90
Enthalpy diff. * suction gas density (kJ/m ³) (and change in order to be equal to CFC-12)	862.6 (1.000)	970.6 (0.889)	881.3 (0.979)	797.7 (1.081)	719.1 (1.200)	645.4 (1.337)
Discharge temperature (satd. vapor -35°C/55°C)	130.2	116.2	115.0	113.7	112.3	110.8
C.O.P.	2.599	2.611	2.624	2.639	2.656	2.677
Material compatibility (steel, copper, al., brass)	Very good	Very good	Very good	Very good	Very good	Very good
PTFE (Teflon/NER/polysulfide (Nylon))	Good	Good	Good	Good	Good	Good
Silicone	Good	Bad	Bad	Bad	Bad	Bad
Fluorinated rubber	Good	Good	Good	Good	Good	Good
Lubricant solubility mineral oil/alkylbenzene	Good	Very good	Very good	Very good	Very good	Very good
Lubricant solubility polyol ester	-	Good	Good	Good	Good	Good
Toxicity (ppm)	1000	s.a.	s.a.	s.a.	s.a.	s.a.
Flammability limits (% vol./bar)	None	1.9-9.2	1.8-9.1	1.8-9.0	1.7-8.9	1.6-8.8
Δh combustion (MJ per kg)	-	50.0	49.9	49.8	49.7	49.6
Life tests performed (C compr.)(A appliance)	(C) (A)	(?) (?)	(C) (?)	(C) (?)	(?) (?)	(?) (?)

Properties (weight percentages)	CFC-12	HC-290/ HC-600 (70/30)	HC-290/ HC-600 (60/40)	HC-290/ HC-600 (50/50)	HC-290/ HC-600 (40/60)	HFC- 134a/ HC- 600a (80/20)	HFC- 152a/ HC-600a (80/20)	HFC- 152a/ HC-600a (70/30)
Molecular formula	CF ₂ Cl ₂	("LPG")	("LPG")	("LPG")	("LPG")			
Molecular weight	120.91	47.54	48.81	50.15	51.56	88.64	64.30	63.45
Critical temperature (°C)	111.8	122.9	128.3	133.8	139.3	99.4	115.4	114.4
Critical pressure (bar)	41.8	48.2	47.8	47.3	46.6	40.5	47.1	45.0
Boiling point (1.013 hPa)	-29.8	-37.0/-24.5	-34.7/-20.0	-32.0/-16.4	-28.7/-12.9	-32.1/-31.7	-27.8/-27.2	-27.9
Vapour pressure at 55 C (bar)	13.72	14.13	12.71	11.40	10.16	16.08	14.04	13.76
Vapour pressure at -25 C (bar)	1.24	1.22	1.04	0.88	0.75	1.37	1.13	1.15
Pressure ratio	11.1	11.6	12.2	12.9	13.6	11.8	12.5	12.0
Enthalpy diff. (suet. 32 C - liquid 32 C) kJ/kg	142.4	356.3	357.7	358.8	359.8	214.5	301.5	305.0
Suction gas density at 32 C (kg/m ³)	6.06	2.34	2.05	1.78	1.54	4.91	2.92	2.94
Enthalpy diff. * suction gas density (kJ/m ³) (and change in order to be equal to CFC-12)	862.6 (1.000)	835.4 (1.03)	731.5 (1.18)	638.5 (1.35)	555.5 (1.55)	1054.223 (0.818)	881.273 (0.979)	895.487 (0.963)
Discharge temperature (substant -35 C/55 C)	130.2	118.3	117.3	116.3	115.2	107.0	123.5	128.4
C.O.P.	2.599	2.561	2.573	2.589	2.608	2.924	2.791	2.859
Material compatibility (steel, copper, al., brass)	Very good	Very good	Very good	Very good	Very good	Very good	Very good	Very good
PTFE (Teflon/NBR/polysulfide (Nylon))	Good	Good	Good	Good	Good	Good	Good	Good
Silicone	Good	Bad	Bad	Bad	Bad	Good	Good	Good
Fluorinated rubber	Good					Bad	Bad	Bad
Lubricant solubility mineral oils/silybenzene	Good	Very good	Very good	Very good	Very good	Not/mise.	Not/mise.	Not/mise.
Lubricant solubility polyol ester	-	Good	Good			Good	Good	Good
Toxicity (ppm)	1000	s.a.	s.a.	s.a.	s.a.	1000	1000	1000
Flammability limits (% vol. / %)	None	1.9-9.2	1.8-9.1	1.8-9.0	1.7-8.9			
Δh combustion (kJ per kg)	-							
Life tests performed [C compr.][A appliance]	[C] [A]	[?] [?]	[?] [?]	[?] [?]	[?] [?]	[C] [?]	[?] [?]	[?] [?]

Table A3.3 Properties of the flammable LPG for different mixture compositions, and for HFC/HC-600a mixtures

ANNEX 4

In a publication by Wiest /Wie94/, results of investigations are reported which involve the application of isobutane, propane and mixtures of these two refrigerants on a refrigerating appliance (which has been a one-temperature refrigerator). The tabulated results which can be found in this publication are once more given here.

Refrigerant Quantity (Refrigerant Mix %)	Charge	Swept Volume Compressor (cm ³)	Energy Consumption (kWh/24h)	Energy Consumption (% comp. to R-12)
R-12 reference	(60 g)	series (3.2)	0.3881	100
R-290	(25 g)	2.3	0.4102	105.70
R-290	(25 g)	2.6	0.4031	103.90
R-290/R-600a (50/50)	(25 g)	3.8	0.385	99.20
R-290/R-600a (72/28)	(25 g)	3.8	0.4056	104.50
R-290/R-600a (60/40)	(25 g)	3.8	0.4028	103.80
R-290/R-600a (72/28)	(25 g)	2.3	0.4146	106.80
R-290/R-600a (72/28)	(25 g)	2.6	0.4044	104.10
R-290/R-600a (40/60)	(25 g)	3.8	0.4314	111.20
R-290/R-600a (50/50)	(20 g)	4.3	0.4598	118.50
R-290/R-600a (60/40)	(25 g)	4.3	0.4079	105.10
R-290/R-600a (72/28)	(25 g)	4.3	0.4285	110.40
R-290/R-600a (50/50)	(25 g)	3.2	0.4222	108.80
R-290/R-600a (72/28)	(25 g)	3.2	0.4054	104.50
R-290/R-600a (28/72)	(25 g)	5.73	0.3682	94.90
R-290/R-600a (40/60)	(25 g)	5.1	0.3618	93.20
R-290/R-600a (50/50)	(25 g)	5.1	0.3754	96.70
R-290/R-600a (28/72)	(21.2 g)	5.93	0.3840	98.90
R-290/R-600a (40/60)	(22.7 g)	5.93	0.3986	102.70
R-600a	(25 g)	4.3	0.4611	118.80
R-600a	(25 g)	6.67	0.4046	104.30
R-600a	(25 g)	6.67	0.4122	106.20
R-600a	(25 g)	6.67	0.4145	106.80
R-600a	(25 g)	5.73	0.3918	101.00
R-600a	(25 g)	5.73	0.3970	102.30
R-600a	(22.5 g)	5.73	0.3580	92.20
R-600a	(22.5 g)	5.73	0.3670	94.60
R-600a	(18.7 g)	5.73	0.3700	95.30
R-600a	(21.3 g)	5.93	0.3846	99.10

Results give rise to the following observations:

- application of roughly 40% in weight compared to R-12 yields good results for all hydrocarbons;
- the results obtained show a very good result for isobutane at 70-80% larger swept volume compared to R-12 (7.8% energy saving);
- the mixture shows relatively good results; best results are obtained if the compressor swept volume is significantly increased compared to R-12;
- the results obtained in applying the mixture vary with increasing swept volume. An increase of the swept volume first yields an decrease in energy consumption; further increase results in an improvement.

The following phenomena may play a role:

- propane and isobutane will both dissolve in the mineral oil; however, the circulating mixture will be different in composition and will most likely have a higher percentage of isobutane. For this reason, a higher swept volume than theoretically required (+20 - 30%) will yield best results;
- it is difficult to state which capillary tube changes have to be made;
- a small overcharging of R-600a (by 2.5 g) easily yields a large increase (in the order of 10%) in energy consumption;
- in these tests, a large number of different compressor volumes have been applied in combination with certain compressor motors. It is not clear in how far the design of the motor influences the results (due to differences in the torque/efficiency curve at the operating point);
- it is not clear whether small changes in the compressor swept volume would have resulted in better energy consumption values for R-12.

It should be underlined here that often a change of components (particularly the compressor) will affect the performance of a system significantly more than the thermodynamic properties of a refrigerant. This will certainly also play a role in the investigation described above.

ANNEX 5

DETAILED CONSIDERATIONS ON FLAMMABLE REFRIGERANTS

A5.1 HC-600a (Isobutane)

A5.1.1 Energy efficiency

Theoretical analysis shows that isobutane can have a slightly higher efficiency than e.g. CFC-12 or HFC-134a; values vary between 5 and 10% dependent on pressure levels. Experimental tests have shown higher efficiencies between 3 and 15%, with optimised systems, including compressor and lubricant optimisation. Good results are also obtained at high ambient temperatures (due to the high critical temperature).

TEWI analyses will be in favour of HC-600a compared to many other refrigerants.

A5.1.2 Design efforts, possibilities and problems

Main Characteristics	Impact on Product	Impact on Process
Much larger compressor displacement (65-80%)	Compressor design changes necessary in order to keep external dimensions (sometimes impossible)	New machinery to produce large displacement models
Lower pressure difference (-40%)	Possible use of lower viscosity oils (additives) (mineral oil)	-
Small changes in capillary tube flow rate	No/small changes needed in CFC-12 designed systems	-
Compatible with conventional desiccants	Better (or same) desiccants need to be used (moisture sensitivity)	-
Low charge	May reduce costs	Very accurate charging equipment
Flammability	Design changes may be necessary	Careful leak detection and adequate storage of refrigerant

A5.1.3 Purity of the refrigerant

Generally, HC-600a with a purity of 99.5% is applied. There are indications that lower purities can be applied without an energy penalty, however impurities should consist of saturated hydrocarbons. Low moisture content is necessary.

A5.1.4 Retrofits

Retrofits of CFC-12 to HC-600a could be carried out. Apart from the aspects mentioned in section 3 (feasibility and safety of a retrofit) it would require the use of a compressor designed for isobutane. Otherwise, the capacity of the system would drop far too much. In case there is no perfect match of compressor, capillary tube, etc., no decrease in energy consumption can be expected.

A5.2 HC-290 (Propane)

A5.2.1 Energy efficiency

Theoretical analysis shows that propane has a more or less equal efficiency to CFC-12. This has been confirmed by experimental tests. A favourable aspect is the low pressure ratio which may have an influence on the compressor temperature. However, the fact that higher viscosity oils will be necessary for reliability reasons might reduce the energy efficiency. There is no real incentive to manufacture propane compressors for small refrigerating appliances.

A5.2.2 Design efforts, possibilities and problems

Main Characteristics	Impact on Product	Impact on Process
Much smaller compressor displacement (-30-35%)	Compressor design changes necessary in order to keep adequate capacities	New machinery to produce small displacement models
Much higher pressure difference (+40%)	Necessary use of high viscosity oils (maybe with additives) and redesign of bearings (mineral)	New machinery to produce newly designed bearings
Higher pressure levels	Stronger electric motors required	-
Changes in capillary tube flow rate	Changes needed in CFC-12 designed systems	-
Compatible with conventional desiccants	Better (or same) desiccants need to be used (moisture sensitivity)	-
Low charge	May reduce costs	Very accurate charging equipment
Flammability	Design changes may be necessary	Careful leak detection and adequate storage of refrigerant

A5.2.3 Purity of the refrigerant

Generally, the purity of the refrigerant should be 99.5% (see for further remarks section 3). A low moisture content is necessary.

No propane based refrigerators have ever been manufactured in large series.

A5.2.4 Retrofits

In principle, retrofits are not possible due to the non-availability of small propane compressors, and are not desirable due to the substantially higher pressure levels in the heat exchangers.

Nevertheless, retrofits of CFC-12 equipment to propane have been carried out and showed reasonable energy efficiency results. This is probably due to (i) the high capacity leading to lower running times which may influence the energy consumption level, (ii) a lowering of the oil viscosity compared to CFC-12, (iii) a higher torque (+30%) on the motor leading to higher efficiency values, in spite of a "misfit" in the design. Retrofits cannot be reliable and more compressor burn-outs could be expected at high loads. This does not even take into account safety concerns (leakage) due to increased pressure levels.

A5.3 HC-270 (Cyclopropane)

A5.3.1 Energy efficiency

Theoretical studies predict efficiency decreases in the order of 3% compared to CFC-12. However, one experimental test performed at the University of Maryland /Kim94/ where the capillary tube was adjusted and the correct refrigerant charge applied, showed a larger increase in energy efficiency (6 - 7%) compared to CFC-12. Further experimental tests need to be done before that a final conclusion can be drawn.

A5.3.2 Design efforts, possibilities and problems

Main Characteristics	Impact on Product	Impact on Process
Slightly smaller compressor displacement (-12%)	No real compressor design changes necessary	-
Higher pressure difference (+10%)	Necessary use of higher oil viscosity (additives) (mineral)	-
High discharge temperatures	Possible need for synthetic lubricants	-
Substantial changes in capillary tube flow rate	Considerable adjustments for CFC-12 designed systems	-
Low charge (48% compared to CFC-12)	May reduce costs	Very accurate charging equipment
Flammability	Design changes may be necessary	Careful leak detection and adequate storage of refrigerant

A5.3.3 Purity of the refrigerant

Generally, HC-270 with a purity of 99% (the best available) should be applied. It may be possible to apply lower purities without an energy penalty, however the impurities should consist of saturated hydrocarbons; a low moisture content is absolutely necessary.

Concerning the chemical stability of HC-270, HC-270 has never been considered as a promising option to replace CFC-12, due to its low chemical stability compared to the straight line hydrocarbons (alkanes). The low availability and the extremely high prices of cyclopropane have also contributed to this effect. However, more recent information gives indications that the stability may be adequate for normal refrigeration purposes, however the disadvantage of the high cost price remains.

No products on HC-270 have ever been manufactured in series.

A5.3.4 Retrofits

In spite of a concern about chemical stability, cyclopropane could be considered as a retrofit candidate. There will be a certain "misfit" of the CFC-12 compressor capacity. However also here the higher cost price and lower availability will be prohibitive for application, particularly in the Article 5(1) countries.

A5.4 E-170 (dimethylether, DME)

A5.4.1 Energy efficiency

Theoretical analysis shows that dimethylether has comparable efficiencies to CFC-12. This has been confirmed in calorimetric compressor testing. Experimental tests on appliances have shown energy consumption levels which varied from slightly lower to slightly higher. In these tests, no perfect tuning of the capillary tube was applied.

TEWI analyses will be in favour of DME compared to other refrigerants such as HFCs.

A5.4.2 Design efforts, possibilities and problems

Main Characteristics	Impact on Product	Impact on Process
Somewhat larger compressor displacement	Real compressor design changes not needed; in fact the HFC-134a compressor design could be used without any change	-
Comparable pressure difference	Use of the same viscosity oils (additives)	-
Small changes in capillary tube flow rate	Small changes needed in CFC-12 designed systems	-
Compatible with conventional desiccants	Better (or same) desiccants need to be used	-
Low charge (approximately 50% of the CFC-12 charge)	Due to the fact that DME is a more or less commodity chemical (propellant), its price level is relatively low	Very accurate charging equipment
Flammability	Design changes may be necessary	Careful leak detection and adequate storage of refrigerant

A5.4.3 Purity of the refrigerant

The same comments as for the hydrocarbons, isobutane and propane are valid. DME is industrially manufactured and applied as a aerosol propellant. It is available at high purity grades without large moisture content at reasonable prices and could therefore be directly applied in small refrigeration systems.

No products on DME have ever been manufactured in series.

A5.4.4 Retrofits

Retrofits from CFC-12 to dimethylether are possible, however result in a somewhat low capacity if the compressor swept volume is not adjusted. Under certain conditions the decrease in capacity could be acceptable. Since DME has comparable properties to the ones of HFC-134a, DME could also be used as a retrofit candidate for HFC-134a with polyolester oil (the solubility in polyolester oil is good); one could also apply mineral oil in this case. It implies that HFC-134a appliance production could be easily converted to DME.

DME has been tested by compressor and appliance manufacturers, however real lifetime tests have not been performed. Its chemical compatibility and stability, as well as its performance on a variety of refrigeration systems should be addressed before that any retrofits are seriously considered. Where it concerns toxicological aspects, no problems can be expected, since DME is applied as a propellant in hair sprays, paints etc.

A5.5 HFC-152a

A5.5.1 Energy efficiency

Theoretical studies indicate that HFC-152a has a comparable (not higher) efficiency compared to CFC-12 (and also compared to HFC-134a). Nevertheless, experimental tests on systems have shown that the energy consumption when using HFC-152a will be reduced by several per cent compared to CFC-12 if the capillary tube and the refrigerant charge are optimised. HFC-152a is also proposed as part of the mixture HCFC-22/HFC-152a which should result in an energy efficiency increase compared to CFC-12, as was shown in Chinese studies.

Based upon TEWI analyses, hydrocarbons such as HC-600a will yield more favourable results.

A5.5.2 Design efforts, possibilities and problems

Main Characteristics	Impact on Product	Impact on Process
Somewhat larger compressor displacement (+12%)	Real compressor design changes not needed; in fact the HFC-134a compressor design could be used without change	-
Not miscible with mineral oil	New lubricant required, preferably polyolester (which requires more stringent control at a production plant) and new desiccants will be required	New dehydration processes and cleanliness and equipment procedures required; may also influence the refrigeration assembling procedures
Large changes in capillary tube flow rate (-30%)	Substantial changes needed in CFC-12 designed systems	-
Higher discharge temperatures (+5%)	Maybe of influence on the lubricant selection	-
Low charge compared to CFC-12 (68%)	May reduce costs	Accurate charging equipment required
Flammability	Design changes may be necessary	Careful leak detection and adequate storage of refrigerant

A5.5.3 Purity of the refrigerant

The purity of the refrigerant needs to be of high grade and any moisture content should be avoided. Requirements are equal to the ones valid for HFC-134a.

No products using HFC-152a have ever been manufactured in series.

A5.5.4 Retrofits

Since HFC-152a will need a change to polyolester oil and since there is no real advantage compared to HFC-134a (HFC-152a being flammable which will complicate servicing procedures), retrofits to HFC-152a are normally not considered.

A5.6 HC-290/HC-600a

A5.6.1 Energy efficiency

Following theoretical analysis, propane/isobutane mixtures are supposed to yield comparable efficiencies to CFC-12. However, experimental results with capillary tube and refrigerant charge optimisation do show generally lower efficiencies for mixtures with a relatively high percentage of propane, combined with CFC-12 compressor capacities.

Higher percentages of isobutane in the mixture contribute to an increase in energy efficiency, however require a substantial increase in the compressor swept volume compared to the application of CFC-12.

The fact that different percentages of propane and isobutane will dissolve in the mineral oil in the compressor, results in a mixture circulating through the system which is characterised by a different percentage than the one which is charged into the system. This is also dependent on the compressor and the related ambient temperature levels.

Where it concerns statements on energy efficiency, these statements can only be made for simple refrigerator models without extra compartments at different temperature levels. Generally, the behaviour of the mixture in more temperature appliances is such that due to the temperature glide and decomposition of the mixture, much higher energy consumption levels result and also malfunctioning of the system can be observed.

An Indian study performed recently /Aga96/ on the optimisation of charge on the capillary tube shows that it is difficult to improve the energy consumption of a system. Real optimisation results in comparable energy consumption levels.

For new production (and servicing in the Non-Article 5(1) countries) the use of mixtures is not considered, due to the enormously difficult optimisation for a wide range of different products (different mixture compositions with differently designed and optimised systems for each product). A second, important effect is that the noise production of propane based fluids is substantially higher than for pure fluids (and significantly higher than for HC-600a).

A5.6.2 Design efforts, possibilities and problems

Main Characteristics	Impact on Product	Impact on Process
Comparable compressor displacement for certain mixtures (high HC-600a mixtures will show substantially lower capacities)	No compressor design changes necessary for certain mixture percentages which result in capacities similar to the ones of CFC-12 (this does not hold for high HC-600a percentages)	-
Comparable pressure differences	Possible use of mineral oils with comparable viscosity to the ones used for CFC-12; higher viscosity oils may be required for higher propane percentages	-
Miscibility with mineral oil perfect	No oil type change (same CFC-12 type may be used)	-
Changes in capillary tube flow rate (higher flow rates)	Substantial changes needed in CFC-12 designed systems	-
Compatible with all conventional desiccants	Better (or same) desiccants need to be used (moisture sensitivity)	-
Low charge (40% of the charge required for CFC-12)	May reduce costs	Very accurate charging equipment
Flammability	Design changes may be necessary	Careful leak detection and adequate storage of refrigerant

A5.6.3 Purity of the refrigerant

Generally, HC mixtures with a purity of 99.5% should be applied. However, there are serious indications that lower purities can be applied without an energy penalty, however impurities should consist of saturated hydrocarbons. A low moisture content of the mixtures is necessary.

A5.6.4 Retrofits

Retrofits from CFC-12 to mixtures of hydrocarbons can be carried out. The following needs to be taken into account:

- if it is assumed that the compressor will not be changed, the mixture percentage should preferably be 60/40 (HC-290/HC-600a); at higher isobutane percentages the capacity will be reduced too much;
- it is not certain whether mixtures with high propane percentages would need a small increase in viscosity. This will very much depend on the propane charge compared to the amount of lubricant applied. Generally it can be assumed that, particularly at high ambient temperatures, no real viscosity change will be needed;
- where it concerns malfunctioning of the mixtures in more temperature refrigerators this applies to both new production and to retrofits, so in fact the mixture is not an adequate retrofit candidate for these types of appliances and will contribute to a significant reduction in quality;
- as is valid for all hydrocarbons, the low charge will require very accurate charging in order not to increase energy consumption levels too much. In practice, it will be very difficult to determine the right amount of charge in a functioning refrigerator with the occurring temperature glide.

A5.7 HC-290/HC-600

A5.7.1 Energy efficiency

No results on energy efficiency have been published in literature. In principle, this mixture is only applied in "LPG quality". This implies that the percentages of HC-290 and HC-600 depend on the supplier and on seasonal variation. It can often be so that the percentage of HC-600 is in the order of 60-70% which would result in significant compressor adjustments necessary.

Nevertheless, the energy efficiency calculated for a HC-290/HC-600 mixture is in the order of the one of CFC-12 if the refrigeration cycle is designed in the proper way (at a 70/30 wt %).

The large temperature glide occurring for all mixture percentages (10-14K) makes application in more temperature refrigerators prohibitive.

A5.7.2 Design efforts

Main Characteristics	Impact on Product	Impact on Process
Comparable compressor displacement for certain, high propane percentage mixtures (most mixtures will show substantially lower capacities)	No compressor design changes necessary for certain mixture percentages; in many cases design changes needed	-
Comparable pressure differences	Possible use of mineral oils with comparable viscosity to the ones used for CFC-12; higher viscosity oils may be required for higher propane percentages	-
Changes in capillary tube flow rate (higher flow rates)	Substantial changes needed in CFC-12 designed systems	-
Compatible with all conventional desiccants	Better (or same) desiccants need to be used (moisture sensitivity)	-
Low charge (40% of the charge required for CFC-12)	May reduce costs	Very accurate charging equipment
Flammability	Design changes may be necessary	Careful leak detection and adequate storage of refrigerant

A5.7.3 Purity of the refrigerant mixture

If the mixture is applied, requirements are similar to other hydrocarbons.

In the case of LPG, a high level of other saturated alkanes, mercaptam, non-condensables and moisture may be present which should be prohibitive for reliable use in a refrigeration cycle.

A5.7.4 Retrofits

Retrofits from CFC-12 to LPG have been reported for the developing country (Cuba); a summary is given by Dijkstra and Tummers /Dijt96/. As stated above, the varying quality of the mixture, the level of impurities and contaminants is stated to be unknown, it is difficult to say whether high levels of butane will yield adequate refrigeration capacity but it may be seriously questioned.

Dijkstra mentions that, in Cuba, no composition is measured, no real energy consumption measurement is performed and no follow-up after servicing occurs. He also mentions that "since an estimated number of 60,000 refrigerators have been converted, it is an indication that the LPG drop-in has shown its usefulness" /Dijt96/.

The information given above underscores that much more needs to be done (particularly experimental tests with adequate monitoring of performance) before that any LPG mixture can be recommended as a suitable drop-in candidate.

A5.8 HFC-134a/HC-600a

A5.8.1 Energy efficiency

This azeotropic mixture has been investigated by one compressor/appliance manufacturer and results were reported in 1995 /Bel95/.

At a level of about 20-25% of isobutane, the mixture of HFC-134a and HC-600a forms an azeotrope (at the applied pressure levels, the weight-percentages of the isobutane vary between 18 and 22%). The azeotrope has a lower boiling character than the pure fluid HFC-134a which means that a volumetric capacity comparable to or higher than CFC-12 can be observed. Compression ratios are close to the ones of CFC-12; the discharge temperatures are lower and are in the range of the temperatures that occur when applying HC-600a.

The energy efficiencies are comparable to CFC-12 or slightly better /Bel95/. Theoretical studies yield higher efficiencies in the order of 10%.

A5.8.2 Design efforts, possibilities and problems

Main Characteristics	Impact on Product	Impact on Process
Smaller compressor displacements	Compressor design changes necessary	-
High HFC content	Use of polyolester oils desirable	-
Miscibility with mineral oil marginal	If the oil type is not changed it will result in high refrigerant pressure levels at equilibrium	-
Small changes in capillary tube flow rate	No/small changes needed in CFC-12 designed systems	-
Not compatible with all conventional desiccants	Change in desiccants needed	-
Flammability	Design changes may be necessary	Careful leak detection and adequate storage of refrigerant

A5.8.3 Purity of the refrigerant

The purity of the mixture should be comparable to the purity of the pure fluids HFC-134a and HC-600a (purity grade 2.5). Very low moisture contents are required.

In the investigation mentioned above, extensive lifetime tests of compressors have been performed which yielded good results (for both mineral oil and polyolester oil) concerning the wear of all imported surfaces. No or very low carbon deposits were observed and general test conclusions were favourable.

A5.8.4 Retrofits

In principle, this mixture could be used for a retrofit, however it would require a conversion to the use of polyolester lubricant in order to keep the pressures in the system low. Furthermore, questionmarks are raised regarding its real drop-in character. However, the mixture could also be applied in systems without changing the lubricant which would result in relatively higher pressures (7 - 10 bars) if the system is switched off for a longer period. During the normal on/off behaviour of a working appliance, pressures will not rise much higher than the pressure level of HFC-134a at the refrigerator evaporator temperature.

Some results on retrofitting refrigerators with a mixture of HFC-134a and HC-600a have been reported /Jan95/, however with a smaller percentage HC-600a which considerably reduced the flammability of the mixture, however also reduced the capacity of the refrigeration system to CFC-12 comparable levels. In these retrofits the mineral oil was not replaced. The small percentage of isobutane applied in the mixture (4 - 6%) was high enough to guarantee a good mineral oil return from evaporator to compressor in many different refrigerator designs. Not enough material is available to make any further statements on the feasibility of retrofits.

A5.9 HFC-152a/HC-600a

A5.9.1 Energy efficiency

This azeotropic mixture has been investigated by a Russian appliance manufacturer; however, reliable results on energy efficiency have never been reported.

At a level of about 30% of isobutane, the mixture of HFC-152a and HC-600a forms an azeotrope. The azeotrope has a lower boiling character than the pure fluid HFC-152a which means that a volumetric capacity comparable to CFC-12 can be observed. Compression ratios are close to the ones of CFC-12; the discharge temperatures are lower and are in the range of the temperatures that occur when applying HC-600a.

The energy efficiency is calculated to be much better than for CFC-12 and slightly higher than for HC-600. Use of the mixture is propagated due to its low global warming potential compared to HFC-134a or mixtures of HFC-134a with hydrocarbons. A second argument which is mentioned is that the flammability of this mixture is lower than the one of the pure hydrocarbons (whether this is an important issue in domestic refrigeration equipment is questionable).

A5.9.2 Design efforts, possibilities and problems

Main Characteristics	Impact on Product	Impact on Process
Comparable compressor displacements	No compressor design changes necessary	-
High HFC content	Use of polyolester oils desirable	-
Miscibility with mineral oil marginal	If the oil type is not changed it will result in high refrigerant pressure levels at equilibrium	-
Small changes in capillary tube flow rate	No/small changes needed in CFC-12 designed systems	-
Not compatible with all conventional desiccants	Change in desiccants needed	-
Flammability	Design changes may be necessary	Careful leak detection and adequate storage of refrigerant

A5.9.3 Purity of the refrigerant

The purity of the mixture should be comparable to the purity of the pure fluids HFC-152a and HC-600a (purity grade 2.5). Very low moisture contents are required.

A5.9.4 Retrofits

In principle, this mixture could be used for a retrofit, however it would require a conversion to the use of polyolester lubricant in order to keep the pressures in the system low. However, the mixture could also be applied in systems without changing the lubricant which would result in relatively higher pressures (7 - 10 bars) if the system is switched off for a longer period. During the normal on/off behaviour of a working appliance, pressures will not rise much higher than the pressure level of HFC-152a at the refrigerator evaporator temperature.

In principle, retrofits are possible for all kind of refrigerator designs since the refrigerant behaves more or less as a pure fluid (virtually no temperature glide). Next to hydrocarbons, this mixture is the most promising one for retrofits.

Theoretical considerations on the mixture HFC-152a/HC-600a yield indications for a high efficiency, where the azeotrope could also be used for retrofits of different types of domestic refrigerators. Compared to the direct warming of HFC-134a, a reduction of 95% could be achieved; together with the possible, even slightly better energy efficiency than HC-600a, the mixture may be a valid candidate for retrofits (however, feasibility of this option in the Article 5(1) countries is doubtful related to questions on availability, in the Non-Article 5(1) countries retrofits are less important and will be more and more on isobutane).

However, any practical evidence is so far lacking.

**MONTREAL PROTOCOL
ON SUBSTANCES THAT DEplete
THE OZONE LAYER**



Technology and Economic Assessment Panel

**PART IV: ASSESSMENT OF THE ECONOMIC VIABILITY OF
METHYL BROMIDE ALTERNATIVES**

**April 1997 Report
Volume II**

**Montreal Protocol
On Substances that Deplete the Ozone Layer**

UNEP Technology and Economic Assessment Panel

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April 1997 Report, Volume II

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ASSESSMENT OF THE ECONOMIC VIABILITY OF ALTERNATIVES TO METHYL BROMIDE

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EXECUTIVE SUMMARY

1 INTRODUCTION

1.1 Decision VII/8 of the Parties requested the UNEP Technology and Economic Assessment Panel (TEAP) to prepare a report to the 9th Meeting of the Parties to enable the Parties to consider further adjustment to the control measures of methyl bromide. In undertaking this task, TEAP was required to address the availability of alternatives to methyl bromide for specific applications. The TEAP instructed its Economic Options Committee to provide information on the economic viability of alternatives to methyl bromide (TEAP Report, June 1996, p. 116).

1.2 Information on the uses of methyl bromide was reviewed to identify those which were likely to be associated with the more significant positive or negative - economic - impacts of phasing out methyl bromide. The information also shows where alternatives are already in use which helps to put the issue of substitution into perspective with respect to different countries and products.

1.3 The Task Force focused on alternatives that are beyond the experimental stage and already in use. As soil fumigation is by far the largest and fastest growing use of methyl bromide, the Task Force gave most of its attention to this use. The quantities of methyl bromide used in post-harvest treatment and for treatment of structures are much smaller, but can have large economic value and therefore these uses were also addressed, but to a lesser degree, by the Task Force. Quarantine and pre-shipment uses are currently exempt from the control schedules of the Montreal Protocol and, therefore, are not addressed in this report.

1.4 External costs, which include environmental effects and human health effects, were addressed, at least qualitatively, in several of the studies reviewed by the Task Force. The Task Force itself was not able to deal directly with the issue of the external costs of methyl bromide alternatives. However, the Task Force recognised that these costs are important and that a close appreciation of their significance is needed to make informed decisions regarding the economics of methyl bromide and its alternatives.

1.5 The Task Force used the information resources available to it particularly the 1997 MBTOC report to TEAP and the 1994 Assessment, the expertise of MBTOC members, and relied on the collective professional experience and judgement of the its members. Microeconomic evaluations of the economics of specific alternatives were carried out and a sector model approach was used to assess the wider economic impacts of switching to methyl bromide alternatives.

2 CONCLUSIONS

2.1 General Conclusions

2.1.1 Progress with alternatives. Where alternatives have been adopted, users have become more efficient as they develop expertise. This learning process is typical when different technologies are introduced. In the case of crop production, yield outcomes become more favourable over time. There are two general reasons for this improvement in the performance of alternatives. First, the technologies themselves improve. That is, incremental improvements take place in aspects such as materials, equipment and application rates (in the case of chemicals). Second, the human agents using the alternatives become more knowledgeable and skilful over time. For example, they may better determine the optimal timing for certain tasks or become more adept at operating new equipment. Over time, these advances have been yield gaps between the alternatives and methyl bromide, and there are examples where yield exceeds that with methyl bromide use.

2.1.2 Technology transfer. The Task Force considered the potential for technology transfer between countries. Some technologies appear to be readily transferable, while others are constrained by factors such as climate (e.g., solarisation), regulation (e.g., pesticide registration requirements), and the knowledge and skills of agricultural workers (e.g., integrated pest management systems). Efforts to increase relevant human capital (e.g., by training agricultural workers) could speed up the transfer and adoption of alternatives. Alternatives are being developed in many places with technology transfer originating from both developed and developing countries.

2.1.3 Dangers of generalisation. The costs of alternatives and methyl bromide will differ over time by crop, over time, and by location. Therefore, one must be careful not to generalise about the economic superiority of specific chemical alternatives, or between chemical and non-chemical technologies.

2.1.4 Technical data. On reviewing available information, the Task Force concluded that the technical and other information required for more comprehensive and rigorous assessments of the relative economic performance were not yet available for specific situations for many methyl bromide alternatives, whilst recognising that ongoing work in many institutions is already making good progress in generating the necessary skills, technical data and other information required for further work.

2.1.5 Production systems. Whilst most of the work undertaken in this assessment addressed the relative economic performance of specific methyl bromide alternatives, the Task Force recognised the advantages of adopting an approach based on identifiable production systems possibly involving combinations of specific alternatives and techniques that might be used if further work on the economic viability of alternatives requested.

2.2 Conclusions of the Microeconomic Evaluation: Soil Fumigation

2.2.1 Dazomet. The Task Force concluded, with input from MBTOC experts, that crop yields might initially decline by up to 10%. However, this yield loss can be overcome within 3 to 4 years as farmers become more familiar with the use of dazomet leading to improved application techniques. However, farmers may need assistance with the substitution process in the form of extension services, advice, and short term financial assistance.

2.2.2 Dichloropropene (1,3 D or Telone) and chloropicrin . The main findings are that (1) the product per unit costs are substantially more expensive than those for methyl bromide; (2) additional costs are incurred to modify equipment to enable implementation of these alternatives; and (3) on the basis of the data available to the Task Force yields are consistently lower with substantial variation in percentage decreases depending on the alternative used and the crop.

2.2.3 Metam sodium. The differences in production costs for metam sodium with respect to methyl bromide are quite varied. They range from +\$1700/ha to +\$800/ha in Colombia for cut flowers (TEAP, 1995); +\$350/ha for strawberries in South Africa (FOE, 1996), and very small differences in Florida (Spren et al. 1995). The switch to metam sodium involves (1) additional costs of equipment, however, no estimates are available; (2) higher risk of crop failure is associated with metam sodium than with methyl bromide, but no estimates of the cost implications are available; and (3) the impact on yields vary.

2.2.4 Integrated pest management (IPM). The studies reviewed on IPM systems report consistently lower production costs than those for methyl bromide. The costs for IPM were estimated by TEAP to be lower by \$1900/ha, or 28% lower (TEAP, 1995); and other estimates were lower by 67% (FOE, 1996). The CSIRO (1995) study estimated only slightly lower costs per square meter using IPM with only one crop and somewhat less than double the cost for one crop when IPM is used to get two crops. Yields using IPM are similar to those using methyl bromide for a single crop, whereas for double cropping yields are about 75% higher for IPM. Profitability is also about 75% higher for IPM with double cropping. Apart from the CSIRO (1995) study, no quantitative impacts are cited for IPM yields although profitability is estimated to be higher in almost all cases.

2.2.5 Soiless substrates (1). The main findings were (1) the costs of substitution will depend on whether the technique is only used for seedlings, or for the full growing of the crop. The estimates are as follows: \$108/ha in Zimbabwe for tobacco seedlings; and \$609/ha in Zimbabwe for paprika seed trays (FOE, 1996); (2) yield impacts are small or positive in switching to this alternative and risks are quoted as consistent with methyl bromide (MBTOC, 1997); and (3) the Danish study (Gyldenkaerne et.al. 1997) for greenhouse grown tomatoes estimates an increase in profitability of \$2 to \$3 per square metre and the pay back periods for investments in the technology are 1.4 to 4 years.

2.2.6 Soiless substrates (2). The use of soiless substrate for seed trays appears to be an attractive alternative for tobacco and some other seedlings, and has been successfully applied in South Africa, the USA and Zimbabwe. This technology is used for several crops and in several countries. Its use for greenhouse tomatoes (Denmark) and for other high-value crops (e.g. strawberries in The Netherlands) is less easily transferable due to capital-intensity and the need to be able to sell in high price markets (e.g., winter tomatoes and strawberries).

2.2.7 Solarisation. The experience with solarisation technology reported from countries with abundant sunshine is encouraging, including several examples of lower production costs than with methyl bromide. The main factors affecting its adoption are that solarisation can only be technically effective where there is sufficient sunshine, soil conditions are favourable, technical assistance is available to local growers; and where the costs of an increased unproductive period can be accommodated.

2.2.8 **Steam.** The main findings are (1) where steam is a high cost alternative to methyl bromide the evidence suggests that it is suitable only in special circumstances where the higher cost is justified by the economic value of the reduced contamination risk e.g., in mother plant beds; and (2) the development of cost-efficient and mobile steam generating equipment is encouraging further uses of steam as an alternative to methyl bromide.

2.2.9 **Reduction of methyl bromide use through virtually impermeable film (VIF).** Improved tarping materials and techniques can reduce application rates by 30% to 50% leading to reduced emissions. Reported implications for production costs vary from cost savings of \$1400/ha to a cost increase of \$400/ha. Those facing cost increases would have an additional incentive to seek cost saving through the adoption of alternatives to methyl bromide.

2.3 **Conclusions on Microeconomic Evaluation of Alternatives: Treatment of Post-Harvest Commodities and Structures**

2.3.1 **Use of heat and phosphine and carbon dioxide.** Use of heat and phosphine and carbon dioxide are prominent among the alternatives used for commodity and structural fumigation. The switch to an alternative may incur additional one-off costs and treatment costs may also be higher or lower. The cost estimates are subject to various site-specific factors that make it difficult to provide estimates of general applicability.

2.4 **Conclusions on Economic Viability of Alternatives: A Sector Approach**

2.4.1 **Sector analyses.** Sector analyses highlight the dynamic nature of agricultural production and trade. Sector models can provide insight into marketing and distributional effects of changes in production systems that cannot be obtained through case studies or budget analyses. Existing patterns of production and trade depend, in part, on production costs associated with the use of methyl bromide. Switches to alternatives having different production costs, together with market forces and trade policies, can lead to forces that could change the location of crop production, trade patterns, consumer prices, jobs and foreign exchange earnings.

2.4.2 **The North American market for specialty winter fresh vegetables (e.g., tomatoes, melons, strawberries).** This market includes producers in the USA (Florida, Texas, California) and Mexico. It accounts for more than 20% of global methyl bromide use for soil fumigation i.e., about 16% of total global methyl bromide use. Using a sector model based on information available in 1994 (Spren et al., 1995), the authors concluded that a rapid phaseout of methyl bromide, given alternatives available at that time, would impose annual economic costs on Florida of \$623 million in shipping point revenues and a total cost of \$1.0 billion. These estimates were substantially reduced in a re-run of the model using information on alternatives as of February 1997; shipping point revenues were reduced to \$300 million.

2.4.3 The European and North African regional market for winter fresh fruits and vegetables. As in the North American market, there has been substantial concern about the potential migration of production to North Africa due to phasing out methyl bromide in the European Union. In principle, the same type of sector analysis as reported for the North America market is also applicable to this market. However, no model of this type is available for the European Union and North African market at present, although simpler quantitative models have been applied to Spain, France and Italy (Bonte, 1996). The results, based on alternatives available as of 1995, suggest economic losses for Spain, France and Italy and increased imports of selected fresh fruits and vegetables, probably from North Africa. Updated results are not available at this time. However, progress with alternatives and their application is likely to lower costs over time in ways that closely reflect the estimates reported for the North American market.

3 PRIORITIES FOR FURTHER WORK

3.1 Technical Data for Agricultural Production Systems. Assessments of the economics of alternatives depend on adequate technical data and other information that must be generated by the experimental work and field testing carried out by agricultural production scientists e.g., estimates of changes in crop yields, production costs, and the risks of crop failure for specific agricultural production systems in specific locations. Technical data on production systems and human capital inputs for IPM systems, whether chemical-free or not, would be of particular interest.

3.2 External Costs. Assessments of alternatives to methyl bromide should include information on economic costs which are not internalised by market prices but are associated with agricultural production and marketing e.g., the effects of toxicity of methyl bromide or alternatives on human health. The Task Force could not address the issue of external costs in this report due to time and resource constraints. However, in further work on assessing the relative economics of methyl bromide and alternatives, the external cost issue should be given high priority.

3.3 Quantitative Estimation of the Economic Viability of Alternatives. The application of quantitative methods to assessments of the relative economics of methyl bromide and alternatives is both important and practicable. The North American model of the winter fresh vegetable market involving the USA, Mexico and Canada demonstrates the value of this approach and the potential for developing further applications to improve (1) assessments of the economic viability of alternatives and (2) estimates of the costs and benefits of phasing out methyl bromide in Article 5(1) countries.

1 INTRODUCTION

1.1 Committee Mandate

- 1.1.1 Decision VII/8 of the Parties to the Montreal Protocol requested the UNEP Technology and Economic Assessment Panel (TEAP) to prepare a report to the 9th Meeting of the Parties to enable the Parties to consider further adjustments to the control measures of methyl bromide. In undertaking this task, the TEAP was requested to address the availability of alternatives to methyl bromide for specific applications.
- 1.1.2 The TEAP instructed the Economic Options Committee (EOC), one of seven constituent Technical Options Committees of the TEAP, to provide information on the economic viability of alternatives to methyl bromide (TEAP, June 1996; p.116).
- 1.1.3 The EOC decided to convene a Task Force including both EOC members and non-EOC experts who were selected for their expertise in the economic assessment of alternatives to methyl bromide. This expert group, referred to as the Methyl Bromide Task Force of the EOC, was convened for the specific purpose of preparing this report in response to the instruction to the EOC from the TEAP. The members of the Task Force are listed in Annex III to this Report.

1.2 Structure of the Committee Report

- 1.2.1 The Methyl Bromide Task Force met in Bangkok, Thailand from 17 to 28 February 1997. In the course of its deliberations, the Task Force reviewed nearly one hundred documents, including case studies. Source documents are referenced in *Annex II* to this report. Overall, the Task Force considers that it has had access to most of the key studies of the impacts and costs or savings of switching out of the use of methyl bromide. It is unlikely that conclusions reached in this report would be changed by information from any existing studies which were not available to the Task Force. Review of these studies led to the overall conclusions drawn from the microeconomic and sector analyses presented in Section 3 and 4 of this report, respectively. There are, however, substantial data gaps in the existing information that limit the completeness of this assessment.
- 1.2.2 The Task Force did not rely solely on documents. The Task Force met, both formally and informally, with members of the Methyl Bromide Technical Options Committee (MBTOC) during the week of 17-21 February 1997 while the MBTOC and the Task Force were meeting concurrently in Bangkok, Thailand. As is the case with any economic assessment, the Task Force members drew upon pertinent economic theory and their professional experience and judgement when analysing the available information. All information, whether in the form of documents or statements by members of MBTOC, was critically assessed from an economic perspective. The Task Force did not evaluate those aspects of the information that was available to it that were outside their expertise; in these cases the task Force consulted with and benefited from technical interpretations and explanations provided by expert members of MBTOC. The Task Force relied substantially on the 1997 MBTOC Report to the TEAP and the 1994 MBTOC Assessment for technical information on performance of methyl bromide and alternatives.

- 1.2.3 The structure of the Task Force's Report is as follows. *Section 1* sets out the Parties' mandate to TEAP, and TEAP's instructions to the EOC, and presents an outline the Report prepared by the Task Force. *Section 2* discusses the concept of relative economic performance, which is not an absolute notion but rather one with several dimensions, some of which can only partly be quantified. The Task Force divided the analysis of viability into two areas; the relative microeconomic performance of specific techniques in specific locations, and the broader sector approach to the performance of a particular set of alternatives that includes employment, trade and other economic indicators. The Task Force also made a distinction between indicators of economic performance for Article 2 countries and Article 5(1) countries. This section goes on to review the basic information available on the use of methyl bromide and its alternatives, and the data problems that the Task Force encountered in interpreting case studies. By this means, the Task Force identified the limitations of the present analysis, especially those issues that could not be addressed but that are of recognised importance to a full assessment of methyl bromide alternatives.
- 1.2.4 *Section 3* presents a review of the major alternatives to methyl bromide that are currently in use. These are divided by technique and by product group for soil applications. In addition, brief assessments are presented on methyl bromide alternatives for commodity fumigation and structural fumigation.
- 1.2.5 *Section 4* presents a sector approach to assessing the impacts of phasing out methyl bromide. Of particular concern are the possible trade effects. In general, this means production moving because of differences in the economics of production in different locations associated with methyl bromide or alternatives use.
- 1.2.6 *Section 5* provides overall conclusions on the relative economic performance of alternatives and methyl bromide based on the information available to the Task Force in February 1997.
- 1.2.7 *Section 6* presents the views of the Task Force on priorities for further work. It is the view of the Task Force that there are substantial gaps in technical data and information that need to be addressed if more comprehensive assessments of the relative economic performance of methyl bromide and its alternatives are required.

2 INDICATORS OF ECONOMIC VIABILITY

- 2.1 **Acceptability of Cost.** Whenever producers are required to phase out the use of a particular technology or substance they will face some costs. Depending on the structure of the markets in which they buy their inputs and sell their outputs, they will be able to pass on part of these costs to suppliers and to consumers. This is what happened with the phase out of CFC's, and methyl bromide is no exception. Hence, the presence of such costs cannot by themselves be considered as an indication of the lack of economic viability of the alternatives. The issue is whether these costs are acceptable; in the sense that they could be much lower by moving to an alternative and in the sense that the burdens on particular social groups - producers, employees, suppliers of chemicals, consumers and society as a whole - are more than would be considered acceptable. These definitions are necessarily subjective; there are no objective indicators of acceptable costs for particular groups.
- 2.2 **Article 5(1) Countries.** The Task Force has also taken a view that the above clarification on "economic viability" needs to be modified when dealing with Article 5(1) countries. For these countries the incremental costs of phase out in accordance with the terms of the Protocol are met through the Multilateral Fund of the Montreal Protocol. The question of economic viability then becomes: (a) are the costs to particular groups that are not compensated by the Fund acceptable, and (b) are the costs borne by the Fund excessive in the sense that they could be reduced by moving to lower cost alternatives. This Report reviews earlier preliminary estimates of the incremental cost of methyl bromide phase out for Article 5(1) countries.
- 2.3 **Elasticities.** The microeconomic costs of phasing out methyl bromide should ideally be measured in terms of the changes in producer and consumer surplus and impacts on input and ancillary markets (including employment). These changes in turn will have a long term and a short term dimension. In the short term, an increase in costs will raise product prices by more than in the long run as supply is more inelastic. This will protect producers to some extent from the cost increases but will mean that consumers will bear a relatively larger part of the cost. In the medium to long term, the prices will not remain as high as supply responses become more elastic, and the costs of alternatives fall. Producers will have to adjust to the higher costs, but over time they will be able to shift resources into other areas which will mitigate some of the effects of smaller price increases.
- 2.4 **Input Markets.** The impacts on employment and other input and ancillary markets will also vary between the short and long run. In the short run, one can expect an employment effect as marginal producers are driven out of business. In the medium to long term it is normally assumed that some or all of these resources will be re-employed in other sectors. Hence, an analysis of the costs should distinguish between the short run and the long run, and between changes in consumer and producer surplus. It should also look at the impacts on employment in the short run and the long run.

- 2.5 **Impact of Substitutes.** In practice, few studies have adequately addressed short and long run differences. Exceptions are the studies by Bonte (1994, 1995) and Spreen *et al.* (1995). Since it is important to evaluate data from other studies as well, it has been necessary to review the impacts of alternatives based on information such as: increases in costs per unit of production, changes in yields, and changes in risks of crop failure. From this information a picture of the likely impacts of substitutes, including any discrepancies in the data, was built up. The Task Force evaluated the impacts of each substitute. These evaluations fed into the assessment of the relative economic performance of the alternatives.
- 2.6 **For Article 5(1) Countries.** Some additional costs and impediments to adoption have to be taken into account. These relate to institutional capacity, the limited availability of skilled labour to apply the alternative techniques, the shortage of capital for the investment in the techniques, and the problems of cash flow which can constrain the adoption of alternatives requiring longer periods between incurring the costs and receiving the income from production.
- 2.7 **Limitations.** The following limitations on the scope of this Report should be noted.
- 2.7.1 *The question of external costs.* The costs of methyl bromide and its alternatives are not just the direct costs (labour, materials, equipment). They also include the external costs for methyl bromide and its alternatives. There was some discussion of potential adverse impacts on soil and water pollution and potential health effects of alternatives which involve toxic substances. The Task Force took the view, however, that it was not possible to review the valuation of and compare these external costs within the constraints of this Report. This issue would not be a concern if the regulatory framework were set so that any external impacts are already optimally regulated. That is unlikely to be the case, and also the Task Force recognises that there may well be positive or negative changes in the social costs of substituting alternatives for methyl bromide that should be taken into account.
- 2.7.2 *The question of regulatory costs.* Some well-developed chemical alternatives to methyl bromide do not have regulatory approval in particular regions. Obtaining approval, *de novo*, is costly and takes time; estimates provided by MBTOC (1995) suggest costs of around \$60-\$100 million and around ten years from initial development to get a product fully approved. In the view of the Task Force this moves consideration of most non-approved substances out of the scope of this Report. However, some materials have not been registered in some countries, but have been in others. Where a full registration package is available, as implied by registration, registration in additional countries can be relatively inexpensive and quick. Non-chemical alternatives, on the other hand, often avoid regulatory costs and delays as they do not generate risks to health, occupational safety and wider environmental concerns.

2.7.3 *Assessment of risk* . MBTOC has emphasised that a major consideration of the comparison between methyl bromide and the alternatives is the different probability each offers of crop failure. Methyl bromide is attractive in many production systems, not because it offers a higher expected yield for a given crop, but because it is considered to reduce the risk of crop failure. In economic terms this reduction of risk has a value – a risk premium – that can be measured in money terms given data on the relevant probabilities. None of the data reviewed provided the Task Force with the necessary information for a formal analysis. In fact, very little is known on this important aspect of methyl bromide and its alternatives and more data are urgently needed. The Task Force has had to rely on qualitative statements of risk, its own knowledge, and discussions with members of the MBTOC.

3 MICROECONOMIC EVALUATION OF ALTERNATIVES RELATIVE TO METHYL BROMIDE

3.1 Introduction

This section reviews studies of alternatives to methyl bromide from a microeconomic perspective. The latter is viewed as looking at individual markets for specific products, assuming that other prices and other markets are not affected.

The discussion is presented as follows. *Section 3.2* presents the basic information on the use of methyl bromide and alternatives in Non-Article 5(1) and Article 5(1) countries for soil treatment, for the most recent years. This shows the areas where methyl bromide use is most significant and therefore where the major economic impacts are likely to be found. It also shows where alternatives to methyl bromide are already in use, so that the issue of substitution can be put into perspective for the different countries and products. *Section 3.3* reports on the analysis of the alternatives that are beyond the experimental stage and already in use. The Task Force assumed that most chemical products not already registered as approved for agricultural application in at least some developed countries are not likely to be available in the time frame for the phaseout of methyl bromide. Furthermore, for some experimental techniques there is virtually no information on which to base a relative economic assessment. They have also been left out of the discussion. The three main non-quarantine and pre-shipment uses of methyl bromide are soil fumigation (76%); durables (13%); and structures (3%). The last two are relatively small uses of methyl bromide. Quarantine and pre-shipment uses are currently exempt from the control schedule of the Protocol. Hence, the Task Force's focus has been on soil fumigation and the other uses have been given less attention.

3.2 Major Uses of Methyl Bromide by Sector and Trends in Use: Non-Article 5(1) and Article 5(1) Countries.

- (i) World use of methyl bromide, as measured by sales (other than use as feedstock for chemical synthesis) was 71,257 tons in 1992, the last year for which UNEP estimates are available. This level represents a significant increase from 1984 when world sales were 45,572 tons.
- (ii) Strong growth in the use of methyl bromide as a soil fumigation treatment was the main course of this increase. Soil treatment accounted for two thirds of methyl bromide use in 1984 and 76% of use in 1992. The other major uses of methyl bromide are post harvest treatment of stored commodities, pre-shipment and quarantine treatment, and treatment of structures. All post-harvest treatments accounted for roughly 22% of use, and treatment of structures about 3%.
- (iii) *Soil Fumigation.* As a soil treatment, methyl bromide is effective against insects, nematodes, and fungal pests and many weeds and weed seeds. Two crops, tomatoes and strawberries, accounted for 35% of the soil fumigation use in 1992 (Table 1). Other crops using significant quantities of methyl bromide are listed in the table.

- (iv) *Post-harvest.* Post-harvest treatment with methyl bromide is used against insect pests for stored grain, dried fruit, and nuts; and as a quarantine measure against some insects and some fungal pests on timber, and for insect pests on fresh fruit and vegetables. Post-harvest treatment of durables and perishable goods used nearly 10,000 tons in 1992.
- (v) *Structures and Transportation vehicles.* Methyl bromide treatments are used against insects including termites in domestic premises. In addition to domestic premises, flour mills and food preparation, facilities are treated. In ships and freight containers methyl bromide is used against rodents and insects pests often as a quarantine or contractual measure. Treatment of structures and transportation is the smallest of the principal uses of methyl bromide. Quantities used rose from 2,166 tons in 1984 to 3,613 in 1989 but have since declined, falling to 1,964 tons in 1992 with further declines reported subsequently due to the increased use of sulphuryl fluoride for fumigation of domestic premises.
- (vi) *Use in Non-Article 5(1) and Article 5(1) countries .* Developing countries use about 18% of methyl bromide produced globally for agricultural and related uses. The main uses are for soil fumigation (about 70%) and disinfestation of durables (about 20%) (UNEP 1995 Assessment). In recent years some developing countries have reduced methyl bromide consumption, while others have shown stable or increased use. Article 2 countries remain the largest consumers of methyl bromide with slightly higher percentage use for soil fumigation and lower percentage used for stored commodities. Methyl bromide use continues in developed countries under annual consumption caps established under the Montreal Protocol at 1991 levels.

Table 1 - Global use of methyl bromide in fumigation by crop in 1992.

	Tomatoes	Strawberries	Cut-flowers	Nursery crops	Tobacco seedbeds
% of global use	22	13	6	6	5
	Melons and cucurbits	Perennial crops	Post-harvest grains	Dried fruits and nuts	Other(*)
% of global use	7	5	8	0.8	27.2

Note: *Includes flour mills (2%), timber (8%) and many other small uses.

Source: MBTOC, 1997. MBTOC Draft Report to TEAP-1997 (19 February 1997: working draft, page 6).

Table 2 - Percentage of selected crop area treated with methyl bromide in selected countries during 1993.

	Tomatoes	Strawberries	Cut flowers	Nursery crops	Tobacco	Melons/curcubits/eggplant
Denmark	34	n/a	5	n/a	n/a	n/a
United Kingdom	10	30	4.4	<1.0	n/a	<1.0
United States(*)	12	68	n/a	n/a	3	59 (eggplant)
South Africa	n/a	67	35	100	100	n/a
Egypt	n/a	5	n/a	n/a	n/a	25 (curcubits)
Malta	100	100	100	n/a	n/a	50 (curcubits)

Notes: *for 1992. n/a: not available

Source: MBTOC, 1995. Montreal Protocol on Substances that Deplete the Ozone Layer. 1994 Report of the Methyl Bromide Technical Options Committee, 1995 Assessment (Table 4.1.4).

Table 3 - Estimated 1992 global usage of methyl bromide by type of fumigation

	Type of fumigation				Total use in agriculture
	Durables (*) (**)	Perishables (*)	Structural (*)	Soil fumigation	
Amount used (tonnes)	9855	6537	2264	57407	76063
% of non-feedstock usage	12.96	8.59	2.98	75.47	100.0

Note:

*in enclosed space

**grains, nuts, dried fruits, timber

Source: MBTOC, 1995. Montreal Protocol on Substances that Deplete the Ozone Layer. 1994 Report of the Methyl Bromide Technical Options Committee. 1995 Assessment. Pg. 48 (based on survey data on use).

3.3 Alternatives for Methyl Bromide in Soil Treatment

Table 4 below lists the alternatives that have been evaluated and the products for which they have been considered. The numbers in table 4 refer to the studies, as referenced in Annex 2. In total, there are around 80 case studies that have been reviewed by the Task Force. Many of these, however, are extremely limited in the quantitative information that they provide; in some cases there is no quantitative information at all. The discussion below is organised by technique, with some general conclusions by product being given at the end of the section.

Table 4 - Economic data used in the analysis of alternatives to methyl bromide for soil treatment

	Bananas	Cucumbers	Cut flowers	Egg plants	Strawberries	Tobacco	Tomatoes
Basamid / Dazomet		6	11, 4		4, 5, 6, 8	13	4, 5, 6, 8
Chloropicrin / dichloropropene / Telone		1		1	1, 13	13	1, 13
Glyphosate	7						
IPM			8, 11, 14		11, 13, 14	13	8, 13, 14
Metam sodium			12		8, 11, 13	11	1
Microbial inoculants							
Soil less substrate		14			13	7, 8, 13	3, 13
Solarisation					8, 13	7, 8, 13	8, 13
Steam		14	5, 8, 11		13	7, 8, 13	13
Reduction in MeBr w/ Tarp			11		11	11	
Biofumigant							13

	Vegetables	Peppers	Melons	Paprika	Onions	Maize	General
Basamid / Dazomet	4	8	4, 5				4
Chloropicrin / dichloropropene / Telone		1					
Glyphosate							
IPM	11						
Metam sodium	11	1					
Microbial inoculants	13						
Soil less substrate		8		8			
Solarisation	10, 13				10	10	
Steam	8						
Reduction in MeBr w/ Tarp	11						
Biofumigant							

Note: numbers in this table refer to the studies in Annex II

3.3.1 Dazomet

3.3.1.1 Dazomet is a widely used chemical for soil fumigation. It is applied in a granular formulation to moist soils where it reacts with water to liberate methyl isothiocyanate (MITC) which is effective against soil borne pests including fungi, nematodes and weeds. Dazomet is also a broad spectrum biocide with a somewhat different range of activity to methyl bromide. It is currently being further developed for pre-plant soil fumigation in food crops.

3.3.1.2 As indicated in table 4, the studies referenced for this technique covered cucumbers, cut flowers, strawberries, tobacco, tomatoes, nursery vegetables, peppers, melons and general vegetable crops (Bonte, 1994; Bonte, 1995a; TEAP, 1995; FOE, 1996; MBTOC, 1997).

3.3.1.3 The dazomet substitute has been evaluated in case studies in South America (FOE, 1996) and Zimbabwe (FOE, 1996). A South American study for cut flowers reports estimates of a cost increase with respect to methyl bromide of \$1000 to \$1600/ha (TEAP, 1995) with no yield effects reported. A Zimbabwe study for strawberries estimates a cost increase of \$1000/ha, also with no yield impacts reported (FOE, 1996). A study for Chile also estimates higher costs for the substitute: \$2000/ha for nursery vegetables, \$2,200 for peppers (FOE, 1996) with no yield effects cited⁸.

3.3.1.4 The dazomet substitute has also been evaluated largely in Europe (Bonte, 1996). The countries studied are: France, Greece, and Spain, and the products analysed were: cut flowers, strawberries, tomatoes, nursery vegetables and melons. The European studies for dazomet have rather different conclusions. These conclusions (Bonte, 1994; Bonte, 1995a; Bonte, 1995b) were:

- (i) costs of the substitutes are lower than methyl bromide by up to 30-40%;
- (ii) “yields” are 25% to 50% lower;
- (iii) in the short run producers will suffer a loss of revenue because, although the price will rise, production will decline by even more. Producers losses are significant;
- (iv) in the short term consumers will lose out because prices of the final products will rise;
- (v) in the long term the prices of final products will revert to international prices, hence there will be no consumer loss but producers will be worse off than in the short run; and
- (vi) there will be considerable loss of employment per product (ranging from 400 - 2000 in France, 1,000-7000 in Spain and 600 - 13,000 in Greece).

3.3.1.5 Given the differences between the European and non-European studies the Task Force decided that the first task was to reconcile these differences. If the European figures are correct, and if dazomet is the alternative of choice, then the impacts on producers and workers are significant and this alternative would be used at substantial cost⁹. If, on the other hand, the non-European figures are correct then the changes could be achieved at modest cost. A more detailed analysis of the European studies by the Task Force revealed that the yield declines were measured as changes in total output – i.e. the change in yield per hectare times the number of producers who cease production because of the changed economic costs and lower yield. This is, of course, not a normal concept of yield loss. Using an estimate of reduced production to determine of a yield loss produces a spuriously high estimate.

⁸ There is some discussion of increased health risk from using dazomet (carcinogenic effects).

⁹ It should be noted that the employment impacts are only the short run direct impacts. In the short term there will be further indirect effects and in the longer term there will be less effects as labour is shifted into other sectors.

- 3.3.1.6 Based on discussions with MBTOC experts, the Task Force concluded that there are likely to be modest initial declines in yield of about 10% in moving to dazomet. As farmers become more familiar with these products, and as the application techniques improve, the yield loss will disappear within 3 to 4 years. On this basis, the magnitude of the costs to producers and consumers, and employment costs, in the European studies has been over-estimated. However, to achieve this transition with low cost, farmers may need assistance through extension services.
- 3.3.1.7 For developing countries, the TEAP study (TEAP, 1995) estimated that 10% of methyl bromide use could be switched to dazomet use at an increased cost of \$1000 to \$1600/ha. The Task Force suggests that this estimate may need to be revisited by assuming declines in yield of around 10% for the first 3-4 years and cost differences for applications that are based on the European studies. In addition to these costs, allowance should be made for the costs of training and education of farmers to adopt the new techniques and the costs of any credit support needed to purchase new capital equipment. Summing these costs would provide an estimate, as per the Multilateral Fund, of the incremental costs for Article 5(1) countries.
- 3.3.1.8 The Task Force has not prepared a revised estimate of the incremental cost for this report; it only pointed out where the existing estimates are reasonable and where they are not. Estimates of the incremental costs of phasing out methyl bromide uses might be addressed in the 1998 Assessment.
- 3.3.1.9 Finally, as a general remark, there is not always an explanation as to why a range of techniques considered for adoption should include some that are high cost options. In those cases where explanations are available, they are provided. Where no explanations are given for the selection of a particular technique, this is pointed out by the Task Force. Dazomet is a relatively expensive option, but if the initial yield effects are as estimated by the Task Force (i.e. around 10%), then it may not be out of line with other techniques. Dazomet is not registered in all developed countries at present.

3.3.2 Dichloropropene¹⁰ (1,3D or Telone) and Chloropicrin

- 3.3.2.1 Telone (1,3-D) is a registered pre-plant fumigation chemical. It is effective against nematodes and suppresses some fungal diseases such as Fusarium and Verticillium wilt. The efficacy of Telone is usually enhanced when mixed with chloropicrin. However, regulatory and trade restrictions could compromise future use of chloropicrin for reasons that have nothing to do with the objectives of the Montreal Protocol.
- 3.3.2.2 The studies reviewed for this alternative (see Table 4) were: cucumbers; eggplants; strawberries; tobacco; tomatoes; and peppers (Spren *et al.* 1995; MBTOC, 1997).

¹⁰ Also referred to as 1,3-D. Telone is a trade name.

3.3.2.3 The studies of the use of these substitutes are from the State of Florida in the USA, USA and Netherlands; Mexico, Costa Rica, Honduras, Morocco, Zimbabwe and Brazil ((Spreen *et al.* 1995; MBTOC, 1997). The main findings are:

- a) The cost differences with respect to methyl bromide generally favours 1,3-D in the Florida studies (Spreen *et al.*, 1995). The USA/Netherlands study (MBTOC, 1997) quotes the cost of chloropicrin as being three times that of methyl bromide. Moreover, all studies reported that some costs will be incurred to modify equipment, although no estimates are provided.
- b) Yields are consistently lower: for 1, 3-D they are 4% less for eggplant, 23% less for tomatoes, 45% less for cucumbers and 18% less for peppers. For strawberries the reductions are less clear. The MBTOC (1997) study cites changes ranging from a reduction of 30% to an increase of 17%. With chloropicrin, the Spreen *et al.*, (1995) study estimates a decline of 25% whereas the MBTOC (1997) study estimates a reduction of only 5-10%.
- c) Consumer prices are estimated to rise in the short run by between 4% (peppers and tomatoes) and 19% (strawberries). While total supply is estimated to decline by 7% to 52% (MBTOC, 1997, Spreen *et al.*, 1995).

3.3.2.4 The Task Force found no reports on the use of this alternative in Article 5(1) countries.

3.3.3 Metam Sodium

3.3.3.1 Metam sodium is a liquid chemical which, when injected in soil, reacts with moisture to liberate methyl isothiocyanate (MITC) which has pesticidal properties as described under dazomet. However, metam sodium requires adequate water/moisture to facilitate its uniform movement and distribution in the soil, which is essential for consistent pest control and efficacy.

3.3.3.2 The studies reviewed for this category were: cut flowers; strawberries; tobacco; tomatoes; nursery vegetables; and peppers. (Spreen *et al.* 1995; Gyldenkaerne *et al.* 1996; Rodriguez-Kabana 1997; CSIRO, 1995; FOE, 1996; MBTOC, 1997).

3.3.3.3 The countries covered are: Colombia (cut flowers), South Africa and USA (strawberries) and Florida (tomatoes and peppers).

3.3.3.4 The main findings from the studies were:

The cost difference estimates with respect to methyl bromide are quite varied. They range from \$1700/ha to +\$800/ha in Colombia for cut flowers, (TEAP, 1995); +\$350/ha for strawberries in South Africa (FOE, 1996), and very small differences in Florida (Spreen *et al.* 1995). The switch to metam sodium

- a) requires changes to equipment, but there is no estimate of the cost of conversion.
- b) The alternative does have a higher risk of crop failure, but this is not quantified.
- c) The impact of switching to metham sodium in terms of yield impacts is varied. Non-US studies cite no yield impact. US studies quote yield effects from 18% to

23% lower than with methyl bromide for tomatoes and peppers (Spreen *et al.* 1995), and 7-30% lower for strawberries (FOE, 1995).

- d) The Florida study (Spreen *et al.* 1995) looks at the substitution of methyl bromide with Telone and metam sodium for tomatoes, cucumbers, peppers and eggplant. Hence, the price and supply impacts cited in 3.5.3 also apply to metam sodium.
- e) Ten percent of methyl bromide in Article 5(1) countries is estimated as being switched to metam sodium (TEAP, 1995), at a cost difference of between - \$1700/ha to +\$800/ha for different crops.

3.3.3.5 The differences in the yields data between the USA studies and the others needs explanation. As with chloropicrin and 1,3-D, it may be that the non-USA studies have not measured yields over a sufficiently long period to allow for a sustainable yield levels to be established. As with these and other products, the price and supply effects are large. In the case of Florida, Spreen *et. al.*, 1995 did not regard, the substitution as feasible. Subsequently, the yield impacts for Florida were re-evaluated to take account of developments since 1994 (VanSickle *et. al.*, 1997) and the revised numbers (see Annex 1) show that these yield loss estimates are now much lower than the 1995 estimates. New technologies and increased knowledge of alternatives to methyl bromide have reduced the impacts to a level that may be acceptable.

3.3.4 Integrated Pest Management¹¹ (IPM)

3.3.4.1 IPM is a systems approach in managing pest problems. The method depends primarily on using resistant varieties, adopting new cultivation practices and judicious use of pesticides. IPM also involves detecting and monitoring pests and beneficial organisms; establishing economically acceptable levels of pest population and selecting least toxic pesticides where biological controls or cultivation techniques cannot control pests. The method offers an effective and environmentally friendly approach to controlling pests and diseases.

3.3.4.2 The studies reviewed for this category were: cut flowers; strawberries; tobacco; tomatoes; nursery vegetables; and perennial crops (Spreen *et. al.*, 1995; FOE, 1996; TEAP, 1995; MBTOC 1997).

¹¹ It should be noted that IPM covers a wide range of techniques, often applied with some chemical products. In this Report practices of crop rotation and fallow with some pest management have been included as IPM. Because of the heterogeneity of techniques comparison across applications is difficult. Also in some cases costs have to be attributed to joint production

- 3.3.4.3 Although there has been considerable discussion of IPM and a large number of studies are cited above, very few of them provided much quantitative analyses. The available data are mainly from Colombia (Banks et al, 1995), Netherlands (CISRO, 1995), Italy (CSIRO, 1995, FOE, 1996), Spain (MBTOC, 1995), USA (MBTOC, 1997) and Zimbabwe (TEAP, 1995). Products are cut flowers (Colombia), strawberry, tobacco seedlings and nursery vegetables (Netherlands, US and Zimbabwe) and tomatoes (Italy)¹².
- 3.3.4.4 The main economic feature of IPM is that the studies give costs that are consistently lower than for methyl bromide. The costs for IPM were \$1900/ha, or 28% less, in the TEAP (1995) study and 67% less in the FOE (1996) study. The CSIRO (1995) study estimated only slightly lower costs per square meter with IPM and one crop, and less than double the cost when IPM is used to get two crops. Yields using methyl bromide and IPM are similar with one crop, but about 75% higher for IPM with two crops. Profitability is also about 75% higher for IPM with two crops, reflecting the more intensive use of fixed equipment. Apart from the CSIRO (1995) study, no impacts are cited for yields although profitability is estimated as being higher in almost all cases.
- 3.3.4.5 The risks of shifting to some IPM systems have been identified in the CSIRO report e.g., the risk of power failure with hydroponic systems in glass houses. There is no other discussion of increased risk with a move to IPM for these products.
- 3.3.4.6 Most production of export cut flowers in Colombia already uses IPM. Transition to IPM is estimated to take 2 years in Zimbabwe for strawberry seedlings (TEAP, 1995). Full commercialisation of IPM for vegetables in North Africa is estimated to take to 2001 according to the same report.
- 3.3.4.7 The attractions of IPM are clear. It is an environmentally friendly method of control, and if it is economically advantageous as well then there is a 'win-win' situation in applying it. The main issues with respect to IPM techniques are: (a) the need for data from further trials to assist development and appraisal of the technique, and (b) a better understanding of the barriers to its adoption.
- 3.3.4.8 The Task Force acknowledged lack of knowledge as possible barriers to the adoption of IPM techniques. Production monitoring costs under IPM are higher, involving equipment, more agricultural workers and training. Access to the requisite knowledge capital is necessary to implement IPM techniques successfully.

3.3.5 Soilless Substrate

- 3.3.5.1 Soilless culture is a method of growing plants on soil-less substrates which provide an anchoring medium that allows nutrients and water to be absorbed by plant roots. These substrates include rock wool, tuff stone, clay granules, foams, glass wool, peat, coconut granules, volcanic stones and pine bark. The introduction of soilless substrate on a large scale requires substantial investment in infrastructure. The methodology of culturing on different kinds of substrates is broadly available, mostly for protected agriculture. It is efficient, performs consistently and increases yields.

¹² The Italian experiment used an IPM system incorporating solarization.

3.3.5.2 The studies reviewed for this category were: cucumbers; strawberries; tobacco seedlings; tomatoes; and peppers. (Gyldenkaerne *et al.* 1996; Rodriguez-Kabana 1997; CSIRO, 1995; FOE, 1996; MBTOC, 1997).

3.3.5.3 The countries covered are: Zimbabwe, South Africa and USA (tobacco); Denmark (tomatoes); Zimbabwe (paprika); USA (strawberries) and “developed countries” (perennial crops) (FOE, 1996).

3.3.5.4 The main findings from the studies were as follows:

- a) the costs of substitution will depend on whether the technique is only used for seedlings, or for the full growing of the crop. Estimates are as follows: \$108/ha in Zimbabwe for tobacco seedlings and \$609/ha in Zimbabwe for paprika seed trays (FOE, 1996);
- b) yield impacts are small or positive in switching to this alternative, and the risks of crop failure are quoted as ‘consistent’ with methyl bromide (MBTOC, 1997); and
- c) the Danish study (Gyldenkaerne *et al.* 1997) for greenhouse grown tomatoes estimates an increase in profitability of \$2-\$3m² and a pay back period for investments in the technology of 1.4 to 4 years.

3.3.5.5 The use of soilless substrate for seed trays can be an attractive alternative for tobacco and some other seedlings, and has been successfully applied in South Africa, the USA and Zimbabwe.

3.3.6 Solarisation

3.3.6.1 Solarisation technology is based on pasteurisation of the soil by means of solar radiation/heat. It is achieved by continuous mulching (broad application) covering the whole field with plastic sheets or by strip mulching whereby each bed is covered separately, thus leaving strips of non-solarised soil in between covered beds. These sheeting techniques correspond closely with those used for methyl bromide, though the plastics may be different. Strip treatment solarisation may increase the chances of reinfestation or recontamination of the treated plots. Thus, although more expensive, continuous mulching is expected to be of higher efficacy than strip mulching. Soil solarisation has a broad spectrum of pest control activity. It is most successful in arid and semi-arid areas with heavier soils and which have intense sunshine, few cloudy days and minimal rainfall, but has been used successfully alone or in combination with other measures under a wide range of conditions.

3.3.6.2 The studies reviewed for this category were: strawberries; tobacco; tomatoes; vegetable nursery, onions; and maize. (Rodriguez-Kabana, 1997; FOE, 1996; Mansour and Sultan, 1991; MBTOC, 1997).

3.3.6.3 The countries covered are as follows: Italy and the US (strawberries) (MBTOC, 1997); Brazil, Israel and the USA (tobacco) (FOE, 1996); Italy (tomatoes) (FOE, 1996); South Africa, Australia, Jordan and USA (nursery vegetables) (EPA, 1995 and MBTOC, 1996); Egypt (onions and maize) (Mansour and Sultan, 1991); and “developed countries” (perennial crops) (TEAP, 1995).

3.3.6.4 The main findings from these studies were:

- a) there is considerable experience from countries with intense sunshine (more than 200 days/year); in general, the results are such that the technique is showing increasing adoption;
- b) studies show lower costs from solarization although with substantial variation. TEAP (TEAP, 1995) presents methyl bromide costs for tobacco seedlings of \$29/ha compared with \$25/ha for solarisation. In Italy, the costs for tobacco seedlings are \$3800/ha for methyl bromide and \$1300 for solarization (CSIRO, 1995). In Chile, the costs are \$3600/ha for methyl bromide and \$4100 for solarization (with dazomet);
- c) for tomatoes, FOE (1995) gives lower costs for solarization of \$2520/ha; and increased profitability of \$2000/ha; and
- d) with other products, the reported costs are consistently favourable to solarization but the range is quite wide. In Jordan, the costs for nursery vegetables were 74% to 86% lower depending on the technique used (black polyethylene versus transparent polyethylene) (Elmore, 1991). Cost differences for onions and maize are not available for Egypt as methyl bromide costs are not given¹³. However, taking typical methyl bromide costs per hectare of around \$6,800/ha (TEAP, 1995), the costs in Egypt for onions/maize/onions rotation (three crops from one parcel of land in one year and a half i.e. three consecutive cropping seasons during 1987-88 (Mansour and Sultan, 1991), and updating and adjusting the data for Egypt to a hectare basis reveals that the cost of solarization is about \$3665/ha., i.e., much lower than the cost methyl bromide;
- e) No yield differences are reported, except for an improved yield in Italy for tomatoes; and no increased risk of crop failure is cited.

3.3.6.5 The use of solarization to replace methyl bromide is attractive in appropriate circumstances. The main issues with regard to its adoption are:

- (a) it is only applicable in areas where the sunshine levels are intense;
- (b) it increases the time required to achieve a full crop cycle by around 6 weeks; and
- (c) as in the case of methyl bromide, there is an environmental problem in disposing of the used plastic sheeting.

¹³ According to Dr Mahmoud E.I. Mansour, a member of the Task Force, methyl bromide is no longer used as soil fumigant in Egypt.

3.3.6.6 The last two problems can be addressed. Part of the profit loss due to the 6 week extension of the crop cycle could be recovered by the lower cost of solarization relative to methyl bromide fumigation. However, in developing countries the increased time interval between costs incurred and payments received may require increased levels of micro credit to those farmers making the switch to solarization. The disposal of plastic sheeting remains a problem. However, new varieties of degradable plastic now offer a feasible option and in other, more difficult, cases a levy on the plastic might be used to fund the collection and proper disposal or recycling of the used plastic. The Task Force also recognised the potential, given the appropriate infrastructure, for using the market value of the used plastic sheeting for recycling purposes to help fund its collection and disposal.

3.3.7 Steam

3.3.7.1 Steam involves injection of water vapour (at between 70 and 80 degrees centigrade) in order to kill soil borne pests and weeds. Effectiveness of treatment depends on soil temperature achieved and the management of the treatment process. Steaming is a well established and effective technique for soil borne pest control and is extensively used for bulk soil or small field treatments within greenhouses and also for some small scale nursery operations.

3.3.7.2 The studies reviewed for this category were for cucumbers; cut flowers, strawberries; tobacco; tomatoes; and vegetable nursery. (Bonte, 1994; Rodriguez-Kabana (1997) ; CSIRO, 1995; FOE, 1996; TEAP, 1995; MBTOC, 1997)

3.3.7.3 The countries covered are Colombia and France for cut flowers; USA for strawberries; Brazil for tobacco; Chile for nursery vegetables; and various developed countries for perennial crops.

The main findings from the studies were:

- a) Steam can be a relatively high cost alternative to methyl bromide. The TEAP (1995) study estimated the additional costs of switching to steam as \$11,700/ha, which represents more than 3 times the cost of methyl bromide. FOE (1995) has similar estimates of the cost differences between methyl bromide and steam. It is currently used in special circumstances, such as where the higher cost is justified by the reduced risk of contamination (e.g. in mother plant beds or where local or national laws prevent methyl bromide use). Up front capital costs can be in the region of \$100,000 per unit of steam generating equipment. Where mobile and energy-efficient steam generating equipment is available, it can help to reduce these costs to the grower;
- b) In general there is no indication that crop yield is lower with steam. The French study (Bonte, 1996) estimates that it is 30% to 50% lower; no other study reviewed by the Task Force suggested yield losses of this magnitude. The Netherlands study estimates a much smaller decline in yield. The US study on strawberries reports that yields will be "lower and variable", although it is not a full field trial.

- c) The French study (Bonte, 1996) estimates, as a consequence of the fall in yields and increased cost that profits will become negative for 50% of growers of cut flowers, with significant loss of income and a loss of around 1700 jobs in the short term. The Task Force noted that these were not replicated in any other study.

3.3.7.4 The Task Force concludes that steam is a relatively high cost option that has specialised uses; for example its strategic, rather than routine, use in Colombia for flower bed fumigation i.e., as part of an IPM system. When used in special applications it can provide a low risk, highly effective, and affordable alternative to methyl bromide.

3.3.8 Reduction of Methyl Bromide Emissions by VIF Tarping

3.3.8.1 The application rates of methyl bromide for soil fumigation are almost always higher than the rate required to compensate for its escape from the soil. Tarping is used to cover the soil so as to reduce the escape of methyl bromide. In most cases, permeable polyethylene tarps have been used for this purpose. However, virtually impermeable tarps (VIF) are now available which allow dosage reductions of 30% to 50% compared to the use of permeable tarps.

3.3.8.2 A review of VIF technology covering tobacco, cut flowers, strawberries and vegetables (TEAP, 1995) describes improved tarping as "good housekeeping" i.e., reducing costs by reducing the application rate of methyl bromide. It has been estimated that use can be reduced by around 30% to 50%. In this way, improved tarping can help countries to reach interim goals for reduction in methyl bromide consumption. Estimates by TEAP (TEAP, 1995) range from a cost saving of \$1400/ha to a cost increase of \$400/ha. Thus, some producers may realise net gains. For those producers that face net losses by using VIF technology, they will have an incentive to consider an earlier switch to methyl bromide alternatives.

3.3.9 Glyphosate

3.3.9.1 Glyphosate ("Roundup") is a broad spectrum herbicide which can effectively control broad leaved weeds and grasses. It is a widely used and commercially accepted herbicide. Where pests are limited to weeds and grasses, glyphosate is an alternative to methyl bromide.

3.3.9.2 The only study examined by the Task Force for this herbicide was for its use in banana production. It reported lower cost, no change in yield and no increased risk of crop failure relative to methyl bromide. However, the use of glyphosate requires a longer period during which the treated land must be out of production. Although this study takes account of the economic cost of leaving productive land idle, this cost could be a practical barrier to the adoption of glyphosate by cash-constrained small farmers. (Rodriguez-Kabana, 1997).

3.3.10 Concluding Comments.

3.3.10.1 The Task Force review of the microeconomic evaluation of the relative economic performance of methyl bromide and alternatives has, by necessity, focused on the results of available reports of field trials, case studies, and other applications of alternative technologies.

3.3.10.2 The studies reviewed by the Task Force tended to give greater emphasis to technical rather than economic aspects of using alternatives. This is not surprising as economic analyses must draw on the results of technical studies and therefore tend to follow rather than lead the publication of technical studies. As a consequence, the economic data are not yet sufficient to clearly establish the economic performance of specific alternatives in a general sense, i.e., across a wide range applications. However, several examples of superior economic outcomes with respect to specific uses of particular alternatives relative to methyl bromide have been presented in this report.

3.3.10.3 While recognising the limitations of the above assessments, the Task Force was able to report particularly favourable economic outcomes for some IPM systems and solarisation relative to methyl bromide use. It should be noted that these alternatives are also likely to score well with respect to economic criteria that could not be covered in this Report i.e., external costs, regulatory costs, and the risk of crop failure.

3.4 Treatment of Post-Harvest Commodities and Structures

3.4.1 Introduction

3.4.1.1 Table 5 below lists the alternatives that have been evaluated and the uses for which they have been considered. As with the use of methyl bromide in soil treatment, the amount of quantitative information is rather limited. Total use of methyl bromide for post harvest treatment accounts for 22% of total world consumption, while 3% of total consumption is for treatment of structures.

3.4.1.2 A substantial proportion of post-harvest use of methyl bromide is likely to be exempt from control under the Protocol under provision for pre-shipment and quarantine use. Though this proportion may vary from country to country, globally it is estimated to be about 19% of use (TEAP Report, 1997). Some countries do have very high levels of use for post-harvest treatment, especially for fumigation of stored commodities which may not be exempt. An example is Peru, where over 85% of use is for this purpose.

3.4.2 Phosphine

3.4.2.1 Phosphine remains the principal alternative to methyl bromide for the disinfestation of durable commodities such as grains, pulses, beans and cheeses. The use of this product is widespread and is usually the material of choice for disinfestation of durables. Many developed countries and developing countries have switched from methyl bromide to phosphine use on stored cereal grain.

- 3.4.2.2 The limited cost data available to the Task Force indicated that phosphine use is more expensive than methyl bromide. However, the prevalence of phosphine use world-wide suggests that these cost data may be representative. These data indicate direct costs of phosphine use as being .21/tonne fumigated/year compared to \$0.75 for methyl bromide. Thus, for a stock of 10 million tons of grain (not untypical for a medium to large country), the additional costs of using phosphine would be around \$4 million a year. There are differences in fixed costs and in losses due to insects compared to methyl bromide. The FoE report (FoE, 1996) cites data for the Philippines which indicate that the additional costs of using phosphine, after taking account of all these factors, to be around \$0.83/tonne for six months storage of milled rice. For some countries, the costs of phosphine use appear to be higher for reasons that are not explained. In Zimbabwe, for example, it is estimated that the direct cost is around three times that of methyl bromide, adding around \$500,000 to the costs of treatment in that country. Furthermore, because phosphine is slower in working, more, or more impermeable, fumigation sheets are needed. The additional costs of these are estimated at \$8.1 million (FOE, 1995). This amounts to \$4.7 more than the cost of methyl bromide for each tonne fumigated. Assuming it applies for one year, it is about 3 times the estimated cost for the Philippines.
- 3.4.2.3 Other issues relevant to the economic evaluation of phosphine are: (a) its longer period of application, and (b) increased fire hazard. It is not clear from existing studies how these factors have been included in the estimates of costs discussed above. TEAP (1995) states that the switch to phosphine can be made within two years in Article 5(1) countries. Some technical assistance in making the transition would be needed but no estimates are available.

3.4.3 Carbon Dioxide

- 3.4.3.1 Carbon dioxide atmospheres of 60% or higher, or atmospheres containing less than 1% of oxygen are effective against all stored product pests. However, longer exposure is required, especially at low temperatures. In general, CO₂ is said to meet quality standards of grain better than methyl bromide or phosphine. In Indonesia, for example, rice stored with CO₂ has a price that is 8% higher than that of rice stored with methyl bromide or phosphine. CO₂ has been used for the fumigation of cereal grains and structures in several countries.
- 3.4.3.2 The cost data for CO₂ indicates that it varies depending on the source of the gas, and on whether recovery methods are used. For structures, TEAP (TEAP, 1995) has estimated methyl bromide costs at \$9 per 1000 cubic feet per year compared with \$10 to \$14 per 1000 cubic feet per year for CO₂. For grains, the costs for 16 months of storage in a sealed enclosure are around \$4.6/tonne with phosphine and \$6.6 with CO₂. However, as noted above, the quality of the grain is better with CO₂ storage. A comparison of direct costs from Malaysia shows that CO₂ is more expensive for shorter periods of storage (4 months) but becomes cheaper for longer periods, and at one year it is around \$2.5/ton for CO₂ compared to \$3.5/ton for phosphine. These figures are not consistent with the Philippines data and no explanation is offered for the difference (FOE, 1996). Other studies of direct costs from Indonesia show that CO₂ has a higher direct cost for periods of up to one year.

- 3.4.3.3 Other issues relevant to the economic evaluation of CO₂ are: (a) costs can be lower if the gas is available from local sources; (b) trials are under way in Germany for recovery of the gas and recycling, although these are still not considered commercially viable.

The use of CO₂ is under trial in Kenya for wheat (vertical silos are fumigated using CO₂ gas from a local geological source); financial data from the trial indicate that CO₂ is about 27% cheaper than phosphine for one treatment per year and about 40% cheaper for a second treatment per year than phosphine (NRI, 1997). CO₂ treatment is in routine large scale use for bags of stored cereal grains in Indonesia. It has been successfully demonstrated in Zimbabwe for the same purpose.

3.4.4 Other Methods of Commodity Fumigation

- 3.4.4.1 Several other methods have been discussed by the MBTOC, although little data are available on the options. These options are as follows.

3.4.4.2 **Ionising radiation** has been used experimentally for the treatment of dried fruit, mainly in the United States. The main issue is that the permitted levels of radiation are too low to achieve full diinfestation, given current storage container size and product density. It is stated by MBTOC that, for developing countries, pilot scale studies would be necessary to determine the cost and efficiency of this method of control. In the US it has been estimated that the costs are significantly higher than for methyl bromide and that the capital investments needed are substantial (around \$4 to \$7 million per facility). The study by Rhodes (Rhodes, 1986) estimated costs of ionisation at \$3 to \$20 per tonne, plus costs of controlled atmosphere of around \$4 to \$5 per tonne. By comparison, the costs of methyl bromide fumigation are around \$0.5 to \$0.9 per tonne. Although the radiation costs may have changed in recent years, one would expect a significant cost differential for this method. Since there are cheaper alternatives, the adoption of this technique will only take place in special circumstances.

3.4.4.3 **Insecticide spray (Fenitrothion, 0.5% or 2% malathion and kerosene)** has been tested in Japan for quarantine treatment of timber and is considered as an alternative to methyl bromide. No information on cost is available.

3.4.4.4 **Use of high temperatures** (c. 60° C) has been used to control or kill pests. It can be used for post-harvest raisins, prunes, dates, walnuts and other dried fruits and nuts and is being increasingly adopted for food processing premises. There have been field trials in the US and Middle East but there are no studies on the costs of heat treatment. In general, it is considered that the method would be expensive, especially when the product is already stored in low temperatures for quality maintenance.

3.4.4.5 **Sulfuryl fluoride** fumigation has been tested for logs and timber fumigation in Japan. It is estimated that about three years are needed to develop the method into a viable procedure in that country and further efforts will be needed to transfer the technique to developing countries. It is considered more expensive than methyl bromide but no cost data are available.

3.4.5 Conclusions on alternatives for commodity and structural fumigation

3.4.5.1 This area of application of methyl bromide has several alternatives in routine use. Prominent among these are heat, phosphine and carbon dioxide. These entail costs of switching and possibly higher costs of treatment. Such cost estimates as are available make it difficult to come up with a firm figure and there are many local factors that could make it lower or higher by a considerable amount.

Table 6 - Alternatives to methyl bromide for commodity and structural fumigation.

Method	Products	Examples of Use, especially Article 5(1) Countries
Phosphine	Grains,pulses,legumes,beans, some cheese	Indonesia, Malaysia, Zimbabwe, Philippines
Carbon Dioxide	Grains, structures	Indonesia, Kenya, Malaysia, Zimbabwe
Insecticide Spray	Timber	Japan
High Temperatures	Dried fruit, food premises	USA, Middle East
Sulfuryl Floride	Logs and timber, domestic premises	Japan

4 RELATIVE ECONOMIC PERFORMANCE OF METHYL BROMIDE AND ALTERNATIVES - A SECTOR APPROACH

4.1 Introduction

- 4.1.1 The budgeting approach used in Section 3 to analyse methyl bromide alternatives is useful for microeconomic analyses of alternative practices relative to methyl bromide. With respect to soil fumigation, it evaluates the impact on total production costs and crop yields to provide estimates of changes in the unit cost of production arising from switching to alternatives. However, the budgeting approach cannot provide estimates of impacts on prices and competitiveness which are essential to determining the effects on consumers and producers as well as on the overall economic performance of the sector in question.
- 4.1.2. A framework for evaluating the overall impact of alternative production practices on the performance of the sector in question can be developed by a sector approach based on the economic concept of a partial equilibrium model that can be quantified to produce estimates of impacts on the producers and consumers participating in a given market. This quantitative framework can be used to estimate the expected impacts that changes in production practices may have on producer prices, the allocation of production across participating geographical areas and also for consumer prices and product availability by geographical area. The value of this approach is that it can be used to estimate the quantitative impacts on producers, consumers, products and areas, respectively, that are central to the process of determining public policy.

4.2 Conceptual Framework

- 4.2.1 Partial equilibrium analyses allow policy analysts to focus on a specific sector without having to model the entire economy. This analytical construct is appropriate where changes in the performance of the sector in question does not materially change the performance of the economy as a whole and, thereby, does not generate significant changes in the overall market demand for the products in question.
- 4.2.2 The empirical use of this approach requires the quantitative modelling of the sector by specifying demand and supply relationships for a set of interrelated products and then estimating the effects of imposed changes in these relationships within the model. As the objective of this exercise is to estimate the effects of these imposed changes on the economic well-being of producers and consumers which will be determined by their responses to imposed change, a mathematical programming model can be used to determine expected behaviour and its economic consequences.

- 4.2.3 The objective function of the programming model is usually specified to maximise the total net revenue of the producers. It is assumed that growers decide on which crops and cropping systems to use in accordance with their objective to maximise total net revenue. Total net returns to growers are defined as total gross returns less the cost of growing, harvesting and marketing the products in question. The critical components of the model are (1) the specification of the demand structure for the crops in question, (2) identification of the production systems used by growers in each area, (3) the pre-harvest costs of these production systems, (4) the post-harvest and marketing costs for these products, and (5) the yield of each crop from each production system in each producing area.
- 4.2.4 This model determines the acres used by each production system in each producing area, the total production of each crop in each producing region, the volume of each crop sold in each geographical area, and the consumer price of each product in each geographical area participating in the consumer markets associated with the sector in question.
- 4.2.5 Estimates of the impacts of imposed changes within the sector (e.g., replacing methyl bromide with best available alternatives) are determined by first solving the model using the model parameters which represent the sector prior to change. These parameters are then changed to reflect the changes in the production systems occurring within the sector; and then the model is solved a second time. The results of the second solution are compared with the results of the first solution to determine the impacts of the changes in the production systems imposed on the sector. This methodology provides a snapshot of sector performance before and after the imposed changes in the production systems of the sector, but does not provide information regarding the transition path from the first to the second solution of the model.

4.3 North American Model

- 4.3.1 A model of the North American market for fresh vegetables was developed to estimate the impacts of using alternatives to methyl bromide for soil fumigation purposes in the context of technology and information available in 1994 (Spren et al. 1995). Production of vegetables in the North American market of Canada, USA and Mexico accounts for more than 90% of the vegetables consumed in this market in the winter season of November through May. Soil fumigation accounts for nearly 80% of the use of methyl bromide and producers in the North American winter fresh vegetable market account for more than 20% of global methyl bromide use for soil fumigation.
- 4.3.2 The model was specified to include supply and demand relationships for tomatoes, peppers, eggplant, cucumbers, squash, watermelon and strawberries. The results suggested that shifts to technologies and practices available in 1994 would result in a 61.4% decline in the production of winter fresh tomatoes by USA growers. The results also predicted strawberry production in the USA would decline 51.9% and that eggplant production would cease altogether in the USA. The model demonstrated the importance of competitive relationships in determining the impact of using alternatives to methyl bromide. Mexico uses very little methyl bromide at present because of its large base of available land, local non-methyl bromide using practices and the opportunity to use crop rotation systems for control of pests. Regulatory restrictions on land use and on water availability make crop rotation practices much less available in most of the winter fresh vegetable growing areas of the USA. These restrictions increase the cost of production and decrease yields for USA growers. A switch to using a combination of chemical alternatives and IPM practices for USA growers could significantly alter competitive relationships in the international market; Spren et al. (1995) expected that alternatives

to methyl bromide would impose significant costs on USA producers to the benefit of those producers in Mexico who do not use methyl bromide.

- 4.3.3 Using 1994 data and estimates of costs of alternatives, the model predicted that consumers in the North American market would also bear some of the costs associated with a switch to methyl bromide alternatives. The amounts of produce made available from these producing areas was estimated to decline from 1.5% for squash to 51.9% for strawberries. Wholesale prices were estimated to increase for all products, except squash, with the largest increase being for strawberries at 18.5%. Certainly, those results predicted that costs would be significant for consumers and producers and that USA producers would bear the largest amount of the costs imposed on producers.
- 4.3.4 Subsequently, that model was updated to include technology and knowledge known to exist as of February, 1997 (Annex 1). Research programmes throughout the world have increased the knowledge available on alternatives to methyl bromide and helped to reduce the cost of using currently available technologies. Two scenarios were estimated, one with marginal improvements in the technology so that medium impacts on yield were imposed with the use of alternatives to methyl bromide, and a second scenario where reduced impacts on yields were imposed. The results indicate that costs predicted to be borne by producers in the USA with use of new technologies would be significantly less, with production of tomatoes in the USA expected to decline only 21.8% if the lower yield impact estimates are used for USA growers, significantly below the 61.4% loss of USA production estimated with data available in 1994.
- 4.3.5 Costs to be borne by consumers are also expected to be considerably less, with no expected change in the availability of tomatoes and only a 9.9% decline in the availability of watermelons. These estimates compare to declines of 7.2% for tomatoes and 40.0% for watermelons using data that was available in 1994. The availability of strawberries in the North American market is estimated to decline by only 7.2% using technologies known to exist in 1997, compared to 51.9% in 1994.
- 4.3.6 These results predict some costs, but those costs are estimated to be less severe than those predicted in 1995 using cost and yield impact data available in 1994. The lesson is that there is a learning curve associated with changes in the production practices associated with new technologies. This learning curve is dependent on the time required to develop new technologies and on the adjustments required of growers in using those technologies. The 1997 re-run of this model indicates that USA growers are into the learning curve for adoption of new technologies that are substantially reducing the costs (if any) of switching to methyl bromide alternatives. Furthermore, new technologies are being modified and developed that are raising yields and reducing production costs. Experience with other products (e.g., CFCs) indicates that the cost of changing to alternative practices can be reduced to similar levels to that of the ODS-using technology, and in certain cases can be even lower allowing cost savings to be realised. The time required to develop and implement alternatives that achieve “a seamless transition” (where technology and market forces motivate the change to alternatives to methyl bromide) cannot be predicted.

4.4 European Union and North African Model

- 4.4.1 The quantitative modelling approach used for the North American market could be used to develop similar analyses for groups of countries with similarly inter-related markets where methyl bromide use is significant. The countries of western Europe and North Africa appear to be candidates for such an effort. ¹⁴ Southern European countries use substantial quantities of methyl bromide for soil fumigation supporting production of strawberries, tomatoes, melons, peppers, cucumbers, and cut flowers. North African countries, notably Morocco, are actual or potential competitors in western European markets for these crops.
- 4.4.2 Three studies for Greece (Bonte, 1995), Spain (Bonte, 1995), and France (Bonte, 1994) used data on per hectare yield and cost effects of switching out of methyl bromide to estimate the economic implications for consumers and producers at the national level as well the effects on jobs and the trade balance. These models used scenarios to estimate national impacts on the production of selected crops, prices, consumer and producer welfare, and direct short-run employment effects. Some scenarios include trade effects, however, estimates were not made of impacts on those economies gaining market share, that is, the competing suppliers using methyl bromide.
- 4.4.3 These studies predicted that without methyl bromide for soil fumigation there is likely to be significant displacement of production from growers in the countries studied to other suppliers e.g., through imports. These results are similar to those reported in the 1995 study of the North American market (Spreen et.al., 1995).and they can be expected to show similar improvements in the relative status of alternatives, if run with more recent data. The findings from the country studies for France, Spain and Greece on the economic performance of farms producing fresh fruits and vegetables assuming (1) a ban on methyl bromide use without alternatives; (2) a ban on methyl bromide use allowing for switches to currently available alternatives; and (3) a 25% cut in the use of methyl bromide by applying improved tarping technology.
- 4.4.4 These country studies address both the short term and medium term effects on the economic performance of producers, employment and on the trade balance. The models allow for the changes in crop yields and production costs resulting from changes in production systems, as well as for the price elasticity of demand for the products concerned. The available alternatives and their estimated respective effects on yields and production costs were assumed to be unchanged over time, and no allowance was made for the possibility of the substitution effect of market price rises on the purchasing decisions of consumers i.e., consumers react to higher prices only by reducing purchases of the products in accordance with the price elasticity of demand. Furthermore, the supply elasticity of imports nor their countries of origin are addressed in these studies.

¹⁴ Professor Luis V. Barcelo, a member of the Task Force, informed the Task Force that the European Commission has commissioned a three-year research project on the economic viability of methyl bromide alternatives to be undertaken by a team of experts from various Member States of the European Union.

- 4.4.5 The models used in these country studies have the advantages of simplicity and modest data requirements compared with the North American model. However, they are capable of throw light on the economic effects of imposing control schedules on the use of methyl bromide in the fresh fruit and vegetable market. However, the results remain highly dependent, as does the North American model, on the availability of acceptable technical data on production costs and yields associated with changes in production systems. It is also important that these data should allow for changes over time as the respective efficiencies of applying existing alternatives improve with experience and improved techniques. These dynamic aspects of the switch to methyl bromide alternatives are especially important for analyses of the medium term and beyond.
- 4.4.6 In their currently specified form, the Bonte models generate substantial economic costs for a methyl bromide ban in terms of (1) the number of hectares taken out of production, (2) job losses, (3) losses in consumer and producer surpluses and (4) deterioration in trade balances. Consumers lose more in the short term through higher prices, whereas producers lose more in the medium term as product sourcing shifts to imports as domestic production falls with resulting job losses. These costs are at their highest for a ban without alternatives and lowest for the 25% cut in methyl bromide use by improved tarping. These results are broadly similar to the 1995 results for the North American model.
- 4.4.7 Unfortunately, the Bonte models have not been updated for technical advances in methyl bromide alternatives since 1994, nor do they contain any dynamic aspects of the process of technical substitution. In particular, there are no results to compare with the February 1997 results for the North American model. As with the North American model, it is highly likely that technical progress on methyl bromide alternatives since 1994 would substantially reduce the estimated yield losses and production costs increases leading to much lower estimates of the economic costs to producers and consumers, and much lower effects on jobs and trade balances.

4.5 Concluding Comments

- 4.5.1 Sector models are well established tools within the science of economics. However, sector models can involve significant data demands and require an empirical understanding of the structure and conduct of relevant markets. Because of the degree of aggregation used in sector models, they are more likely to give consistent results than the budget approach case studies. The sensitivity of the sector model results to the specified parameters and assumptions is generally transparent. Annex I suggests how sector models might be used to inform discussion on the application of the concept of acceptable cost, as presented in paragraph 2.1 above, to the performance of methyl bromide alternatives.

- 4.5.2 Whilst the budgeting approach is relevant to decisions facing individual producers, the sector approach provides insight into the issues of the economic performance and political acceptability of the economic costs associated with switching to methyl bromide alternatives.

5 OVERALL CONCLUSIONS ON ECONOMIC VIABILITY

5.1 Conclusions

- 5.1.1 **Information and Analysis.** The Task Force used all the information resources available to it to respond to Decision VII/8, including the 1997 MBTOC Report to TEAP. The Task Force drew on a wide range of documents, the expertise of MBTOC members, the application of economic theory, and the collective professional experience and judgement of its members. The Task Force commented on the relative economic performance of specific alternatives to methyl bromide in soil fumigation uses and fumigation of durable commodities and structures, and examined quantitative sectoral models used to estimate the wider economic impacts of switching to methyl bromide alternatives. These efforts led the Task Force to the following overall conclusions.
- 5.1.2 **Soil Fumigation.** The Task Force focused on the economics of methyl bromide alternatives for soil fumigation. Soil fumigation is the largest use of methyl bromide and it is on this use that much of the research is focused. Furthermore, the growth in world consumption of methyl bromide is concentrated in soil fumigation. Quantities of methyl bromide used in post-harvest treatment and for treatment of structures are much smaller, but still have large economic value. Quarantine and pre-shipment uses are exempt from the control schedules of the Protocol.
- 5.1.3 **Dangers of Generalisation.** The costs of alternatives and methyl bromide will differ by crop, over time, and by location. Therefore, one must be careful not to generalise about the economic superiority of specific chemical alternative, or between chemical and non-chemical technologies.
- 5.1.4 **Progress with Alternatives.** Where alternatives have been adopted, users have become more efficient as they develop expertise. This learning process is typical when different technologies are introduced. In the case of crop production, yield outcomes become more favourable over time. There are two broad reasons for this improvement in the performance of alternatives. First, the technologies themselves improve. That is, incremental improvements take place in aspects such as materials, equipment, and application rates (in the case of chemicals). Second, the human agents utilising the alternatives become more knowledgeable and skilful over time. For example, they may better determine the optimal timing for certain tasks or become more adept at operating new equipment. Over time, these advances have narrowed yield gaps between alternatives and methyl bromide, and there are examples where yield exceeds that with methyl bromide use.
- 5.1.5 **Technology Transfer.** The Task Force considered the potential for technology transfer between countries. Some technologies appear to be readily transferable, while others are constrained by factors such as climate (e.g. solarization), regulation (e.g., pesticide registration requirements), and the knowledge and skills of the people (e.g., IPM systems). Efforts to enhance human capital could facilitate the transfer and adoption of alternatives. Alternatives are being developed in many places with transfer coming from both developed and developing countries.

- 5.1.6 **Sector Analyses.** The sectoral analyses highlight the dynamic nature of agricultural production and trade. Sectoral models can provide insight into marketing and distributional effects which case studies and a budget analysis approach cannot. Clearly, existing patterns of production and trade depend, in part, on the price and availability of methyl bromide. The phase out of methyl bromide and the suitability of alternatives in conjunction with market forces and trade policies can change the locations of where specific crops are produced, trade patterns, and the market prices faced by consumers. Little empirical work exists on the primary and secondary effects of these changes. Yet, they are of critical importance in determining economic costs of phasing out methyl bromide.
- 5.1.7 **External Costs.** External costs, which include environmental and human health effects, were addressed in several studies. As noted in Section 2, circumstances have not permitted the Task Forces to review and compare external costs associated with alternatives. However, the Task Force emphasised that external costs are important and that estimation of their magnitude and who bears these costs is needed if societies are to make well-informed decisions on alternatives to methyl bromide.
- 5.1.8 **Technical Data.** On reviewing available information, the Task Force concluded that the technical and other information resources required for a more comprehensive and rigorous assessments of the relative economic performance of methyl bromide alternatives were not yet available for specific situations for many methyl bromide alternatives, whilst recognising that the ongoing work of many institutions is already making good progress in generating the necessary skills, technical data and other information required for further work.
- 5.1.9 **Production Systems.** Whilst most of the work undertaken in this assessment addressed the relative economic performance of specific methyl bromide alternatives, the Task Force recognised the advantage of adopting an approach based on identifiable production systems possibly involving combinations of specific alternatives and techniques that might be used if further work on the economic viability of alternatives were to be requested.

6 PRIORITIES FOR FURTHER WORK

This section records the views of the Task Force on their suggested priorities for further work on the relative economic performance of alternatives and methyl bromide.

- 6.1 Technical Data on Agricultural Production Systems.** Economic assessments of alternatives to methyl bromide depend on the availability of adequate technical data and information on technically feasible alternatives. Such information is generated by the experimental work of agricultural production scientists, preferably in collaboration with economists. The required data includes estimates of changes in crop yields, production costs, and the risks of crop failure for specific agricultural production systems as they are applied in specific locations. The information should also include data on inputs of financial and human capital, and other input costs required to ensure the effective implementation of specific alternatives. It is the view of the Task Force that technical data on human capital inputs as applied to specific IPM systems, whether or not they are chemical-free, is of particular importance.
- 6.2 External Costs.** Assessments of methyl bromide itself and of alternatives to methyl bromide should include information on those economic costs to society that are not captured by market determined costs but which are generated by agricultural production and marketing activities. Such non-market costs include the effects of chemical toxicity on human health whether acting indirectly through emissions to atmosphere (whether stratospheric in the case of ozone depletion or ground-level) or through the leaching of chemicals through the soil to contaminate water supplies. These non-market costs, classified as externalities in economic analysis, are an essential part of economic assessments of alternatives and of methyl bromide. This may require the valuation of relevant externalities in monetary terms. The Task Force decided not to address the issue of external costs in this Report due to time and resource constraints. However, it is the view of the Task Force that further work on the external costs of alternatives and of methyl bromide is of importance.
- 6.3 Quantitative Estimation of the Economic Costs of Phasing Out Methyl Bromide.** It is the view of the Task Force that the application of quantitative economic modelling to assessments of the relative economic performance of alternatives and methyl bromide is both important and practicable. In the report of the Task Force, the applications of the North American model of the fresh vegetable market involving Mexico, the USA and Canada demonstrated the value of this approach. Furthermore, it is the view of the Task Force that the conceptual framework and the empirical implementation of the quantitative economic model demonstrates the potential for developing further applications of such models to improve both (1) the assessment of the relative economic performance of alternatives and (2) estimates of costs to the Multilateral Fund of phasing out methyl bromide in Article 5(1) countries. Further application of this approach to assessments of the relative economic performance of alternatives to individual countries or to groups of countries with interdependent markets in products that currently use methyl bromide in their agricultural production systems is feasible.

ANNEX I

ECONOMIC VIABILITY OF ALTERNATIVES TO METHYL BROMIDE FOR SOIL FUMIGATION - AN ANALYSIS OF THE NORTH AMERICAN WINTER FRESH VEGETABLE MARKET

Soil fumigation accounts for nearly 80% of the world-wide use of methyl bromide according to figures collected by UNEP (1995). Tomatoes and strawberries account for more than half of that use with 35% and 20% of all soil fumigation applied on tomato and strawberry production, respectively.

The USA accounted for 22,716 metric tons of the global total of 50,913 tons of methyl bromide used for soil fumigation purposes in 1992 (UNEP, 1995). The crops of tomatoes, strawberries, peppers, cucurbits and eggplant accounted for 10,264 tons used for soil fumigation purposes in the USA. Growers of these crops have used methyl bromide for nearly 30 years and have yet to embrace any alternative as an economically viable replacement.

Spreen, et al. (1995) completed a study that analysed the impact of phasing out the use of methyl bromide in the winter fresh vegetable industry of North America. The analysis involved identifying next best alternatives to methyl bromide and then estimating their impact on costs of production and yield in the context of technology and knowledge available in 1994. These data were then used in a partial equilibrium economic model to determine the impacts that a switch to these alternative practices would have on the North American fresh vegetable industry.

The objective of the analysis was to quantify the economic impact from a change in the production system to an alternative that did not use methyl bromide. The important considerations included in the model were the following.

1. All crops of the production system where methyl bromide impacts their economic outcome are included. Critical to this evaluation are the impacts on the primary crop that uses methyl bromide and on any following crops whose economic outcome is dependent on methyl bromide being applied to the first crop.
2. Seasonality of production and demand were accounted for by developing a monthly model of production and demand for each crop.
3. Regional production and demand of products grown using methyl bromide before switching to alternative production systems were accounted for by specifying production systems in the major producing areas for these crops and demand models for each of the major consuming areas.

A mathematical model of the North American winter fresh vegetable market was developed to estimate the impact a phase out of methyl bromide would have on producers of these crops in the North American market. The model was specified as a spatial equilibrium model that separated production by area and demand by region within the market area. Vegetables included in that study were tomatoes, bell peppers, strawberries and eggplant. Other crops included in the model were squash, cucumbers and watermelons grown as second crops in double cropping production systems that utilise inputs from a first crop that included methyl bromide. Production areas included in the study were the States of Florida, California and Texas from the USA and the State of Sinaloa in Mexico. These areas provide more than 90% of the supply going to North American markets for these crops in the winter season from November to May. The months included in the model were November through May for tomatoes, peppers, eggplant, cucumbers

and squash. Strawberries were included for the months of December through March and watermelons were considered for May. Areas devoted to producing these crops in the winter season of 1992/93 are shown in table 1.

Table 1 - Planted acres of land devoted to production of selected vegetable crops in the North American winter market, 1992/93.¹⁵

Crop	Area	Acres
Tomatoes	Florida	48,400
	Mexico	55,068
Strawberries	Florida	5,100
	California	7,608
Cucumbers	Florida	15,800
	Mexico	13,720
Peppers	Florida	21,100
	Texas	5,865
	Mexico	12,236
Eggplant	Florida	2,150
	Mexico	1,916
Squash	Florida	9,245
	Mexico	14,491
Watermelon	Florida	42,000

Acres of USA land devoted to these crops in the winter season and their comparison to the total acres of production in the USA which are treated with methyl bromide are contained in table 2. These data indicate the importance of this market in the use of methyl bromide in the USA. Land devoted to these crops in the winter season account for more than 90% of the total land in the USA using methyl bromide in 1992. Total methyl bromide used in the USA on land devoted to these crops was estimated to be 10,264 metric tons in 1992¹⁶, or 45% of the total methyl bromide used for soil fumigation purposes in the USA in 1992. The larger impact on growers from a switch to alternatives to methyl bromide will be felt by growers of these crops in these areas.

††††¹⁵Source: Spreen et al. (1995)

¹⁶Total methyl bromide used on these crops was estimated by weighting the total methyl bromide used on each crop in the USA as estimated by UNEP (1995) by the proportion of this crop grown in the winter season. Areas with more than 100% of the area were given the total estimate of methyl bromide used on that crop.

Table 2 - Planted acres of US A land devoted to producing crops with methyl bromide in the winter market and their comparison to planted acres in the annual USA market.¹⁷

<u>Crop</u>	Winter U.S. Total	Annual U.S. Total	Winter acreage as % of U.S. Annual
Tomatoes	48,400	55,021	88.0%
Strawberries	12,708	33,717	37.7%
Peppers	26,965	22,960	117.4%
Cucumbers	15,800	5,300	298.1%
Eggplant	2,150	2,000	107.5%
Total	115,935	118,998	97.4%

Mathematical Model of the North American Fresh Vegetable Market

The Spreen et al. model was developed to account for regional demand in the North American market and the cost of growing and marketing these crops from the major producing areas of the USA and Mexico . The objective function for the model was to maximise the net returns to growers. It is assumed that growers make decisions on which crops and cropping systems to use and that their decisions are driven by their objective to maximise total net revenues . Total net revenues are the total returns realised by growers for crops included in the analysis less growing, harvesting, post harvest and marketing costs.

Total returns were specified as the total revenues received by growers of these crops, such that total returns equals the sum of the products of average price received for each product in each market and total volume of the product sold in each market . The price received is determined by the demand structure of the products in question . Demand is typically specified as a quantity dependent function where the amount of product demanded is determined by the price of product supplied, prices for alternative products, the income of the economy where the product is consumed and other factors that can influence demand (e.g., quality attributes) . An inverse demand structure specifies the demand relationship as the price of the products of interest being a function of quantities rather than quantities being a function of prices . Using the inverse demand approach, total returns can be specified as the sum of revenues received for each crop from each producing area in each market:

$$1) \quad TR = \sum_{ijk} [P_{ik} * Q_{ijk}]^{18}$$

where TR is total revenues for the set of products sold, P_{ijk} is the average price received for product i sold in consuming market k and Q_{ijk} is the total volume of product i sold in consuming market k from producing region j. P_{ik} is determined by the structure of the demand system such that

$$2) \quad P_{ik} = f(Q_{ik}, Q_{ak}, I, X)$$

¹⁷Some crops show more than 100% for two reasons. First, several acres of many crops are planted as second crops following the production of a first primary crop but were not recorded as using methyl bromide even though the second crop benefits from the methyl bromide applied to the first crop. A second reason that the total may be more than 100% is that some acres of these crops have not been treated with methyl bromide.

¹⁸The notation of \sum_{ijk} is used to represent the summation of the terms inside the following brackets across the i, j and k subscripts. This notation structure is followed throughout this text.

where the price of product i in consuming market k is a function of the total quantity of product i supplied in market k , quantity of alternative products supplied (Q_{ak}), income (I) and a set of exogenous factors (X) that influence demand. The exogenous factors would include any measure of quality that may influence the demand for the product.

The cost of growing the products is driven by the pre-harvest cost of each production system that produces the crops in question and the post harvest and marketing costs. Pre-harvest costs are dependent on the production system used to produce the crop. Production systems include all crops that are produced on each unit of land that shares inputs that impact the success of the enterprise. It is not uncommon for double cropping to occur on land where inputs from the first crop are used to successfully produce a second crop. Methyl bromide has been a chemical used to ensure the productivity of land for growing second crops. As such, production of the second crop has been dependent on inputs used in the production of the first crop, i.e., the production system must account for all costs of growing both crops and the output is the total of all production from both crops.

An example of a production system with multiple crops would be a first crop of tomatoes followed by a second crop of cucumbers that are dependent on the condition of the land after the tomato harvest has been completed. Given suitable land conditions, the second crop of cucumbers will use inputs remaining from the production of tomatoes. The economic returns of the enterprise may therefore be dependent on the successful use of the double cropping production system. As such, a single crop of tomatoes is treated as a different activity than a double crop of tomatoes followed by cucumbers.

The pre-harvest costs are the sum of the pre-harvest cost per acre of each production system multiplied by the number of acres committed to each production system in each area, i.e.,

$$3) \quad PRH = \sum_j [PRC_{aj} * A_{aj}]$$

where PRH is the total pre-harvest cost for producing the crops in the sector, PRC_{aj} is the per acre pre-harvest cost of producing one acre of production system a in region j and A_{aj} is the total acres of production system a produced in producing region j .

The total harvest and post harvest costs are the sum of the products of the per unit harvest and post harvest costs multiplied by the total number of units produced, i.e.,

$$4) \quad PH = \sum_{ij} [PH_{ij} * Q_{ij}]$$

where PH is the total of all harvest and post harvest costs of producing all crops, PH_{ij} is the per unit harvest and post harvest cost of producing product i in producing region j and Q_{ij} is the total units of product i produced in region j .

The total marketing costs are the sum of the products of the amount of product sold from each producing region to each consuming area in the market multiplied by the per unit cost of marketing and shipping the product from the producing area to the consuming market, i.e.,

$$5) \quad MC = \sum_{ijk} [MC_{ijk} * Q_{ijk}]$$

where MC is the total of all marketing costs, MC_{ijk} is the per unit cost of marketing product i from producing area j to consuming market k and Q_{ijk} is the amount of product i produced in region j sold in consuming market k .

The model is closed by first specifying that total production of each product in each producing area is equal to the sum of the products of yield of each product from each production system in each producing area and acres of each production system in each area, i.e.,

$$6) \quad Q_{ij} = \sum_a [YLD_{ija} * A_{aj}]$$

where YLD_{ija} is the yield per acre of product i in the producing region j using cropping system a and where Q_{ij} and A_a are as defined before.

Finally, the total amount of production sold to the consuming markets must be equal to the total production in each producing area, i.e.,

$$7) \quad Q_{ij} = \sum_k [Q_{ijk}]$$

The objective function for this model is to maximise the net returns to producers, i.e.,

$$8) \quad \text{Maximise } NR = TR - PRC - PHC - MC$$

subject to the constraints for yield (equation 6) and allocation of production across consuming markets (equation 7), where NR is the net revenues received by growers of these crops and the other variables are as defined before. The decision variables in this model used to maximise net returns are the acres of each production system produced by growers in each of the producing areas (A_{aj}).

The data requirements to solve this model are the parameters of the inverse demand equation, the per acre cost of producing each acre of each production system (PRC_{aj}), the per unit harvest and post harvest cost of each product grown in each production area (PH_{ij}), the cost of marketing each unit of production from each producing area to each consuming market (MC_{ijk}) and the expected yield of each product from each production system in each production area (YLD_{ija}).

The results of the model with the prescribed parameters determine the optimum number of acres of each production system in each producing area. Other data provided in the results are the production of each product in each production area, the amount of product sold from each producing area to each consuming market and the price of each product in each consuming market.

The impact of any change in the sector can be estimated by changing the parameters associated with that change and then re-estimating the model. The impact of the change in the sector is the difference in the results of the base model before the change and the results in the model after the parameters have been changed.

The effects of changing production systems to use alternatives to methyl bromide are assumed to be changes in the pre-harvest costs of production for each production system in each production area (PRC_{aj}) and the yields of each product in each production area for each production system (YLD_{ija}). Estimates of these parameters are required to estimate the effects of changing to alternative practices.

The North American market model used by Spreen et al. was specified with 4 separate demand regions whose central delivery points were New York City, Chicago, Atlanta and Los Angeles. Inverse demand equations were estimated for each product in each consuming market. The demand flexibilities derived from these estimations provided the demand parameters used in the mathematical model of the North American vegetable market.

Pre-harvest and post harvest production costs were estimated for each production system within each production area. The State of Florida in the USA uses several double cropping systems that produce a primary crop and then uses inputs from the primary crop to grow a second crop on the same unit of land. These cropping systems are listed in table 4 with the resulting yield impacts that were estimated by production scientists (those involved in the search for alternatives to methyl bromide) to occur if methyl bromide were removed and growers were forced to use alternatives that had the least impact on yield and cost of production. The production systems in Mexico are not listed because they grow primarily single crops that currently do not rely on methyl bromide in their production process.

The analysis of the impact that a phase out of methyl bromide would have on the North American market was conducted in two parts. First, the model was solved with parameters that assumed the continued use of methyl bromide. This solution provided the baseline for comparison to a second solution that provided results with parameters changed to reflect changes in the cost of production and yield when the next best alternatives to methyl bromide are used. The yield and cost parameters used for the alternatives were estimated in 1994 by production scientists involved in research programmes evaluating alternatives to methyl bromide.

The results of that analysis indicate that use of alternatives to methyl bromide in the context of the technology and knowledge available in 1994 would have devastating impacts on the North American fresh vegetable market. Table 3 lists the results of the analysis that indicates produce availability in the North American winter market would decline from 1.5% for squash to 51.9% for strawberries. Prices paid by consumers would increase across all markets, with average increases ranging from 0.9% for squash to 18.5% for strawberries.

The results also indicate that the dynamics of the market would change significantly. Production in Florida would decline for all crops but squash with a total loss of all eggplant production. Production of tomatoes, strawberries and peppers would all decrease by more than 60% in Florida while cucumbers and watermelon would decline by more than 40%. California also becomes a net loser when considering a phase out of the use of methyl bromide. Production of strawberries in California in the winter market declines 42.9%. Because Texas does not use methyl bromide in the production of winter bell peppers, production of bell peppers increased 143.1% in Texas. The biggest winner in the winter market would be Mexico however, with increased production of all crops but squash. Increases in production ranged from 7.4% for cucumbers to 123.2% for eggplant. Mexico does not use significant quantities of methyl bromide because of the large amount of land they have available for crop rotation. The phasing out of methyl bromide changes the competitive nature of the market, benefiting those who rely less on methyl bromide and having significant consequences for those whose costs and yields are more influenced by a phasing out of methyl bromide use.

Table 3 - The effect on the North American market from a ban on the use of methyl bromide.

Crop	Consumption		Production			
	Volume	Price	Florida	California	Texas	Mexico
	% of Change					
Tomatoes	(7.2)	3.8	(61.4)			82.7
Strawberries	(51.9)	18.5	(68.7)	(42.7)		
Cucumbers	(20.6)	8.1	(46.4)			7.4
Peppers	(8.7)	4.0	(63.5)		143.1	54.4
Eggplant	(15.9)	8.4	(100.0)			123.2
Squash	(1.5)	0.9	4.8			(6.6)
Watermelon	(40.0)	11.2	(40.0)			

Note: Figures in parentheses represent declines.

Source: Spreen et al., 1995

A third step in the analysis has been completed to update the information related to costs and yield to reflect improvements in technology and knowledge gained since the 1995 analysis was performed. Research at various institutions has resulted in the development of alternatives to methyl bromide that results in smaller impacts on yields for these crops. The parameters of the model using alternatives to methyl bromide were changed to reflect these improved technologies and the information gained from various research trials since the original study was completed. The yield parameters used in this analysis are contained in tables 4 and 5. The parameters for yields were adjusted to reflect a low impact on yield (table 4) and then a medium impact on yield (table 5). The model was then re-estimated to measure the potential impact that alternatives to methyl bromide would have given the improved technologies identified in 1997.

The results of this third step analysis are contained in tables 6 and 7. The results show that improvements in technology and knowledge since methyl bromide was listed by the Montreal Protocol have reduced the predicted impact on consumers and producers significantly. The results in scenario 2 (table 7) show that marginal improvements in technology (medium impact) with reduced impacts on yields lowers the loss in produce available to consumers and the increase in wholesale prices, as compared to the original results shown in table 3. It also reduces the shift in production across regions. If optimistic results from scientific trials are to be accepted and yield impacts are low (table 4), then impacts on consumers will be significantly smaller, with produce availability never reducing more than 9.9% and wholesale prices never increase more than 3.3%. Florida still loses market share to Mexico in this scenario because no impact on yield is felt by Mexican producers, but the loss in market share is not nearly as dramatic as that estimated by Spreen et al.(1995), and all areas remain strong competitors in the market. California actually increases production of strawberries when reduced impacts on yield are considered.

These results are significant in demonstrating the returns that USA producers are realising from the intensive research program mes that have been committed to finding alternatives to methyl bromide. These results indicate that the impact from phasing out methyl bromide use would not be seamless (i.e., impacts on consumers and producers are still significant) if technology improvements do not continue, but the gains realised from research program mes over the last 3 years have been significant and will greatly reduce the impact on consumers and producers from those estimated impacts that were published by Spreen et al. in 1995 before the advances in new technology which have followed the listing of methyl bromide as a controlled substance under the Montreal Protocol in 1992 as part of the Copenhagen Amendment.

Conclusions

Estimation of economic viability for alternatives that are currently available for methyl bromide can be done using proper modelling techniques . Experience in estimating the economic impacts of alternatives to methyl bromide in the North American market indicate that use of currently available alternatives is expected to have significant impacts on consumers and producers . It is important to note however, that the magnitude of predicted impacts have been significantly reduced because of the large investments made to improve the technology available to growers for replacing methyl bromide . The results indicate that producers are making progress in finding economically viable alternatives to methyl bromide.

Table 4 - Per acre yields of crops by cropping system and production area using alternatives to methyl bromide with low impacts on yield, scenario 1.

Crop/cropping system	Florida				California
	Dade County	Palm Beach	West Central	Southwest	
Tomato/single (25 pound cartons/acre)	1040 ¹⁹ (20)	780 (40)			
Tomato/fall single			1100 (0)	1400 (0)	
Tomato/spring single			1100 (0)	1400 (0)	
Tomato/tomato-cukes		780 (40)	1100 (0)	1400 (0)	
Tomato/tomato-squash			1100 (0)	1400 (0)	
Tomato/tomato-melon			1100 (0)	1400 (0)	
Peppers/single (28 pound bushels/acre)		950 (5)			1000 (5)
Peppers/fall single			950 (5)		
Peppers/spring single			950 (5)		
Peppers/pepper-cukes					1000 (5)
Peppers/pepper-squash			950 (5)		1000 (5)
Peppers/pepper-melon			950 (5)		
Cucumbers/tomato-cukes (55 pound bushels/acre)		570 (5)	570 (5)	570 (5)	
Cucumbers/peppers-cukes		570 (5)		570 (5)	
Squash/tomato-squash (42 pound bushels/acre)			260 (5)	260 (5)	
Squash/pepper-squash			260 (5)		
Eggplant/single (33 pound bushels/acre)		1425 (5)			
Melon/tomato-melon (cwt./acre)			285 (5)	304 (5)	
Melon/pepper-melon			285 (5)	304 (5)	
Strawberries/single (12 pound flats/acre)			1900 (5)		2375 (5)

¹⁹Expected yield using an alternative to methyl bromide is listed above the percentage loss this yield represents (in parentheses) when switching to a methyl bromide alternative.

Table 5 - Per acre yields of crops by cropping system and production area using alternatives to methyl bromide with medium impacts on yield, scenario 2.

Crop/cropping system	Florida				California
	Dade County	Palm Beach	West Central	Southwest	
Tomato/single (25 cartons/acre)	1040 ²⁰ (20)	780 (40)			
Tomato/fall single			1045 (5)	1330 (5)	
Tomato/spring single			1045 (5)	1330 (5)	
Tomato/tomato-cukes		780 (40)	1045 (5)	1330 (5)	
Tomato/tomato-squash			1045 (5)	1330 (5)	
Tomato/tomato-melon			1045 (5)	1330 (5)	
Peppers/single (28 pound bushels/acre)		900 (10)			945 (10)
Peppers/fall single			855 (10)		
Peppers/spring single			855 (10)		
Peppers/pepper-cukes					945 (10)
Peppers/pepper-squash			855 (10)		945 (10)
Peppers/pepper-melon			855 (10)		
Cucumbers/tomato-cukes (55 pound bushels/acre)		540 (10)	540 (10)	540 (10)	
Cucumbers/peppers-cukes		540 (10)		540 (10)	
Squash/tomato-squash			248 (10)	248 (10)	
Squash/pepper-squash (42 pound bushels/acre)			248 (10)		
Eggplant/single (33 pound bushels/acre)		1350 (10)			
Melon/tomato-melon (cwt./acre)			270 (10)	288 (10)	
Melon/pepper-melon			270 (10)	288 (10)	
Strawberries/single (12 pound flats/acre)			1700 (15)		2125 (15)

²⁰Expected yield using an alternative to methyl bromide is listed above the percentage loss this yield represents (in parentheses) when switching to a non methyl bromide alternative.

Table 6 - The effect on the North American market from alternatives to methyl bromide, scenario 1 with low impacts on yield.

Crop	Consumption		Production			
	Volume	Price	Florida	California	Texas	Mexico
	% of Change					
Tomatoes	(0.1)	(0.4)	(21.8)			35.8
Strawberries	(7.2)	3.3	(28.3)	4.2		
Cucumbers	(4.2)	0.8	(1.1)			(7.4)
Peppers	(5.8)	1.9	(34.0)		65.0	28.5
Eggplant	(4.3)	2.2	(17.9)			18.3
Squash	(2.2)	0.6	4.2			(7.1)
Watermelon	(9.9)	2.8	(9.9)			

Note: Figures in parentheses represent declines.

Table 7 - The effect on the North American market from alternatives to methyl bromide, scenario 2 with medium impacts on yield.

Crop	Consumption		Production			
	Volume	Price	Florida	California	Texas	Mexico
	% of Change					
Tomatoes	(1.5)	0.5	(43.8)			68.5
Strawberries	(25.6)	10.1	(66.3)	(3.5)		
Cucumbers	(6.5)	1.9	(7.0)			(5.9)
Peppers	(7.3)	3.0	(49.5)		70.5	51.2
Eggplant	(7.2)	3.7	(31.0)			32.1
Squash	(2.3)	0.7	4.2			(7.4)
Watermelon	(30.1)	8.4	(30.1)			

Note: Figures in parentheses represent declines.

ANNEX II

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ANNEX III

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