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Abstract Executive Summary of the 2006 Chemicals TOC Assessment Report

What has been Achieved

Process Agents

CTOC has taken over the work of the Process Agents Task Forces, providing information to Parties on nominations of Process Agents. Taking into account Table A in decision XVII/7 and Table A bis in decision XVII/8, there are now 68 nominations to be assessed.

Feedstocks

Feedstock uses were summarized in the 2005 CTOC Progress Report. ODSs such as CTC and methyl chloroform are feedstocks for the production of CFCs and HCFCs, the latter continuing in use in Article 5 countries until 2040. Methyl bromide and halon 1301 can be used as feedstocks in manufacture of detergents and pharmaceuticals. Estimated ODS emissions from feedstocks were on the order of 3,500 metric tonnes or 1,619 ODP tonnes in 2002.

Laboratory and Analytical Uses

Advice has been provided on essential uses of CFC-113 and CTC. A review was carried out of potential laboratory and analytical uses of methyl bromide. Methyl bromide can be used in laboratories as a ‘methylating agent’. Alternatives to methyl bromide are generally available, but replacements in analytical applications can be more difficult to find.

Aerosol Products, Non-medical

Today more than 99.5% of non MDI aerosols use non-CFC formulations worldwide. The CFC consumption in this sector in 2003 and 2004 was around 2,000 tonnes in Article 5 countries and it is on the decline. There are no technical barriers to global transition to non-ODS alternatives, and many aerosol products have been replaced by not-in-kind substitutes such as mechanical pumps (finger or trigger pumps), sticks, roll-ons, brushes, etc as well as by non-ODSs.

Carbon Tetrachloride (CTC)

TEAP and CTOC provided a report on sources of CTC emissions and opportunities for reductions in 2006. Based on the calculation for the CTC demand 2002-2009, CTC emissions have been estimated. The discrepancy between emission data calculated from atmospheric concentrations and those derived from consideration of industrial activity is due possibly to under-estimation or under-reporting of the latter.
Solvents

Over 90% of ODS solvent uses (based on the peak consumption of 1994-95) have been reduced by substitution to not-in-kind technologies and conservation. The remaining less than 10% of the ODS market is shared by several in-kind solvent alternatives.

Destruction and Other Issues

Under the decision XII/8, TEAP set up two separate task forces - Task Force on Collection, Recovery and Storage (TFCRS) and Task Force on Destruction Technologies (TFDT). Large amounts of CFCs are contained in refrigeration equipments. CFC-11 remains in installed foams, and halons 1301 and 1211 in firefighting equipment. Some 16 of 45 ODS destruction technologies considered to meet the environmental and economic screening criteria adopted by the TFDT.

What is Left to be Achieved

Feedstocks

Halon 1301 is a very useful feedstock for preparation of bioactive compounds such as Fipronil, a broad-spectrum insecticide. A new development of non-ozone depleting trifluoromethylating agent will provide an option for resolution.

Laboratory and Analytical Uses

The reasons for slow progress in replacing ODS have been explored. It is estimated that laboratory uses of ODS could be reduced by 37% (over the 2003 figure) by 2008.

Solvents

The major challenges to total phase out are: providing access to information on already identified alternatives, overcoming economic considerations and identifying the small and medium users who, collectively, make up a major portion of the solvent market.

The Way Forward

Process Agents

The existing Process Agent nominations will be reviewed for the 19-MOP in 2007. Tighter collaboration between the Executive Committee (ExCom) and the TEAP will be important to clarify the real figures of process agent applications in Article 5 countries.

Feedstocks

TEAP and CTOC will continue to investigate on all feedstock uses, levels of emission and methods to limit emissions. The CTOC will keep monitoring feedstock uses of ODS that may not have been recognized formerly.
Laboratory and Analytical uses

Opportunities to reduce the use of ODS in preparative and analytical laboratories will arise as adoption of Green Chemistry practices. Meanwhile, the CTOC will maintain a watching brief on possible uses and report to Parties from time to time.

Aerosols, Non-medical

The completion of global CFC phase-out will occur in the near future as the reduction schedule mandated by the Montreal Protocol comes into force in Article 5 countries.

Carbon Tetrachloride (CTC)

Three potentially significant areas require further investigation to get better data for industrial emissions to enable resolution of the discrepancies with atmospheric measurements; the first area is to identify the production of CTC as a by-product and its subsequent use; the second area is to identify any other requirements for CTC and the third is the emission of CTC from sources such as landfills.

Solvents

Regulatory changes will continue to impact use of solvents. In some cases, this may require solvent and/or equipment change or a new cleaning process. The CTOC will investigate the Essential use Exemption of CFC-113 for aerospace applications by the Russian Federation for the years 2007 to 2010.

Destruction and Other Issues

One of the main synergies with the Basel, Rotterdam and Stockholm Conventions will be in the implementation of best practices in order to reduce and eliminate the use of certain chemicals and their waste, also reducing the pollution to the environment.
ES. Executive Summaries of All Chapters

ES1. Process Agents

The TEAP established Process Agents Task Forces (PATF) three times, first in 1997, in 2001 and in 2004, responding to the request of the Parties to review process agent uses applied by the Parties. In 2003, decision XV/7 provided a new list of 26 process agent applications to be reconsidered at the seventeenth Meeting of the Parties in 2005. With further 11 nominations for process agent uses from 8 Parties in 2004-2005, the 2004 PATF presented a report of its assessment to the Sixteenth Meeting of the Parties (2004). In 2006 the TEAP/CTOC considered two further applications for process agent designation, the one concerning the use of excess BCM in a reaction where a small part of this ODS was consumed as feedstock, and the other involving reduced energy consumption in the production of vinyl chloride monomer when small quantities of CTC were present in the reaction mixture. The 2006 TEAP Progress Report described the recommendation that both of these be considered process agent uses.

A guidance note with pro-forma has been prepared by the CTOC (Appendix 6-1 on page 102-105 in the 2005 TEAP Progress Report) to help Parties provide all necessary information when making nominations and submitting data for process agent applications to the Ozone Secretariat and the TEAP according to the decision XVII/6 paragraph(2) and paragraph (4).

Through intensive discussions on the findings of the PATF, three important decisions have been adopted on process agents at the seventeenth Meeting of the Parties (2005). Decision XVII/7 listed a revised Table A with 39 entries, and decision XVII/8 presented an interim Table A-bis (29 new entries) subject to reconfirmation at the Nineteenth Meeting of the Parties in 2007.

Decision XVII/6 has called on Parties to submit necessary data of the process agent uses listed in decisions XVII/7 and XVII/8 before 31 December 2006 to the Secretariat and the TEAP. With these information, the TEAP/CTOC will investigate all the applications listed in decision XVII/7 and in decision XVII/8 and report to the 27th OEWG in 2007, and every other year thereafter and make recommendations to the Parties at the twentieth Meeting in 2008, and every other year thereafter, on process agent use exemptions; on insignificant emission associated with a use, and process agent uses that could be added to or deleted from table A of decision X/14 according to decision XVII/6 paragraph (7). Further, the TEAP/CTOC will review in 2008 and every other year thereafter, emissions of table B of decision X/14, taking into account and data reported by the Parties and will recommend any reductions to the make-up and maximum emission on the basis of that review.

It will be important to consider how to reduce the emissions of ODS from the process agent uses. Some of the more emissive uses of process agents have been modified, either by improving emission controls, by substituting a non-ozone depleting (or at least a less-ozone-depleting) substance for the original process agent, or by ceasing the process altogether. Further opportunities will exist for improving controls and for substituting by less harmful substances. For example, TEAP considers that in some instances HCFCs could offer the unique properties required in these chemical processes i.e. non flammable, good chemical and physical properties, excellent solvency, etc. in place of fully halogenated ODS, which have higher ODPs.
Also important is a tighter collaboration between the Executive Committee (ExCom) and the TEAP to clarify the real figures of process agent applications in Article 5 countries.

**ES2. Feedstocks**

Feedstock uses were summarized in the 2005 CTOC Progress Report in detail under Decision X/12. CTC, CFCs and HCFCs can be feedstocks either by being fed directly into the process as a raw material stream or they can be produced as an intermediate in the synthesis of another product.

Major feedstocks in chemical industries include HCFC-22, CFC-113 and HCFC-142b as raw materials for manufacturing a variety of fluorinated polymers and elastomers. Historically CTC was a major feedstock for CFC-11 and CFC-12, but as the phase-out of CFC production continues, volumes of CTC for this application will diminish. Instead some HCFCs and CFCs have been used as feedstocks for producing alternative CFCs like HFC-125.

1,1,1-Trichloroethane (TCA) is converted to HCFC-141b and HCFC-142b, which can continue until 2040 at high volume for emissive uses mainly in Article 5 countries. Methyl bromide and trifluoromethyl bromide can be used as feedstocks in manufacture of detergents and pharmaceuticals.

The ODS emissions from feedstock applications were estimated on the order of 3,500 metric tonnes or 1,619 ODP tonnes with an assumption of 0.5% emission based on the quantity of the feedstock used in the production according to the IPCC recommendation.

Recently the HTOC raised a question that there has been use of Halon 1301 as a feedstock and the CTOC found that Halon 1301 is a very useful feedstock for preparation of bioactive compounds such as Fipronil, a broad-spectrum insecticide. (TEAP 2006 Progress Report) Under the Montreal Protocol, feedstock uses of ODS are exempt from control measures. Production of halon-1301 reported to the Ozone Secretariat for this feedstock use has averaged 400 tonnes per annum in France and approximately 160 tonnes in 2004 in China. This feedstock production raises some concerns because production for fire protection uses stopped in non-Article 5 Parties in January 1994 and will likely cease in Article 5 Parties in 2008, and feedstock use was not envisioned. The continued production of halon-1301 for feedstock use raises some serious issues that Parties may wish to consider and evaluate options to resolve.

A Party defines its own feedstock uses and exercises a range of stringency in reducing and eliminating unnecessary emissions of ODSs. TEAP and CTOC have become aware of a feedstock use that could jeopardize protection of the ozone layer and continue to investigate on all feedstock uses, levels of emission and methods to limit emissions. A watching brief will be maintained by the CTOC for feedstock uses of ODS that may not have been recognized formerly.

**ES3. Laboratory and Analytical Uses**

Under Decision IX/17 an Essential Use Exemption for laboratory and analytical uses of ODS was introduced. Decision X/19 extended this exemption until 31 December 2005. In 2003, the Fifteenth Meeting of the Parties, in Annex 1.B, approved the essential use of 1.025 metric tonnes CFC-113 and CTC for Poland in 2004.
Under Decision XVII/10, the Parties agreed to consider certain uses of methyl bromide as laboratory and analytical uses for the year 2006. In that same decision, Parties requested the TEAP to review those and other potential laboratory and analytical uses of methyl bromide, and, at the same time, to consider the criteria that had been previously adopted for laboratory and analytical uses of Annex A, B and C substances, in order to assess their relevance of those criteria to the laboratory and analytical uses of methyl bromide.

Methyl bromide is one of the most chemically reactive of the ozone depleting substances, and it finds use in laboratories as a ‘methylating agent’. Alternatives are available for many of these uses, and they often come into use when supplies of methyl bromide held in research laboratories are exhausted and difficulty is encountered in the purchase of quantities of 10-20 kg, as had been past practice.

Replacements for methyl bromide in analytical applications can be more difficult to find, but uses of this type are generally on a larger scale and there may be significant emissions. This is especially while methyl bromide uses continue to be permitted (CUN, QPS) and there are requirements for calibration or comparison with potential replacements.

The reports of laboratory uses of ODS received by the Ozone Secretariat in the period 2002-2005 are summarized in the table below. Small quantities (<0.005 MT) of CFC-12, CFC-124, BCM and HBFC-2281 are not included in the table.

**Laboratory Uses of Quantities of Ozone Depleting Substances (MT) Reported to the Ozone Secretariat**

<table>
<thead>
<tr>
<th>Year</th>
<th>Parties Reporting</th>
<th>Category</th>
<th>CTC</th>
<th>CFC-11</th>
<th>CFC-113</th>
<th>Methyl chloroform (TCA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005</td>
<td>1</td>
<td>Production</td>
<td>47</td>
<td>0.78</td>
<td>0.02</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Import/consumption</td>
<td>0.78</td>
<td>0.02</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2004</td>
<td>4</td>
<td>Production</td>
<td>81.7</td>
<td>54.9</td>
<td>2.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Import/consumption</td>
<td>5.09</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>1.81</td>
</tr>
<tr>
<td>2003</td>
<td>4</td>
<td>Production</td>
<td>69.2</td>
<td>3.12</td>
<td>9.50</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>Import/consumption</td>
<td>3.23</td>
<td>3.12</td>
<td>9.50</td>
<td>0.02</td>
</tr>
<tr>
<td>2002</td>
<td>3</td>
<td>Production</td>
<td>85</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>Import/consumption</td>
<td>16.52</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>9.11</td>
</tr>
</tbody>
</table>

Decision XV/8 asked TEAP to report annually on the development and availability of laboratory and analytical procedures that can be performed without using the controlled substances in Annexes A, B, and C (groups II and III). There has been only slow progress in replacing ozone depleting substances (ODS) that are used in laboratory and analytical procedures with substances that are less harmful to the ozone layer. In most cases this is due to the availability of ODS at favorable prices under the EUE and failure of alternative candidates to meet the demanding specifications that have brought about the use of ODS in the first place.
In 1996 the United States EPA compiled a list of institutions that develop laboratory standards, procedures, instructions and regulations that require the use of ODS, and also a list of those institutions that are investigating, researching or developing alternative procedures that do not require ODS. A section of the report listed 45 procedures that employed ODS (CTC, CFC-11, TCA, CFC-12, CFC-113, bromochloromethane, and HCFC-21), thus bringing to attention some opportunities for substitution.

A report commissioned by the EC and received in 2005 identified 125 laboratory procedures in which ODS were used – CFC-113>CTC>TCA, with smaller quantities of other CFCs and halons – mostly in extraction steps. The laboratory uses of ODS in 2003 totaled 9.933 ODS tonnes. It was estimated that this figure could be reduced by 37% by 2008 through the use of feasible non-ODS alternatives.

Opportunities to reduce the use (and therefore emissions) of ODS in preparative and analytical laboratories will arise as adoption of Green Chemistry practices – good laboratory practices and environmentally sound management of chemical reactions - spreads from the initial development in the USA and could eventually be enshrined in regulation.

While much as been discovered in the last few years, Parties need to be aware that there could be laboratory and analytical uses of ODS that have not yet come to attention. The surveys conducted by the United States and the European Union may be consulted to identify similar uses in other countries. Such uses may be discovered when orders are placed with suppliers of these chemicals, but volumes are usually small, and so some years may elapse before an on-going use comes to light.

Members of the CTOC and other Technical Options Committees that report to the TEAP will maintain a watching brief on possible uses and report to Parties from time to time.

**ES4. Aerosol Products, Non-medical**

Worldwide aerosol fillings have grown over the last years and were close to 11 billion cans in 2005, the largest number ever. Today more than 99.5% of non MDI aerosols use non-CFC formulations worldwide. There are no technical barriers to global transition to non-ODS alternatives in all these applications, which require either low flammability or specific pharmaceutical approval.

The latest CFC consumption in the aerosol sector reported by Parties in 2003 and 2004 was around 2,000 tonnes in Article 5 countries, down from the estimated use of 4,300 tonnes in 2001. Currently available alternatives for CFCs used in non-MDI aerosols as propellants include hydrocarbon aerosol propellants (HAPs), dimethyl ether (DME), HFCs (HFC-152a, HFC-134a and HFC-227ea), HCFCs (HCFC-22 and HCFC-142b) and compressed gases (CGs) such as compressed air, CO₂, N₂ and N₂O. HAPs and DME are both flammable and explosive and strict safety measures are required. HFCs are non-ODS but should be used only where they provide important safety, functional or health benefits for the users due to greenhouse gases.

There are many alternatives to replace ODS used as solvents or as active ingredients in non-MDI aerosols. These replacements can be hydrocarbons, high boiling HFCs like HFC-43-10mee, and HFC-245fa, high boiling HCFCs like HFC 141b, and other solvents like HFEs or even water. Many aerosol products have been replaced by such not-in-kind substitutes as mechanical pumps (finger or trigger pumps), sticks, roll-ons, brushes, etc.
In 2005 the residual CFC consumption was only due to the use in Article 5 countries. The main groups of non-MDI aerosol products still using ODS (CFC/HCFC) are:

- local anesthetics, vaginal foams, wound sprays, throat and nasal sprays, traditional Chinese medicines;
- Industrial/technical aerosols (dusters, electronics cleaners, freeze sprays, spinnerette sprays, anti-spatter sprays, tire inflators, fluorinated greases deposition etc.);
- Insecticides and disinfectants for aircrafts etc.

It is expected that the completion of global CFC phase-out in non-MDI aerosols will occur in the very short term as the reduction schedule mandated by the Montreal Protocol comes into force in Article 5 countries.

The residual ODS phase-out in the non-MDI aerosol sector will require:

- Efforts by national environmental facilities and governmental bodies, including national legislation and enforcement;
- Technical/financial assistance for reformulation;
- Educational assistance in alternatives choice and handling;
- Sufficient time for the conversion of medical aerosols that must be clinically tested and approved by national health and drug authorities.

**ES5. Carbon Tetrachloride (CTC)**

In accordance with decision XVI/14, TEAP and CTOC provided ‘a report on sources of carbon tetrachloride emissions (CTC) and opportunities for reductions’ in 2006. The main sources of CTC emissions were initially its feedstock applications – conversion into fluorocarbons such as CFC-11 and CFC-12. CTC demand for the production of CFC-11 and CFC-12 exceeded 1 million tonnes in 1987. More recently, it has been used as feedstock for the production of a number of alternative CFCs like HFCs. By 2010, new HFCs can be estimated, using data in IPCC/TEAP 2005, to exert a demand of some 54 kilo- tonnes per annum of chemical intermediate CTC into HFC-245fa, HFC-236fa, and HFC-365mfc. In addition, there are a number of designated essential uses for CTC in pharmaceutical and agrochemical applications together with a large list of approved process agent uses for CTC.

The calculation for the CTC demand 2002-2009 was based on the CFC production for basic domestic needs for the period 2003-2009, an estimate of the “make-up” figure for process agent use contained in Decision X/14, and a forecast of the CTC use as a feedstock for HFCs through to 2015 on the future requirements of the foam insulation market (IPCC/TEAP Report, 2005). (cf. TEAP Progress Report 2006, p78-90)
### Estimated total CTC requirements for assumed demands (tonnes)

<table>
<thead>
<tr>
<th>Year</th>
<th>2002</th>
<th>2003</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFC Feedstock</td>
<td>126,240</td>
<td>108,425</td>
<td>96,837</td>
<td>74,903</td>
<td>51,353</td>
<td>26,476</td>
<td>21,441</td>
<td>14,247</td>
<td>0</td>
</tr>
<tr>
<td>Emissive uses</td>
<td>36,426</td>
<td>33,784</td>
<td>30,700</td>
<td>32,958</td>
<td>34,636</td>
<td>36,414</td>
<td>38,299</td>
<td>40,297</td>
<td>41,920</td>
</tr>
<tr>
<td>Other Feedstock</td>
<td>3,295</td>
<td>23,649</td>
<td>32,412</td>
<td>38,231</td>
<td>42,342</td>
<td>44,399</td>
<td>46,422</td>
<td>48,376</td>
<td>50,285</td>
</tr>
<tr>
<td>TOTAL</td>
<td>165,961</td>
<td>165,858</td>
<td>159,949</td>
<td>146,092</td>
<td>128,331</td>
<td>107,289</td>
<td>106,162</td>
<td>102,920</td>
<td>92,205</td>
</tr>
</tbody>
</table>

The possible CTC emissions from these requirements were calculated between 13,728 and 21,960 metric tonnes in 2006 with reasonable assumptions.

According to the calculated emissions estimated from the historically observed CTC concentrations, annual CTC emissions peaked at approximately 130,000 tonnes in the mid-1980s, but then declined to about 80,000 tonnes by the late 1990s. Given the range of lifetimes considered for CTC, these figures could involve uncertainties of ±30%. Recent data from the IPCC/TEAP Report, 2005, estimate emissions in 2002 to be 64,000-76,000 kilo-tonnes.

There is an emerging conclusion that the discrepancy between emission data calculated from atmospheric concentrations and those derived from consideration of industrial activity is due to under-estimation or under-reporting of the latter.

The foregoing conclusion may need reconsideration if the behavior of CTC in the atmosphere is reassessed by the Science Assessment Panel. As for additional formerly unrecognized sources, there is the possibility that CTC is emitted from landfills, which have come to attention recently as temporary sinks from which a number of chemicals substances can be released to the atmosphere. In the case of CTC, the substance might have entered the landfill as a component of wastes, or possibly been generated in the landfill by chemical or (more likely) microbiological action. No reports are available of such emissions but the attention being paid to landfills in recent times could provide confirmation or refutation of this hypothesis.

Three potentially significant areas require further investigation to get better data for industrial emissions in Article 5 and non-Article 5 countries to enable resolution of the discrepancies with atmospheric measurements; the first area is that of CTC production in order to identify, in particular, the production of CTC as a by-product and its subsequent use, re-cycling or destruction; the second area is to identify any other requirements for CTC and the third is the emission of CTC from sources such as landfills.

### ES6. Solvents

Over 90% of ODS solvent uses (based on the peak consumption of 1994-95) have been reduced by substitution to not-in-kind technologies and conservations and the remaining less than 10% of the ODS market is shared by several in-kind solvent alternatives.

Not-in-kind alternatives options include no-clean mainly in electronics and aerospace, aqueous systems in degreasing and precision cleaning, hydrocarbon in precision mechanics and oxygenated solvents in diverse cleaning applications. The primary in-kind substitutes for 1,1,1-trichloroethane (TCA) and CTC cover chlorofluorocarbon alternatives such as...
trichloroethylene, perchloroethylene and methylene chloride. Also, a brominated substance, n-propyl bromide, with similar solvent properties to those of the chlorinated solvents, has taken a significant market share in recent years for defluxing, general cleaning and adhesives applications in spite of its ozone depleting potential and toxicity. The in-kind substitutes for CFC-113 and CFC-11 are fluorinated alternatives such as hydrochlorofluorocarbons (HCFC-141b and HCFC-225ca/cb), perfluorocarbons (primarily C6F14), hydrofluorocarbons (HFC-43-10mee, HFC-365mfc and HFC-245fa, HFC-c447ef) and hydrofluoroethers (HFE-449s1, HFE-569sf2). HFCs are available in all regions but their uses have been primarily in non-Article 5 countries due to relatively high cost and importance of high tech industries. Their growth is expected to be minimal due to the increasing concern about their high GWP. In Article 5 countries, use of HCFC-141b is still increasing especially in China, India, and Brazil and its consumption exceeded 5,000t in 2002 (AFEAS, 2002). The HCFC total consumption phase-out for Article 5 countries is scheduled for 1 January 2040 with a freeze of consumption in 2015. But some countries are accelerating this for solvents (e.g., Malaysia, Thailand) – while applications that utilize HFC or HFE may be interchangeable transitions from HFCs and HFEs as to hinder conversions. Further barriers to transition occur where complex and crucial components are involved.

The challenges that are facing the world are phase out of ozone depleting substances in Article 5 countries. Preferable alternatives have been identified throughout the world and are generally readily available but the major drawbacks to the implementation are primarily access to information, and knowledge about what are the acceptable alternatives. A second major hurdle to be overcome is the economic considerations. However, the biggest problem is being able to identify the small and medium users who, collectively, make up a major portion of the solvent market.

Progress in achieving the phase-out in Article 5 countries has been good, given the widespread use of ozone-depleting solvents and the variety and complexity of their applications. Of the various uses, the large-scale electronics industry has progressed furthest towards a complete phase-out, although this is not the case with smaller units. Full phase-out for metal cleaning applications is hampered by the large number of small users, many of whom are undercapitalised. In precision cleaning applications, users have been aggressively implementing alternatives. Yet, in some cases, they are still searching for solutions for cleaning precision parts that are especially vulnerable to residues or reactions, or that have unusually stringent cleanliness criteria.

The regulatory changes continue to impact use of solvents as well as containment, emission, safety, health and recycling requirements. In some cases, they may require solvent and/or equipment change or a new cleaning process.

**European Regulation Changes**

It is important to note that HFC solvent uses have not been restricted in any way in Europe by the April 2006 Regulation on F-gases. By now the 1999 VOC Directive limiting emission of solvents in industrial uses including surface cleaning, has been fully implemented in EU 15. The new European chemical policy called REACH (Registration Evaluation and Authorization of Chemicals) will come as a new regulation mid 2007. It could impact substances availability for certain uses (including solvents) in cases where low sales volumes cannot support the testing regime required by REACH or where the re-assessed properties of the substance mitigate against its use.
Japanese Regulation Changes

PRTR (Pollutant Release and Transfer Register) regulation came into effect in 2002. The law requires reporting of release and transfer of 354 substances including all ODSs and chlorinated solvents. The other new regulation which will have a major effect in controlling cleaning operation is the VOC (volatile organic compound) regulation. It came into effect from April 2006. The VOCs emitted in industrial cleaning in 2002 was 141,000 tons. Of those VOCs emitted, 66% was chlorinated solvents such as methylene chloride (34%), trichloroethylene (23%) and perchloroethylene (9%). In order to achieve reduction in emission, various combinations of cleaning equipments, operating manuals and peripherals to suit the processes are needed and efforts are made to develop such systems.

The selection of the alternative technologies to ODS solvents for Article 5 countries should be:

- "No-clean", keep-clean
- Aqueous/hydrocarbon-surfactant cleaning
- Organic solvent cleaning (with solvents less toxic than non-ozone-depleting halogenated solvents)
- Non-ozone-depleting halogenated solvents (HFC, HFEs, TCE, PCE)
- Organic solvent cleaning (with solvents more toxic than non-ozone-depleting halogenated solvents)
- HCFC-225
- HCFC-141b
- PFCs

All applications to the Multilateral Fund that propose the use of aqueous or hydrocarbon surfactant cleaning should include funding for pollution prevention, recycling, waste water treatment, shower and eye-wash facilities and drying equipment, as appropriate. Applications that involve the use of organic and hydrogenated solvents should include containment equipment, adequate ventilation control, and/or low emission equipment. The guidelines for all processes should include requirements for personnel safety, for example, the use of eye guards and other personal protection equipment by workers who perform the cleaning operation and means for the measurement of operator exposure.

The CTOC will investigate the Essential use Exemption of CFC-113 for aerospace applications by the Russian Federation for the years 2007 to 2010.

ES7. Destruction and Other Issues

Under the decision XII/8, TEAP set up two separate task forces and reported to the Parties at MOP-14 in 2002 (Report of the TEAP April 2002 Volume 3; Report of the Task Force on Collection, Recovery and Storage (TFCRS) and Report of the Task Force on Destruction Technologies (TFDT). The TFCRS estimated the amounts of CFC contained in refrigeration equipment to be between 350,000 and 400,000 ODP-tonnes in 2002, 1.25 million ODP-tonnes of CFC-11 still remaining in installed foams in 2010 and Halon 1301 and halon-1211 installed in firefighting equipment to be 450,000 and 330,000 ODP-tonnes, respectively in 2002. The barriers to collection, recovery and storage are, for example, (1) lack of appropriate legislation and infrastructures, (2) financial resistance where manufacturer or owner has to pay, (3) ineffective collection of rigid construction foam within building
structures, (4) restriction of trans-boundary movements of waste. The TFDT reviewed criteria for approval of the destruction facilities and assessed their environmental and economic performance. 16 ODS destruction technologies met the screening criteria among 45 considered.

In 2005, TEAP established the Task Force on Foam End-of-Life Issues, in response to decision XVII/10. The report in May 2005 was mainly focused on the description of the technical and economic aspects of blowing agent recovery and destruction from appliance and building insulation foams and proposed a new parameter, recovery & destruction efficiency (RDE) which would be valuable to accommodate the whole recovery and destruction chain, and concluded that currently practiced recovery and destruction process have the potential to reach an RDE of greater than 85%-90% with a net cost of recovery of $25-40/kg. The existing banks of CFCs and HCFCs are estimated to be 1.5 million and 0.75 million tones, respectively.

Under the decision XVII/18 and decision 47/52 of the ExCom of MLF, foam, halon and refrigerant banks on the basis of recoverable ODS were discussed in order to assess the current and future requirements for the collection and disposition of non-reusable and unwanted ozone-depleting substances in Article 5 countries. In addition to non-reusable CFCs from refrigeration (3,500 metric tonnes), there is likely to be an excess of CTC production in the near future, and the excess will need to be destroyed. However, ODS recovery and destruction in these cases will not be achievable without any additional stimulation which may arise from other environmental agreement and economic imperatives.

Under the decision XVII/17(3), the CTOC reviewed possible synergies with other conventions, such as Basel, Rotterdam and Stockholm Conventions which are related to Montreal Protocol in several issues as environmentally sound management of ozone-depleting substances and their wastes. One of the main synergies between them will exist in the implementation of best practices in order to reduce and eliminate the use of certain chemicals and their waste, also reducing the pollution to the environment.
1 Introduction

This is a first assessment report of the Chemicals TOC (CTOC) since the reorganization of the former ATOC (Aerosols, Sterilants, Miscellaneous Uses and CTC TOC) and STOC (Solvents, Coatings and Adhesives TOC) to the present CTOC in 2005. Its membership incorporates solvent, feedstock, and laboratory and analytical use experts mainly from the former STOC; and CTC, non-medical aerosol and miscellaneous uses experts from the former ATOC. In addition the experts on process agents and destruction technologies have been invited from the former task forces. Furthermore some new members have been recruited mainly from Article 5 countries to get balanced expertise.

The CTOC is responsible for annual progress updates on Solvents, non-Medical Aerosol and Miscellaneous Chemical Uses, and also for completing assessments requested by the Parties on Process Agents, Feedstocks, Laboratory and Analytical Uses, Carbon Tetrachloride (CTC), Destruction Technologies as well as new chemicals such as n-Propyl Bromide (n-PB).

The 2006 assessment report will describe the progress being made during these four years in phasing out ODSs in each sub-sector which is included in the CTOC activities.
2 Process Agents

2.1 Narrative of the Process Agent Determinations

The use of ozone-depleting substances in ways that were not primarily emissive was considered by the Fourth Meeting of the Parties (1992), and Decision IV/12 stated 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;*

The Decision went on to urge Parties to minimize such emissions and to request the TEAP to estimate the total emissions derived from such uses.

The TEAP established the first Process Agent Task Force (PATF), which submitted its report in April 1997. At the Tenth Meeting of the Parties in 1998, Decision X/14 established Table A, containing at that time 25 uses of controlled substances as process agents, and Table B, in which emission limits for such uses were established. It was noted that Parties may propose additions to the list, and that following investigation and recommendation by the TEAP, such uses could be added to Table A. The Decision also determined that 'Parties should not install or commission new plant using controlled substances as process agents after 30 June 1999, unless the Meeting of the Parties has decided that the use in question meets the criteria for essential uses under Decision IV/25'.

Decision X/14 requested the TEAP and the Executive Committee to review Tables A and B and report to the Thirteenth Meeting of the Parties in 2001. To meet this request, the TEAP established the second PATF and included its findings in the 2001 TEAP Progress Report. The report included criteria that a particular use of a controlled substance would need to meet if it were to be adjudged a process agent use. The 2001 PATF endorsed the determination of the 1997 Task Force that 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
   - vapor 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.
7. To minimize undesirable by-product formation.
Decision XIII/13 recognized the work of the TEAP and requested it to finalize its report the following year. Then TEAP carefully reviewed previous TEAP/PATF reports as well as newly available information and listed up 45 applications of process agents in an updated Table A, and categorized these uses in the following four groups in the 2002 TEAP Progress Report (Chapter 9).

**Category 1:** Process agents with negligible emissions. These uses meet the technical criteria of the 1997 PATF report, and their emissions have been reduced to negligible levels.

**Category 2:** Process agents with non-negligible emissions. Although these uses meet the technical criteria of the 1997 PATF report, their emissions have not been reduced to negligible levels.

**Category 3:** Insufficient information to decide whether these are process agent uses or not.

**Category 4:** Not process agents because the technical criteria are not met.

The TEAP noted that Parties may apply for Emergency Exemption or Essential Use Exemption for uses in categories 3 and 4, or the uses may be classified as feedstock. In the updated Table A, 11 uses fell in category 1, 24 in category 2, and 10 in category 3.

The Fifteenth Meeting of the Parties in 2003, in Decision XV/6 accepted a revised Table A with 31 entries, and in Decision XV/7 listed a further 26 process agent applications and requested the TEAP to review them for the Seventeenth Meeting of the Parties.

### 2.2 Process Agents Task Force (PATF) 2004

When further nominations for process agent uses were received, the TEAP once again established a Process Agents Task Force, and its report was presented to the Sixteenth Meeting of the Parties in 2004. The definitions and criteria adopted in 1997 were reiterated in the 2004 PATF Report, and details of other definitions commonly used in the chemical process industry were presented.

The PATF reported in detail on the nine applications that had been referred to it for recommendation, but it also reported that many applications for process agent use did not provide sufficient information and requests for such information were needed before the PATF could give full consideration to an application. On the advice of the PATF, letters requesting more information were sent to Parties by UNEP to satisfy the requirements of the Process Agents Task Force. These letters indicated the need for the following information:

- Plant start up date.
- Installed capacity and actual production in the last three years.
- Description of chemicals and reactions involved in every step of the process.
- Detailed Process Flow Chart.
- Efforts made to replace the ODS including listing and description of alternative processes.
- Actual emissions of controlled substances.
- Description of measures to reduce emissions.

The PATF recognized that some of the information it was requesting would be regarded by manufacturers as confidential business information, and that the Parties (their governments) would not be at liberty to disclose such information. Nonetheless, the PATF (and later the CTOC and the TEAP) members were able to satisfy themselves that sufficient information had been disclosed that a decision to recommend was possible.
The PATF made some additional comments in the Conclusions section of its report, as follows:

- The Task Force notes that there are opportunities to switch to ODS-free alternatives for all process agent uses which have significant emissions of controlled substances and were reviewed in their report.
- Inclusion of a process agent use in Table A of Decision XV/7 for an Article 5(1) Party does not necessarily assure that the same use can be considered a process agent for a non-Article 5(1) Party. This is the case when there are feasible non-ODS alternatives for that use, but inclusion in Table A allows the Article 5(1) Party to become eligible for funding in accordance with the rules and guidelines of the Executive Committee of the Multilateral Fund.
- Parties may wish to consider whether, in the case of non-Article 5(1) Parties, adding a new Process Agent to Table A should have any impact on Table B of Decision X/14, which lists the maximum emissions allowed per region/country for Process Agents.
- Parties may wish to clarify the criteria used to define when an ODS use falls under the Laboratory and Analytical Exemption. Possible criteria could be the nature of the activity i.e. research investigation or analytical measurement, as opposed to scale or venue.

Although positive recommendations were brought to the Meeting of the Parties by the TEAP on all the applications reviewed, no decision on Process Agents was taken at the Sixteenth Meeting. The TEAP recommendations were considered again at the Seventeenth Meeting of the Parties in 2005, which made several decisions regarding process agents. Decision XVII/6, among other matters, called on Parties to furnish emissions and other data before 31 December 2006. Decision XVII/7 adopted a revised Table A with 39 entries, and Decision XVII/8 presented an interim Table A bis (29 entries) subject to reconfirmation at the Nineteenth Meeting of the Parties in 2007.

2.3 Analysis of the Process Agent Uses

In the Table A adopted by Decision XVII/7, the most common ODS being used as a process agent was carbon tetrachloride (CTC). This accounted for 32 of the 39 applications, most of them being for use of CTC as a specialized reaction solvent in the manufacture of agricultural and pharmaceutical chemicals. One application not of this type involved the use CTC to remove the dangerous impurity, nitrogen trichloride (NCl₃) from elemental chlorine produced in electrolytic cells, and another was a specialized use of small volumes of CTC in the production of the medical diagnostic material, radio-labeled cyanocobalamin.

Four of the applications involved the use of CFC-113 (CF₂Cl-CFCl₂) as a reaction solvent with unique properties that made possible high yields and suppression of side-reactions. Similar reasons dictated the use of CFC-11 (CFCl₃), CFC-12 (CF₂Cl₂) and bromochloromethane (BCM, CH₂BrCl) in one application each.

Unresolved Applications

Following the Seventeenth Meeting of the Parties, the TEAP and its Chemical Technical Options Committee (CTOC) considered two further applications for process agent designation, the one concerning the use of excess BCM in a reaction where a small part of
this ODS was consumed as feedstock, and the other involving reduced energy use in the production of vinyl chloride monomer when small quantities of CTC were present in the reaction mixture. The 2006 TEAP Progress Report contains the recommendation that both of these be considered process agent uses.

Regarding Table A bis (Decision XVII/8), the TEAP was informed – but too late for consideration before the writing of its 2006 Report – that several of these applications would be withdrawn by the Party because they were feedstock applications. The CTOC agreed that the specified applications were feedstock, and this will be further considered by the TEAP. (See Appendix 1 for the revised Table A in Decision XVII/7 and the Table A-bis in Decision XVII/8.)

Changes to Process Agent Uses

Some of the more emissive uses of process agents have been modified, either by improving emission controls, by substituting a non-ozone depleting (or at least a less-ozone-depleting) substance for the original process agent, or by ceasing the process altogether.

Further opportunities exist for improving controls and for substituting by less harmful substances. For example, where CTC is used as a solvent in the preparation of an acid chloride to form a carboxylic acid and thionyl chloride, the solvent function can be performed by excess thionyl chloride which is recovered at the end of the reaction. While chemical engineering adjustments would need to be made to the process to take account of differences in some properties of thionyl chloride and CTC (for example, heat transfer and viscosity), the boiling points of the two substances are similar (78.8°C and 76.5°C, respectively), and thionyl chloride is an excellent solvent for organic chemicals. Thionyl chloride is used in this way, for example, in the last step of the synthetic sequence leading to the production of DV acid chloride (permethric acid), a precursor of synthetic pyrethroids.

TEAP considered that in some instances HCFCs could offer the unique properties required in these chemical processes i.e. non flammable, good chemical and physical properties, excellent solvency, etc.

TEAP is aware of at least a proposed use of a low-ODP HCFC as a “Process Agent” for the production of fluoropolymers. The HCFC would be a substitute for the use of an ODS process agent with a much higher ODP. In this case the HCFC would be partly "consumed" through a chain transfer reaction into the product, and the unreacted excess HCFC would be recovered.

There may be other cases where HCFCs can serve as process agents in place of fully halogenated ODS, which have higher ODPs. Parties may wish to consider that it may not be necessary to allow the exempted use of fully halogenated ODSs as process agents in those applications where partially-halogenated ODSs or non-ODS substances can be used as process agents.

In parallel with the TEAP consideration on process agent uses, the Executive Committee authorized the Fund Secretariat at its 44th Meeting to hire a consultant to catalogue process agent uses in Article 5 countries and their related emission levels.
The results are referred to UNEP/OzL.Pro/ExCom/45/53, which identified 18 processes that have not been included in Decisions XV/6 and XV/7, and also identified a large discrepancy between the figures provided by Article 5 countries in annual reports to the Fund Secretariat and to the Ozone Secretariat. This clearly indicates the tighter collaboration between the ExCom and the TEAP for collecting the real figures of process agent applications in Article 5 countries.

**Emissions Reported in Table B**

The emissions of ODS being deployed as process agents are required to be reported annually by Parties.

*Table B: remains unchanged from its original inclusion in Decision X/14 (quantities are metric tonnes per year):*

<table>
<thead>
<tr>
<th>Country/region</th>
<th>Make-up or consumption</th>
<th>Maximum emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>European Community</td>
<td>1000</td>
<td>17</td>
</tr>
<tr>
<td>United States of America</td>
<td>2300</td>
<td>181</td>
</tr>
<tr>
<td>Canada</td>
<td>13</td>
<td>0</td>
</tr>
<tr>
<td>Japan</td>
<td>300</td>
<td>5</td>
</tr>
<tr>
<td>Hungary*</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>Poland*</td>
<td>68</td>
<td>0.5</td>
</tr>
<tr>
<td>Russian Federation</td>
<td>800</td>
<td>17</td>
</tr>
<tr>
<td>Switzerland</td>
<td>5</td>
<td>0.4</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>4501</strong></td>
<td><strong>220.9</strong></td>
</tr>
</tbody>
</table>

* These country totals should now be included in the EC figures.

Note that the maximum emissions of the total make-up or consumption in Table B are equal to 4.9% of all the estimated emissions in Table A.
### Appendix 1

**Decision XVII/7: List of Uses of Controlled Substances as Process Agents**

To adopt the following uses of controlled substances as a revised table A for decision X/14;

**Table A: List of uses of controlled substances as process agents**

<table>
<thead>
<tr>
<th>No.</th>
<th>Process agent application</th>
<th>Substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Elimination of NCl3 in the production of chlorine and caustic</td>
<td>CTC</td>
</tr>
<tr>
<td>2.</td>
<td>Recovery of chlorine in tail gas from production of chlorine</td>
<td>CTC</td>
</tr>
<tr>
<td>3.</td>
<td>Manufacture of chlorinated rubber</td>
<td>CTC</td>
</tr>
<tr>
<td>4.</td>
<td>Manufacture of endosulphan (insecticide)</td>
<td>CTC</td>
</tr>
<tr>
<td>5.</td>
<td>Manufacture of isobutyl acetophenone (ibuprofen – analgesic)</td>
<td>CTC</td>
</tr>
<tr>
<td>6.</td>
<td>Manufacture of 1-1, bis (4-chlorophenyl) 2,2,2- trichloroethanol (dicofol insecticide)</td>
<td>CTC</td>
</tr>
<tr>
<td>7.</td>
<td>Manufacture of chlorosulphonated polyolefin (CSM)</td>
<td>CTC</td>
</tr>
<tr>
<td>8.</td>
<td>Manufacture of poly-phenylene-terephtal-amide</td>
<td>CTC</td>
</tr>
<tr>
<td>9.</td>
<td>Manufacture of fluoropolymer resins</td>
<td>CFC-113</td>
</tr>
<tr>
<td>10.</td>
<td>Manufacture of fine synthetic polyolefin fibre sheet</td>
<td>CFC-11</td>
</tr>
<tr>
<td>11.</td>
<td>Manufacture of styrene butadiene rubber</td>
<td>CTC</td>
</tr>
<tr>
<td>12.</td>
<td>Manufacture of chlorinated paraffin</td>
<td>CTC</td>
</tr>
</tbody>
</table>
| 13. | Photochemical synthesis of perfluoropolyetherpolyperoxide (precursors of Z-perfluoropol 
|     |   yethers and difunctional derivatives)                                                   | CFC-12        |
| 14. | Reduction of perfluoropolyetherpolyperoxide intermediate for production of 
|     |   perfluoropolyether diesters                                                              | CFC-113       |
| 15. | Preparation of perfluoropolyether diols with high functionality                            | CFC-113       |
| 16. | Production of Bromohexine hydrochloride                                                    | CTC           |
| 17. | Production of Diclofenac sodium                                                           | CTC           |
| 18. | Production of Phenyl glyicine                                                             | CTC           |
| 19. | Production of Cyclodime                                                                  | CTC           |
| 20. | Production of chlorinated polypropene                                                     | CTC           |
| 21. | Production of chlorinated EVA                                                              | CTC           |
| 22. | Production of methyl isocyanate derivatives                                                | CTC           |
| 23. | Production of 3-phenoxo benzaldehyde                                                      | CTC           |
| 24. | Production of 2-chloro-5-methylpyridine                                                    | CTC           |
| 25. | Production of Imidacloprid                                                                | CTC           |
| 26. | Production of Buprofenzin                                                                 | CTC           |
| 27. | Production of Oxadiazon                                                                  | CTC           |
| 28. | Production of chloradized N-methylaniline                                                 | CTC           |
| 29. | Production of Mefenacet                                                                   | CTC           |
| 30. | Production of 1,3-dichlorobenzothiazole                                                    | CTC           |
| 31. | Bromination of a styrene polymer                                                          | BCM           |
| 32. | Synthesis of ascorbic acid                                                                | CTC           |
| 33. | Synthesis of ciprofloxacin                                                                | CTC           |
| 34. | Synthesis of norfloxacin                                                                  | CTC           |
| 35. | Synthesis of 2,4-dichlorophenoxyacetic acid                                               | CTC           |
| 36. | Synthesis of diperoxydicarbonate                                                          | CTC           |
| 37. | Production of sodium dichloroisocyanurate                                                  | CTC           |
| 38. | Production of radio-labelled cyanocobalamin                                               | CTC           |
| 39. | Production of high modulus polyethylene fibre                                            | CFC-113       |
Decision XVII/8: List of Uses of Controlled Substances as Process Agents
To adopt the following uses of controlled substances as an interim table A bis for decision X/14, subject to reconfirmation and inclusion in a reassessed table A for decision X/14 at the Nineteenth Meeting of the Parties in 2007;

Table A-bis: Interim list of uses of controlled substances as process agents

<table>
<thead>
<tr>
<th>No.</th>
<th>Process agent application</th>
<th>Substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.</td>
<td>Production of p-Bromobenzaldehyde (intermediate)</td>
<td>Probably CTC</td>
</tr>
<tr>
<td>41.</td>
<td>Production of fenvalerate (pesticide)</td>
<td>CTC</td>
</tr>
<tr>
<td>42.</td>
<td>Manufacture of Losartan Potassium</td>
<td>BCM</td>
</tr>
<tr>
<td>43.</td>
<td>Production of 1,2-Chloro-1,4-Naphthoquinone (pharmaceutical)</td>
<td>CTC</td>
</tr>
<tr>
<td>44.</td>
<td>Production of Prallethrin (pesticide)</td>
<td>CTC</td>
</tr>
<tr>
<td>45.</td>
<td>Production of 2-Methoxybenzoylchloride (pharmaceutical)</td>
<td>CTC</td>
</tr>
<tr>
<td>46.</td>
<td>Production of o-Nitrobenzaldehyde (dyes)</td>
<td>CTC</td>
</tr>
<tr>
<td>47.</td>
<td>Production of Salimusk (perfume)</td>
<td>CTC</td>
</tr>
<tr>
<td>48.</td>
<td>Production of Epoxiconazole (pesticide)</td>
<td>CTC</td>
</tr>
<tr>
<td>49.</td>
<td>Production of benzophenone (chemical)</td>
<td>CTC</td>
</tr>
<tr>
<td>50.</td>
<td>Production of Picloram; Lontrel (pesticides)</td>
<td>CTC</td>
</tr>
<tr>
<td>51.</td>
<td>Production of 3-Methyl-2-Thiophenecarboxaldehyde (pesticide, pharma.)</td>
<td>CTC</td>
</tr>
<tr>
<td>52.</td>
<td>Production of Difenoconazole (pesticide)</td>
<td>CTC</td>
</tr>
<tr>
<td>53.</td>
<td>Production of 2-Thiophenecarboxaldehyde (intermediate)</td>
<td>CTC</td>
</tr>
<tr>
<td>54.</td>
<td>Production of 2-Thiophene ethanol (pharmaceutical)</td>
<td>CTC</td>
</tr>
<tr>
<td>55.</td>
<td>Production of 5-Amino-1,2,3-thiadiazol</td>
<td>CTC</td>
</tr>
<tr>
<td>56.</td>
<td>Production of Levofoxacin (pharmaceutical)</td>
<td>CTC</td>
</tr>
<tr>
<td>57.</td>
<td>Production of Cinnamic acid (intermediate)</td>
<td>CTC</td>
</tr>
<tr>
<td>58.</td>
<td>Production of Ertaczo (pharmaceutical)</td>
<td>CTC</td>
</tr>
<tr>
<td>59.</td>
<td>Production of 3,5-Dinitrobenzoyl chloride (3,5-DNBC) (intermediate)</td>
<td>CTC</td>
</tr>
<tr>
<td>60.</td>
<td>Production of Fipronil (pesticide)</td>
<td>CTC</td>
</tr>
<tr>
<td>61.</td>
<td>Processing of Aluminium, Uranium</td>
<td>CTC, CFC</td>
</tr>
<tr>
<td>62.</td>
<td>Production of Furfural (volume chemical)</td>
<td>CTC</td>
</tr>
<tr>
<td>63.</td>
<td>Production of 3,3,3-trifluoropropene (volume chemical)</td>
<td>CTC</td>
</tr>
<tr>
<td>64.</td>
<td>Production of Triphenylmethylchloride (intermediate)</td>
<td>CTC</td>
</tr>
<tr>
<td>65.</td>
<td>Production of Tetrachlorodimethylmethane (volume chemical)</td>
<td>CTC</td>
</tr>
<tr>
<td>66.</td>
<td>Production of 4,4`-difluorodiphenylketone (intermediate)</td>
<td>CTC</td>
</tr>
<tr>
<td>67.</td>
<td>Production of 4-trifluoromethoxybenzenamine</td>
<td>CTC</td>
</tr>
<tr>
<td>68.</td>
<td>Production of 1,2-benzisothiazol-3-ketone</td>
<td>CTC</td>
</tr>
</tbody>
</table>
3 Feedstocks

3.1 What are Feedstocks?

Carbon tetrachloride (CTC), 1,1,1-trichloroethane (TCA or methyl chloroform), chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) can serve as chemical building blocks in the preparation of other chemicals. In their use as a raw material, they are converted to other products except for minimal residues. As a result, their environmental impact is avoided with the exception of very small amounts. These could be residual levels in the ultimate product (which are typically miniscule) or by fugitive leaks in the production, storage and/or transport processes.

The Montreal Protocol defines “Production” as follows: “Production means the amount of controlled substances produced, minus the amount destroyed by technologies to be approved by the Parties and minus the amount entirely used as feedstock in the manufacture of other chemicals. The amount recycled and reused is not to be considered as Production.” Based on this definition, substances controlled by the Montreal Protocol are not subject to phaseout regulations while being used in feedstock applications. Therefore, it is expected that production of some of these controlled substances will continue for the foreseeable future.

3.2 Where they are Used

CTC, CFCs and HCFCs can be feedstocks either by being fed directly into the process as a raw material stream or they can be produced as an intermediate in the synthesis of another product. Losses can occur during production, storage, transport, if necessary, and transfers. Intermediates are normally stored and used at the same site and so fugitive leaks are somewhat lower in this case.

Common feedstock applications include, but are not limited to the following:

- Conversion of HCFC-21 in the synthesis of HCFC-225 which finds application as a solvent
- Conversion of CFC-113 to chlorotrifluoroethylene. The latter is subsequently polymerized to polychlorotrifluoroethylene, a barrier resin used in moisture-resistant packaging.
- Conversion of CFC-113 and CFC-113a to HFC-134a and HFC-125. As this is the route to much of the HFC volumes, it is a high volume use.
- Conversion of HCFC-22 to tetrafluoroethylene (TFE). TFE forms the building block of many fluoropolymers both by homopolymerization and copolymerization. This is a very high volume use.
- Conversion of 1,1,1-trichloroethane (through 1,1-dichloroethylene) to HCFC-141b and HCFC-142b. This can continue until 2040 at high volume for emissive uses of these products and can continue long-term for uses related to conversion to polymers as noted below.
- Conversion of HCFC-142b to vinylidene fluoride which is polymerized to polyvinylidene fluoride or to copolymers. These are useful as specialty resins and elastomers. This use of HCFC-142b is not subject to phaseout and is likely to continue long term.

- Conversion of carbon tetrachloride (CTC) to CFC-11, CFC-12, etc. This has historically been a very high volume application. However, as the phasedout of CFC production continues, volumes of CTC for this application will diminish.

- Conversion of HCFC-123 in manufacture of pharmaceuticals which is a long term use not subject to phaseout.

- Conversion of HCFC-123 to HFC-125. While this usually occurs as an intermediate, it is possible that this could be done using HCFC-123 as a starting material. We are not aware of using HCFC-123 as a starting material at this time.

- Conversion of methyl bromide in the production of non-ionic detergents.

- Conversion of trifluoromethyl bromide (CF3Br or Halon 1301) in manufacture of pharmaceuticals.

Recently the HTOC raised a question about use of Halon 1301 as a feedstock. The CTOC investigated this matter and reported the finding that Halon 1301 is very useful feedstock for preparation of bioactive compound in the 2006 TEAP Progress Report. Trifluoromethyl thiophenol, trifluoromethyl trialkylsilanes, trifluoromethyl sulfenyl chloride and trifluoromethyl sulfonic acid are very important intermediates for preparation of agricultural chemicals and pharmaceuticals, and those compounds are all prepared from trifluoromethyl bromide (Halon 1301). In a particular case, Fipronil, a broad-spectrum insecticide used to control multiple species of thrips on a wide range of crops, is produced by treatment of specifically substituted pyrazole with trifluoromethyl sulfenyl chloride or by another suitably substituted pyrazole with trifluoromethyl bromide. In China both of processes are in operation in agricultural companies. The estimated annual production volume of Fipronil is about 400 tonnes in China and at least 800 tonnes in Germany.

3.3 Estimated Emissions of ODS

The IPCC recommends that emissions can be estimated from production facilities at 0.5% for HFCs and 0.2% for SF6. This includes fugitive and transport emissions. If one accepts that 0.5% is an appropriate guidance level for products transported and used as raw materials, calculations from 2002 production data suggest that:

ODS used in production of HFCs = 334,000 tonnes
Emission volume of ODS = 1670 tonnes
ODP impact of emissions = 1336 ODP tonnes

Production of fluoropolymers = 225,000 tonnes
Emission of ODS = 1125 tonnes
ODP impact of emissions = 62 ODP tonnes
Methyl chloroform used in production of HCFCs = 95,000 tonnes (2003)
Emission volume of ODS = 475 tonnes
ODP impact of emissions = 48 ODP tonnes

CTC used in production of CFCs = 107,000 tonnes (yr. 2000)
Emission of ODS = 214 tonnes
ODP impact of emissions = 235 ODP tonnes

These data are only for emissions associated with manufacture and do not include any emissions related to uses. Therefore, total emissions from feedstock use are on the order of 3500 tonnes and contribute about 1619 ODP tonnes.
4 Laboratory and Analytical Uses

Any consideration of laboratory and analytical uses of methyl bromide needs to be informed by previous decisions of the Parties concerning all Ozone Depleting Substances (ODS). Decision VII/11 included several clauses of direct relevance to the present discussion. These were: (i) adoption of the illustrative list of laboratory uses shown in Annex IV of the report of the Seventh Meeting of the Parties, (ii) exclusion of several uses of ODS from the global exemption (of relevance here are use for preservation of publications and archives, and sterilization of materials in a laboratory), (iii) replacement of ODS wherever possible in standard procedures, and (iv) agreement that controlled substances used for laboratory and analytical purposes should meet the standards for purity as specified in Decision VI/9.

The purity standards and other requirements placed on laboratory and analytical uses are given in Annex II of the report of the Sixth Meeting of the Parties including the following: (i) purity requirement for ‘other controlled substances with boiling point below 20°C and of at least 99.0%’; (ii) criteria that controlled substances for laboratory and analytical uses shall be supplied only in re-closable containers or high pressure cylinders smaller than three litres or in 10 millilitres or smaller glass ampoules; and (iii) advice concerning preparation of mixtures containing the controlled substances, labeling, recovery and reuse, and annual reporting of activities.

The intention behind Annex II of the report of the Sixth Meeting of the Parties seems to restrict the use of relevant ODS to analytical and laboratory synthesis applications, and effectively to exclude its use in many other situations. For example, the high cost and inconvenience of using small containers of CFC-12 would discourage the use of the substance to recharge automobile air conditioners designed to use CFC-12 but not yet retrofitted to use ozone-safe refrigerants. Thus, the high purity standard, carrying with it increased cost, and the restriction on the size of container in which the substance can be supplied, militate against the use of such material in large scale operations.

Under Decision IX/17 an Essential Use Exemption for laboratory and analytical uses of ODS was introduced. Decision X/19 extended this exemption until 31 December 2005. Decision XV/8 asked TEAP to report annually on the development and availability of laboratory and analytical procedures that can be performed without using the controlled substances in Annexes A, B, and C (groups II and III).

In 2003, the Fifteenth Meeting of the Parties, in Annex 1.B, approved the essential use of 1.025 metric tonnes CFC-113 and CTC for Poland in 2004.

4.1 Methyl Bromide

Under Decision XVII/10, the Parties agreed to consider certain uses of methyl bromide as laboratory and analytical uses for the year 2006. In that same decision, Parties requested the TEAP to review those and other potential laboratory and analytical uses of methyl bromide, and, at the same time, to consider the criteria that had been previously adopted for laboratory and analytical uses of Annex A, B and C substances, in order to assess their relevance of those criteria to the laboratory and analytical uses of methyl bromide. The TEAP was requested to report to the 26th OEWG in 2006. The following details are drawn from that review.
Laboratory Uses

Methyl bromide is one of the most chemically reactive of the ozone depleting substances, and it finds use in laboratories where the synthesis of organic chemical substances is studied. The chemical bond between the bromine and the methyl group is easily broken, and the usual outcome of such a chemical reaction is the transfer of the methyl group to the molecule of some other chemical reactant at the point where its molecule contains a nitrogen, oxygen, sulfur or phosphorus atom. Transfer of the methyl group to carbon or a metal is also possible in certain cases. In all such reactions the methyl bromide is referred to as a ‘methylating agent’. Such reactions are carried out in research laboratories of universities, institutes and industry. In a typical case, methyl bromide (MeBr) may react with an amine, R3N: to give a quaternary ammonium salt with structure R3MeN⁺ Br⁻. This same kind of reaction is conducted on an industrial scale for the preparation of substances with particular desired properties. In such cases methyl bromide is classified as feedstock and would not meet the requirements for exemption as a laboratory or analytical use. Methyl bromide is also used in research laboratories for transfer of the methyl group via an organometallic intermediate such a Grignard reagent as CH₃MgBr. Alternatives are available for many of these uses, and they often come into use when supplies of methyl bromide held in research laboratories are exhausted and difficulty is encountered in the purchase of quantities of 10-20 kg, as had been past practice. In formation of Grignard reagents, methyl iodide is often a suitable replacement, and this substance along with other methylating agents such as trimethyl phosphate, dimethyl sulfate or methyl sulfonates can also be used in other procedures. If bromide salts are explicitly required as products, then anion exchange of the initial product (iodide, phosphate, sulfate or sulfonate) would be required and no controlled substance would be required for this step.

Thus, alternatives are usually available to the use of methyl bromide in synthesis although some modification to experimental methods may be needed when the published procedure being followed was based on the use of methyl bromide. However, such replacement needs not be a priority due to small scale and essentially non-emissive in use.

Analytical Uses

Replacements for methyl bromide in analytical applications can be more difficult to find, but uses of this type are generally on a larger scale and there may be significant emissions. This is especially while methyl bromide uses continue to be permitted (CUN, QPS) and there are requirements for calibration or comparison with potential replacements. The following cases were considered as representative of such uses.

- Experiments reported by one Party involved the treatment of goods such as mattresses, toys, and medical devices to see how much methyl bromide is retained after fumigation. The amounts needed were minute. Similarly, small quantities of methyl bromide have been used in testing for gas distribution in commodities and for plant damage during fumigation.
- Methyl bromide may be needed as a calibrant for analytical purposes, including calibration of instruments involved in fumigation trials in which an alternative is to be benchmarked against MB, for determining residue levels, for measurement of levels at fumigation sites, and for studies of emissions from fumigation chambers or films - virtually impermeable and low permeable films (VIF and LPF, respectively).
• Methyl bromide may be used as a test gas to measure sensitivity of organisms, in particular where levels of effectiveness are to be determined for quarantine purposes, and where newly identified organisms are studied or where damage to plant material or retention in commodities is being studied.
• Methyl bromide may be used in a small gas chamber to disinfect plants which may be used as host for biological control by known organisms (a range of - possibly unidentified - organisms having been eliminated by the methyl bromide treatment).
• Methyl bromide may be used as a test gas for toxicological studies such as those for inhalation toxicology associated with permitted uses, including tests of its retention in an activated carbon canister.
• Methyl bromide must necessarily be used as a calibrant when testing for recycle and destruction of MB.

In all of these applications, many of which are emissive uses, the scale of the operation may vary greatly. The criterion of scale as specified in Annex II of ‘reclosable container or high-pressure cylinders smaller than three litres’ could be maintained for methyl bromide laboratory and analytical uses. The option is available, as observed above, to include any larger quantities in a Critical Use Nomination.

One of the uses of methyl bromide which was reviewed was a field trial to evaluate its effectiveness for soil disinfestations and to benchmark alternatives. The weight of opinion is not in favor of classifying such a trial as a laboratory or analytical use. For the field trial to be of any extent, a large number of 3 litres or 10 millilitres containers would need to be opened and this goes against the spirit of the exemption but these sizes would be adequate for QPS test purposes. For such operations, any methyl bromide required could be included by the Party in the Critical Use Nomination, and one Party is known to do this.

4.2 Other ODSs

Laboratory Uses

There has been only slow progress in replacing ozone depleting substances (ODS) that are used in laboratory and analytical procedures with substances that are less harmful to the ozone layer. In most cases this is due to the availability of ODS at favorable prices under the EUE and failure of alternative candidates to meet the demanding specifications that have brought about the use of ODS in the first place. Some information about laboratory uses has been obtained from research laboratories in universities, research institutions and industry laboratories. The ODS may play the role of reaction solvent, such that if the situation were an industrial one, and use commenced before June 1999, there would be a case for classification of the ODS use as Process Agent. It is likely that alternative solvents could be found to allow the disuse of ODS in these situations. In other laboratory uses, the ODS would be regarded as feedstock, since it is wholly or partly destroyed in the reaction as a result of the incorporation of all or some portions of the ODS molecule into the product of the chemical reaction. This would be the case, for example, where carbon tetrachloride (CTC, CCl₄) was used in a free radical-initiated reaction which results in the incorporation of a CCl₃- fragment into a new molecule. In such cases the ODS play unique roles which depend on the fine details of their chemical structures and on the reactivity of the groups of atoms they contain, and so it is difficult to see how they could be replaced in these reactions by alternative, non-ODS substances. In general, compared with industrial uses and their concomitant emissions, the emissions of ODS from these laboratory uses are very small and therefore not of major
concern under the Montreal Protocol. Opportunities to reduce the use (and therefore emissions) of ODS in Preparative and analytical laboratories will arise as adoption of Green Chemistry practices – good laboratory practices and environmentally sound management of chemical reactions - spreads from the initial development in the USA and could eventually be enshrined in regulation.

**Analytical Uses**

A similar situation is found with analytical uses, although few of these have quite the specificity of the preparative uses of ODS. Some changes have been reported where the ODS was formerly used as a solvent just because it possessed convenient properties such as solvent power and liquid range (difference between freezing and boiling point). There is one ASTM method, for the analysis of volatiles in coal, in which CTC has been replaced by hexane. Compilations of standard methods such as those maintained by the American Society for Testing Materials (ASTM), the United States Environmental Protection Agency (US EPA), and the United States National Institute of Occupational Health and Safety (US NIOSH) and probably others would need to be searched for cases where ODS are employed in testing and analyses, and investigations made of possible replacements. This would be a major task, and there are reasons of cost as well as the desire of the relevant professional community to maintain consistency of the reporting of analytical results that such a search has not been undertaken. CTC is used in analyses for total hydrocarbons extracted from water, wastewater and sediments, using method ASTM D-3921, with quantitation by means of infrared (IR) spectroscopy. Similarly, it is used in hydrocarbon extraction from water and soils, by method APHA AWWA-WPCF 5520C (IR method). CTC is also used in iodine value (Wijs method) determination of fats and oils, by method AOCS Cd 1b-87, and in simeticone extraction and cleaning of NaCl cells for FTIR analysis and in viscosity coefficient determination. CTC also finds use as a solvent in nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy, for example in method USP XXIII in pharmacy. It is used as a gas chromatography (GC) standard in method EPA 1311, for waste analysis by TCLP (Toxicity characteristics, Leaching Procedure), and for determination of specific weight of cement, according to the one national method although this use can be replaced by kerosene or gasoline. 1,1,1-Trichloroethane (TCA) is used in bromine index determination of hydrocarbons by potentiometric titration (ASTM D 2710-99 and ASTM D 2710). CFC-113 is used in oil, grease and hydrocarbon determinations from wastewater with quantitation by partition infrared method No 5520C (Standard Methods for Water and Wastewater), and for hydrocarbon extraction from water (ASTM D 3921). In some cases known to the TEAP, there are special features of the analytical procedure that would make it hard to replace the ODS with an alternative non-ODS substance. Such is the case in tests in which petroleum hydrocarbons are collected and dissolved in CFC-113 (CCl2F-CF2Cl) before estimation of the amount of hydrocarbon by means of infrared spectroscopic analysis. The key requirement for the test is that the solvent, CFC-113, have no infrared absorption in the region where C-H vibrational frequencies are found, so that a clear assay can be made of the intensity of the hydrocarbon C-H peaks. Alternatives solvents with no C-H bonds are either ODS (such as CTC) or substances such as carbon disulfide which is unlikely to be adopted because of its high volatility and on the grounds of its occupational health and safety features including flammability, toxicity and unpleasant odor. Preliminary data from a survey in one Article 5(1) country showed that analytical uses of CTC, TCA and CFC-113 amounted to 10-20 litres per year, with typical analyses employing 100-200 millilitres.
Surveys of Use

In 1996 the United States EPA compiled a list of institutions that develop laboratory standards, procedures, instructions and regulations that require the use of ODS, and also a list of those institutions that are investigating, researching or developing alternative procedures that do not require ODS. A section of the report listed 45 procedures that employed ODS (CTC, CFC-11, TCA, CFC-12, CFC-113, bromochloromethane, and HCFC-21), thus bringing to attention some opportunities for substitution.

A report commissioned by the EC and received in 2005 identified 125 laboratory procedures in which ODS were used – CFC-113>CTC>TCA, with smaller quantities of other CFCs and halons – mostly in extraction steps. The laboratory uses of ODS in 2003 totaled 9.933 ODS tonnes. It was estimated that this figure could be reduced by 37% by 2008 through the use of feasible non-ODS alternatives.

Reports to Ozone Secretariat

The reports of laboratory uses of ODS received by the Ozone Secretariat in the period 2002-2005 are summarized in the table below. Small quantities (<0.005 MT) of CFC-12, CFC-124, BCM and HBFC-2281 are not included in the table.

Laboratory Uses of Quantities of Ozone Depleting Substances (MT) Reported to the Ozone Secretariat

<table>
<thead>
<tr>
<th>Year</th>
<th>Parties Reporting</th>
<th>Category</th>
<th>CTC</th>
<th>CFC-11</th>
<th>CFC-113</th>
<th>Methyl chloroform (TCA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005</td>
<td>1</td>
<td>Production</td>
<td>47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Import/consumption</td>
<td>0.78</td>
<td>0.02</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2004</td>
<td>4</td>
<td>Production</td>
<td>81.7</td>
<td>54.9</td>
<td>2.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Import/consumption</td>
<td>5.09</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>1.81</td>
</tr>
<tr>
<td>2003</td>
<td>4</td>
<td>Production</td>
<td>69.2</td>
<td>3.12</td>
<td>9.50</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>Import/consumption</td>
<td>3.23</td>
<td>9.50</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>2002</td>
<td>3</td>
<td>Production</td>
<td>85</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>9.11</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>Import/consumption</td>
<td>16.52</td>
<td>9.11</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5 Aerosol Products, Non-medical

Worldwide aerosol fillings have grown over the last years and were close to 11 billions cans in 2005, the largest number ever. Today more than 99.5% of non MDI aerosols use non-CFC formulations worldwide.

In 2005 the residual CFC consumption in the sector was only due to the use in Article 5 countries. It is expected that the completion of global CFC phase-out in non-MDI aerosols will occur in the very short term as the reduction schedule mandated by the Montreal Protocol comes into force in Article 5 countries.

There are no technical barriers to global transition to non-ODS alternatives in all non-MDI aerosol applications, which require either low flammability or specific pharmaceutical approval.

Currently available alternatives for CFCs used in non-MDI aerosols as propellants covers hydrocarbons (HAPs), dimethyl ether, HFCs, HCFCs and compressed gases (CGs).

There are many alternatives to replace ODS used either as solvents or as active ingredients in non-MDI aerosols. These replacements can be hydrocarbons, high boiling HFCs like HFC-4310mee, and HFC-245fa, high boiling HCFCs like HFC-141b, and other solvents like HFEs or even water. The suitability of the alternative depends heavily on the specifics of the formulation.

Many aerosol products have been replaced by such not-in-kind substitutes as mechanical pumps (finger or trigger pumps), sticks, roll-ons, brushes, etc.
6 Carbon Tetrachloride (CTC)

Decision XVI/14 entitled “Sources of carbon tetrachloride emissions and opportunities for reductions” requests the Technology and Economic Assessment Panel to assess global emissions of carbon tetrachloride being emitted from a range of different sources.

Carbon tetrachloride can be produced by three main processes (chloromethane, perchlorination and CS₂ processes), all of which involve the reaction of elemental chlorine with substances having 1-3 carbon atoms in their molecules.

Carbon tetrachloride was initially used as a solvent, notably in dry-cleaning and metal cleaning applications (where there is still believed to be small residual use in DPR Korea for instance), but its feedstock applications into fluorocarbons are the most important. At its peak in 1987, when CFC-11 and CFC-12 production exceeded 800 kilo tonnes, CTC production was over 1 million tonnes. More recently, CTC has been used as feedstock for the production of a number of HFCs.

There are, or have been, some process applications for CTC notably in the manufacture of chlorinated rubbers and paraffins (which continue in China and India, for instance), and there are a number of designated essential uses into pharmaceutical and agrochemical applications, and in chlorine plants.

There is a large list of approved process agent uses for CTC that is under constant review by the Meeting of the Parties to the Montreal Protocol as alternative process agents gain acceptance. These applications are described in Table A of Decision XVII/7 and in Table A-bis of Decision XVII/8.

Calculated CTC Demand 2002-2009

The calculation for the CTC demand 2002-2009 was based on the CFC production for basic domestic needs for the period 2003-2009, an estimate of the “make-up” figure for process agent use contained in Decision X/14, and a forecast of the CTC use as a feedstock for HFCs through to 2015 on the future requirements of the foam insulation market (IPCC/TEAP Report, 2005). (cf. TEAP Progress Report 2006, p78-90)

Estimated total CTC requirements for assumed demands (tonnes)

<table>
<thead>
<tr>
<th>Year</th>
<th>2002</th>
<th>2003</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFC Feedstock</td>
<td>126,240</td>
<td>108,425</td>
<td>96,837</td>
<td>74,903</td>
<td>51,353</td>
<td>26,476</td>
<td>21,441</td>
<td>14,247</td>
<td>0</td>
</tr>
<tr>
<td>Emissive uses</td>
<td>36,426</td>
<td>33,784</td>
<td>30,700</td>
<td>32,958</td>
<td>34,636</td>
<td>36,414</td>
<td>38,299</td>
<td>40,297</td>
<td>41,920</td>
</tr>
<tr>
<td>Other Feedstock</td>
<td>3,295</td>
<td>23,649</td>
<td>32,412</td>
<td>38,231</td>
<td>42,342</td>
<td>44,399</td>
<td>46,422</td>
<td>48,376</td>
<td>50,285</td>
</tr>
<tr>
<td>TOTAL</td>
<td>165,961</td>
<td>165,858</td>
<td>159,949</td>
<td>146,092</td>
<td>128,331</td>
<td>107,289</td>
<td>106,162</td>
<td>102,920</td>
<td>92,205</td>
</tr>
</tbody>
</table>

The possible CTC emissions from these requirements were calculated between 13,728 and 21,960 metric tonnes in 2006 with reasonable assumptions.
Atmospheric Concentrations of CTC

According to the back-calculations based upon new findings from the observed CTC concentrations reported in the international Scientific Assessment of Ozone Depletion: 2002 (Montzka and Fraser), annual CTC emissions peaked at approximately 130,000 tonnes in the mid-1980s, but then declined to about 80,000 tonnes by the late 1990s. Given the range of lifetimes considered for CTC, these figures could involve uncertainties of ±30%. Recent data from the IPCC/TEAP Report, 2005, estimate emissions in 2002 to be 64,000-76,000 tonnes. In summary, the calculated annual emissions are:

- Mid-1980s maximum: 130±40 kilo tonnes
- Late 1990s: 80±25 kilo tonnes

There is an emerging conclusion that the discrepancy between emission data calculated from atmospheric concentrations and those derived from consideration of industrial activity is due to under-estimation or under-reporting of the latter.

The foregoing conclusion may need reconsideration if the behavior of CTC in the atmosphere is reassessed by the Science Assessment Panel. As for additional formerly unrecognized sources, there is the possibility that CTC is emitted from landfills, which have come to attention recently as temporary sinks from which a number of chemical substances can be released to the atmosphere. In the case of CTC, the substance might have entered the landfill as a component of wastes, or possibly been generated in the landfill by chemical or (more likely) microbiological action. No reports are available of such emissions but the attention being paid to landfills in recent times could provide confirmation or refutation of this hypothesis.

Three potentially significant areas require further investigation to get better data for industrial emissions in Article 5 and non-Article 5 countries to enable resolution of the discrepancies with atmospheric measurements; the first area is that of CTC production in order to identify, in particular, the production of CTC as a by-product and its subsequent use, re-cycling or destruction; the second area is to identify any other requirements for CTC and the third is the emission of CTC from sources such as landfills.
7 Solvents

7.1 Background

On an ozone-depletion weighted basis, solvents constituted approximately 15% of the market for chemicals targeted for phase-out under the Montreal Protocol. Of the four most common ODS chemicals used as solvents – CFC-113, CFC-11, carbon tetrachloride (CTC) and 1,1,1-trichloroethane (TCA; also known as methyl chloroform) – the vast majority of use in non-Article 5 countries consisted of CFC-113 and TCA in industrial applications and used in industrial cleaning equipment. Use of CTC was predominately in dry cleaning of textiles or in cold cleaning, although it was – and still is – used in hot spray cleaning in a few Article 5 countries. The three major end uses that in the past employed CFC-113 and TCA were metals cleaning, electronics cleaning, and precision cleaning. Metals cleaning applications usually involve removing cutting oils and residual metal filings from metal surfaces, and the maintenance and repair of equipment and machinery. This sector relied principally on TCA. Precision and electronics cleaning used mostly CFC-113. Electronics cleaning, or defluxing, consists mainly of the removal of flux residue that remains after a soldering operation for printed circuit boards and other contamination-sensitive electronics applications. Other electronics applications include the development of wet and dry film photo-resists with TCA, but these materials have been largely replaced by products developed in basic aqueous solutions or oxygenated solvents.

The Solvent Technical Options Committee’s 1998 report estimates that 90% of ODS solvent use (based on the peak consumption of 1994-95) has been reduced by substitution to not-in-kind technologies and conservations. The remaining 10% of the ODS market is shared by several organic solvent alternatives. In non-Article 5 countries, almost all ODS solvents (CFC-113, CFC-11, CTC and TCA) have been eliminated by either not-in-kind technology (no-clean flux, aqueous, semi-aqueous or hydrocarbon solvents) or other organic solvents.

7.2 Not-In-Kind Alternatives Options

These are numerous including no-clean, aqueous, hydrocarbon and oxygenated solvents and correspond to the fragmented market with a large number of small users in very diverse industries. Each presents “trade-offs” between effectiveness in use, cost, safety, and environmental properties.

No-clean: The use of no-clean flux is the preferred option in electronics and can be used for practically all types of printed circuit boards even for some applications in aerospace, aeronautics and military (recognizing the crucial reliability and safety issues). Even high tech printed circuit boards for automotive controls use it in their vast majority (>70%), but this approach requires very tight control of incoming materials, adapted chemicals for soldering and skilled operators to master the process. Overall 85% of printed circuit boards were assembled with a no-clean process, in developed as well as in developing countries (IPC, 2004). Total process costs are reduced and environmental impact is very low with no direct greenhouse gas emissions. However, there is now a significant trend, with increased miniaturisation of electronics and the use of lead-free soldering, requiring higher soldering temperatures, for a resurgence of the need for cleaning. Often, such cleaning is very difficult because of small component spacing and stand-off. It has been shown that lead-free soldering without cleaning may seriously engender a number of reliability problems, such as the formation of dendrites and conductive anodic filaments.
Also classed as “no-clean”, evaporative machining, drawing and pressing lubricants enjoy some popularity for metal working. They are generally suitable for some applications where it is possible to capture Volatile Organic Compounds (VOCs) before they are emitted outside the place where they are used. Some of them may have moderately high Global Warming Potentials (GWP).

**Hydrocarbon solvent cleaning:** This process has proven to be a good solution with paraffin hydrocarbon formulations; cleaning is efficient but the non-volatile or less-volatile residues can be incompatible with some downstream manufacturing or finishes. Some cases of materials incompatibility are also known. Their environmental impact is low (low GWP, no ODP) but they are generally classified as VOC. Their toxicity is also low. Due to their combustibility (flashpoint > 55°C), they have to be used in open tank equipment at a temperature at least 15°C below their flashpoint. After cleaning, rinsing has to be done by fresh solvent. To reduce the solvent consumption it is recommended to recycle on site by vacuum distillation. In some cases, safety considerations and emissions reduction demand a closed machine with a vacuum system. This is not always compatible with high throughput processes. Their use in precision mechanics (injectors, bearings etc.) has developed in the last 3 years, but it involves a drastic change of process and medium to high investment as well as good training of the operators.

**Oxygenated solvent cleaning:** Oxygenated organic solvents are compounds based on hydrocarbons containing appendant oxygen (alcohols and ketones), integral oxygen (ethers), or both (esters). These substances have been used for many years in diverse cleaning applications. Their cost and environmental impact are low (low GWP, no ODP) but they are classified as VOCs and may contribute to ground level ozone pollution. Many of the oxygenated compounds are flammable as neat products or the mixture may become flammable in use, hence precautions for handling flammables must be considered, e.g. explosion proof equipment.

**Aqueous cleaning:** These processes can be good substitutes for metal degreasing or even precision cleaning when corrosion of the materials is not an issue. For some tasks, where finish is a crucial issue, the number of required washing and rinsing baths and the quality of the water might be a deterrent. The availability of good quality water and water disposal issues need to be taken care of, right from the start of the process conception. Some aqueous cleaning processes have a low environmental impact (no VOC, low GWP, no ODP) and a low toxicity. However, others involving additives may emit VOCs and use toxic and corrosive chemicals. As a general rule, all aqueous processes require waste water treatment and some of the recovered pollutants are hazardous waste and must be disposed of according to national or state regulations. The process is generally not forgiving; any error in operation or maintenance could result in quality problems. Investment costs can be high but operating costs are generally lower than those with solvents alternatives.

### 7.3 In-Kind Alternatives

The primary in-kind substitute for 1,1,1-trichlorehthane (TCA) and CTC has been the chlorocarbon alternatives such as trichloroethylene, perchloroethylene and methylene chloride. These substitutes have very small (0.005-0.007) ozone depletion potential, generally classed as zero-ODP, and similar cleaning properties. Also, a brominated solvent, n-propyl bromide, introduced a decade ago, has similar properties as the chlorinated ODS solvents and
has taken a significant market share for defluxing, general cleaning and adhesives applications. n-Propyl bromide is ozone depleting and is considered as toxic (see below).

The in-kind substitutes for CFC-113 and CFC-11 are fluorinated alternatives such as hydrochlorofluorocarbons (HCFC-141b and HCFC-225ca/cb), perfluorocarbons (primarily C6F14), hydrofluorocarbons (HFC-43-10mee, HFC-365mfc and HFC-245fa, HFC-c447ef) and hydrofluoroethers (HFE-449s1, HFE-569sf2). HCFC-141b and HCFC-225ca/cb have properties similar to TCA and CFC-113 respectively; hence, have been preferred where in-kind alternatives were required. In particular, HCFC-141b with its low cost and good solvency initially captured a significant market share of ozone depleting solvents. However, HCFCs are transitional substances due to their ODP. Their use is declining in non-Article 5 countries but still increasing in Article 5 countries.

Most of the electronics cleaning market converted to not-in-kind alternatives such as no-clean processes; aqueous and semi-aqueous cleaning. Oxygenated solvents (e.g. alcohols, glycols, ethyl lactate) also have replaced CFC-113 in some portions of the electronics cleaning market. A very small segment of the market went to the HCFC alternatives and their azeotropic blends.

A part of the metal cleaning applications, particulate removal, medical and miscellaneous also went to aqueous, semi-aqueous, HCFCs and chlorocarbons alternatives. Some of these applications have recently switched to a newer brominated solvent, nPB, an ODS not yet controlled by the Montreal Protocol, although toxicity concerns have limited its development in certain countries. Most of the displacement drying applications switched to either hot air drying or an alcohol-drying system. A part of the drying application sector also went to HCFCs. The cleaning applications (electronics, metal and particulate removal) and carrier solvents are the focus of this section.

In late 1980s and early 1990s, PFCs (primarily C6F14) entered into some of the CFC-113 markets with limited use in precision and electronics and computer disk cleaning and coating. Use was mostly limited, because of cost and the very high GWP, to high-performance, precision-engineered applications where no other alternatives were technically feasible due to performance or safety requirements. Other alternatives such as HFCs and HFEs have been developed with better cleaning performance, significantly lower GWP and lower cost. PFCs are no longer considered technically necessary for most applications except vapour phase soldering and reflow, the cleaning of inertial guidance systems and some computer disk media cleaning and coating.

In the long term, HFCs and PFCs are expected to take a very small share of the ODS solvent market. The IPCC’s 3rd Assessment Report (TAR) projects less than 3% of the possible CFC solvent demand will be replaced by HFCs and PFCs. Some of the reasons for these low uses are the higher cost of HFCs and PFCs, ready availability of other low cost and acceptable alternatives, and limited solvency of the common soils in these solvents. Because of such a low use of HFC and other fluorinated alternatives, the EU Commission does not include any HFC solvent use restriction in its recent proposed regulation on certain fluorinated gases (COM(2003) 492 – C5-0397/03 – 2003/0189 COD).

**Chlorinated Solvents:** Chlorinated solvents such as methylene chloride, trichloroethylene and perchloroethylene have been used for a century in cleaning applications. The implementation of the Montreal Protocol motivated a return to the use of these traditional
solvents. Chlorinated solvents are used as replacements for CTC, CFCs, TCA and HCFCs in a variety of cleaning applications due to their high solvency. While the boiling points of trichloroethylene (87°C) and tetrachloroethylene (121°C) limit their use in some applications, they also provide an advantage in cleaning some soils such as resins and waxes. However, in some instances, the solvent strength of the chlorinated solvents may cause incompatibility with the components to be cleaned. They mostly require the addition of corrosion inhibitors and their use in low emissions machinery has presented a new problem, inhibitor exhaustion. This has resulted in the need for users to titrate the solvent periodically and add fresh inhibitor to maintain the product quality.

The chlorinated solvents are non-flammable but have toxicological profiles that necessitate low exposure guidelines. The time-weighted average (TWA) exposure guidelines for methylene chloride, trichloroethylene and perchloroethylene are 50 ppm, 50 ppm and 25 ppm, respectively. Worker exposure to these solvents needs to be minimised in order to use them safely. EU has reclassified the trichloroethylene as “may cause cancer” (risk phrase R45, July 2002; 22nd amendment of annex of directive 67/548/EEC).

**HFC Alternatives:** There are two HFC solvent alternatives commercially available. They are HFC-43-10mee (C₅H₂F₁₀) and HFC-c447ef (heptafluorocyclopentane;C₅H₃F₇), and two other HFCs are coming into the solvent markets.

HFC-43-10mee is a non-flammable, non-VOC (US definition) solvent with low toxicity. The atmospheric life of HFC-43-10mee is 15.9 years and GWP-100 of 1610. HFC-43-10mee readily forms azeotropes with many desirable alcohols, chlorocarbons and hydrocarbons to give blends enhanced cleaning properties. It has better solvent properties than PFCs. The neat material is used as a carrier fluid, particulate removal and other miscellaneous applications. The blends are used in applications such as precision cleaning, defluxing flip chips and printed wiring board (PWB) and oxygen system cleaning.

HFC-c447ef (C₅H₃F₇) is a non-flammable, non-VOC solvent (US definition) with a boiling point of 82 °C (Zeon Corporation, 2004). Its atmospheric life is 3.4 years with GWP-100 of 250 that is lower than that of most HFCs and some HFEs. However, because of its high freezing point (21.5 degrees C), its neat use is limited. Some azeotropic mixtures with alcohol and ketone or mixtures with terpenes are provided for the application of degreasing of metal parts and flux cleaning of PCBs. The use of this solvent is low and most current users are in Japan, but marketing has started in the US.

Two other HFC candidates, although primarily developed for foam blowing applications, have been promoted in some solvent applications. They are HFC-365mfc (pentafluorobutane) (Solvay, 2004) and HFC-245fa (pentafluoropropane) (Honeywell, 2004).

HFC-365mfc is a non-VOC solvent (US definition) with an atmospheric life (9.9 yrs.), GWP-100 of 782 and very low toxicity (exposure guide of 500 ppm). The manufacturers data sheet (Solvay’s ) indicates it is flammable (flashpoint = -24°C) and, hence, it is used primarily in blends with other non-flammable HFCs or HFEs to suppress its flammability. The current cost of HFC-365mfc is lower than that of other HFCs and HFEs, consequently, its use is increasing to form low cost non-flammable blends (with HFCs and HFEs) for some applications.
HFC-245fa has relatively low boiling point (15°C) which limits its use in conventional degreasers. At this time its use has been limited to aerosol blends; its use in cold cleaning is also envisaged, though also limited due to its rapid evaporation rate.

Although HFCs are available in all regions their uses have been primarily in non-Article 5 countries, due to relatively high cost and importance of high tech industries. Also, with increasing concern about their GWP, uses are focused in critical applications with no other substitute. Therefore, growth is expected to be minimal.

**PFC Alternatives:** PFC solvents such as C$_6$F$_{14}$ have physical properties similar to that of CFC-113. The atmospheric lifetime and GWP of PFCs are very high (C$_6$F$_{14}$ atmospheric lifetime of 3200 years and GWP-100 of 7400). However, the very limited solubility of organic soils in these materials has restricted their use in cleaning to particulate removal and cleaning of fluorinated oils and greases. Due to the high cost, the availability of substitutes and regulations restricting or banning use, PFC use has been limited primarily to niche applications in non-Article 5 countries (Japan, USA and Western Europe) with virtually no use in Article 5 countries or CEIT. For example in the US, PFC use is restricted to only those applications where no other alternative meets performance or safety requirements. In Germany, CFCs, HCFCs, HFCs and PFCs solvent use is prohibited, “except the pertinent authority can allow for high-quality applications provided negative environmental impacts and impacts on the climate are not expected and only if state-of-the-art technology does not allow the use of any fluorine-free solvent.”

Limited published data are available regarding consumption of C$_6$F$_{14}$. Volumes are known to have decreased since mid-1990s due to replacement with lower GWP compounds.

**HCFC Alternatives:** The only HCFC solvents used are HCFC-141b and HCFC-225ca/cb with ODP of 0.11 and 0.025/0.033 and GWP-100 of 713 and 120/586, respectively (IPCC/TEAP special Report, Chapter 2, Table 2.1). HCFC-141b’s major use is in foam blowing, and its use as a solvent represents less than 10% of global use in 2002.

As a solvent, HCFC-141b use in non-Article 5 countries is widely banned, with very few derogations. Use from existing stockpiles is, however, allowed in the US. Now that HCFC-141b inventory is getting low, conversion to non-ozone depleting alternatives has accelerated.

In Article 5 countries, use of HCFC-141b is still increasing especially in China, India, and Brazil, as economic growth rates are high, even if process containment and recycling are developed; it could have exceeded 5000 t in 2002 (AFEAS, 2002). This is often the most cost-effective substitution to 1,1,1-trichloroethane or CFC-113. The decrease in non-Article 5 countries, especially as foam-blowing use is phased out, will lead to production restructuring, which could create shortages in 2010-2015.

HCFC-225ca/cb use has always been directed to niche applications in precision cleaning and as a carrier solvent. Major sales occur in Japan and USA respectively (around 2,000 t in 2002).

The HCFC total consumption phase-out for Article 5 countries is scheduled for 1 January 2040 with a freeze of consumption in 2015. But some countries are accelerating this for solvents (e.g., Malaysia, Thailand) –while applications that utilize HFC or HFE may be
interchangeable transitions from HFCs and HFEs as to hinder conversions. Further barriers to transition occur where complex and crucial components are involved.

**Hydrofluoroethers Alternatives:** HFE-449s\(^1\) and HFE-569sf\(^2\) are segregated hydrofluoroethers with the ether oxygen separating a fully fluorinated and a fully hydrogenated alkyl group. Both of these compounds are used as replacements for CFCs and HCFCs. The pure HFEs are limited in utility in cleaning applications due to their mild solvent strength. However, the HFEs are also used in azeotropic blends with other solvents (such as alcohols and trans-1,2-dichloroethylene) and in co-solvent cleaning processes giving them broader cleaning efficacy. HFE-449s\(^1\) and HFE-569sf\(^2\) are non-flammable and have relatively high exposure guidelines (750 ppm and 200 ppm, respectively) allowing them to be used safely in many cleaning applications. These HFE compounds are available in most regions. The relatively high cost of these materials limits their use compared to lower cost solvents such as the chlorinated solvents and hydrocarbons (UNEP STOC, 2003).

HFE-347pcf: This compound is a non-segregated hydrofluoroether with oxygen separating two partially fluorinated alkyl groups. The material is a new compound and has only recently become commercially available. Very little information is available regarding the performance of this material in cleaning applications.

**Normal-propyl bromide Alternative:** n-Propyl bromide (1-bromopropane, nPB) is a non-flammable, brominated alkane. Its high solvent strength makes it effective in a variety of cleaning applications including both vapour degreasing and cold cleaning. In some instances, n-propyl bromide may be incompatible with the components to be cleaned.

The direct greenhouse gas emissions from n-propyl bromide are very low due to its very low GWP. The ODP of n-propyl bromide varies depending upon the latitude at which it is emitted. The current calculations indicate a range of ODPs from 0.013 to 0.105.

n-PB has low acute toxicity but its complete toxicological profile necessitates a low exposure guideline. Current exposure guidelines set by n-PB manufacturers range from 5 to 100 ppm. The ACGIH has recently reduced its recommended AEL to 10 ppm. However, recent toxicological studies continue to raise concerns regarding its chronic toxicity (both reproductive and central nervous system effects) causing some organizations to suggest even lower exposure guidelines are required to protect workers (CDHS, 2003). The EU has decided to reclassify its toxicity as altering fertility and dangerous for the fetus (risk phrases R60 and R63, amendment in 2004 of Directive 67/548/EEC). There is anecdotal evidence that dermal uptake may cause severe neuropathy.

n-PB is available in most regions, including Asia, with local productions in China, France, Israel, Jordan and the USA. World production capacity for the manufacture of n-PB has continued to increase, resulting in a lowering of bulk prices to a level comparable to the upper range of chlorinated solvents. The global annual production capacity is estimated to exceed 20,000 t, of which about 5,000 t are probably used as a pharmaceutical intermediate or process agent. The consumption, as a solvent, is growing at a rate of 15-20% per year in USA (5,000 t), Japan (1,260 t) and other Asian countries.
In Europe, nPB use has rapidly increased in metal and precision cleaning until 2005 to reach a plateau around 1,200 tonnes; since then it is being progressively phased out because of its labelling reclassification as

R 11 Highly flammable.
R 36/37/38 Irritating to eyes, respiratory system and skin
R 48/20 Harmful: danger of serious damage to health by prolonged exposure through inhalation
R 60 May impair fertility
R 63 Possible risk of harm to the unborn child
R 67 Vapors may cause drowsiness and dizziness.

This substitution is not only due to this classification but also to the 1999 VOC Directive which forces the reduction of emissions of volatile organic compounds.

7.4 Consumption / Emissions

Most solvent uses are emissive in nature with a short inventory period of a few months to 2 years (IPCC Good Practice Guidance, 2001). Although, used solvents can and are distilled and recycled on site, all quantities sold are eventually emitted. The IPCC Good Practice Guidance recommends a default emission factor of 50% of the initial solvent charge per year (IPCC Good Practice, 2002). A report by the U.S. Environmental Protection Agency (USEPA) uses the assumption of 90% of the solvent consumed annually is emitted to the atmosphere (US EPA, 2004). Thus distinction between consumption and emission is typically not significant for these applications.

Emissions Reduction Options

Most of the new solvent handling equipment is designed for very low emissions, partly because of the higher cost of the HFC, PFC and HCFC solvents and partly due to increased environmental awareness and zero or low emission regulations in some countries for all solvents. The new tight machines generally have higher free boards, dual temperature cooling coils, automated work transport facilities, welded pipe joints, hoods or sliding doors, and superheated vapour-drying system. Likewise, it is possible to reduce emissions to a minimal level by implementing good handling practices, such as reducing drag-out losses of solvent from system by keeping the workload in the vapour zone long enough to drain and drop any entrapped or remaining solvent. It is also possible to minimise evaporative losses by improving the design of solvent bath enclosures and of vapour recovery condensing systems. The so-called “zero-emissions” machines employ a chamber to contain the parts to be cleaned. It is then hermetically sealed and the solvent is pumped in to the chamber in hot, cold and vapour phases. A filtered vacuum pump removes any residual solvent before the chamber is opened to remove the cleaned parts. The capital cost is typically 50-100 per cent higher than a modern open-top degreaser but this difference is easily amortised by reduced solvent losses, especially if fluorinated solvents are used. These machines suffer from a lower throughput for a given volume capacity.
7.5 Regulatory Changes

Regulatory changes will continue to impact use of solvents as well as containment, emission, safety, health and recycling requirements. In some cases, they may require solvent and/or equipment change or a new cleaning process. Some of the recent regulatory changes are given below.

European Regulation Changes

It is important to note that HFC solvent uses has not been restricted in any way in Europe by the April 2006 Regulation on F-gases. This information would be clearer to write “Finally it is important to say that not fluorinated solvent uses have not been restricted in any way in Europe by the April 2006 Regulation on F-gases.”

By now the 1999 VOC Directive limiting emission of solvents in industrial uses including surface cleaning, has been fully implemented in EU 15. VOC definition is different from the US one and is: “any organic compound having at 293.15 K a vapour pressure of 0.01kPa or more”.

It sets 2 kinds of limits for VOC components’ emission during use:
- in mg/m3 (from 2 to 75 depending on the type of solvents) in the general aspiration system or chimney of the workshop.
- In % of the total solvent consumption for the “fugitive” emissions (outside the previous system) = solvent lost in air, soil, parts etc.

Spray uses or buckets uses are also being monitored as the companies have to present a yearly solvent management plan showing reductions of total solvents’ emissions. This directive has led, in cleaning, to a partial substitution of “opened” equipment for “semi closed” or “closed” ones with high internal recycling rate. It has also reduced uses of “toxic” products such as n propyl bromide or trichloroethylene as these 2 solvents have been reclassified in the last 2 years.

It forces substitution of these substances or, if it is not possible for technical reasons, it fixes a very low limit in the gas effluents of 2mg/m3.

The new European chemical policy called REACH (Registration Evaluation and Authorization of Chemicals) will come as a new regulation mid 2007. It could impact substances availability for certain uses (including solvents). Finally it is important to note that HFC solvent uses has not been restricted in any way in Europe by the April 2006 Regulation on F-Gases.

Japanese Regulation Changes

PRTR (Pollutant Release and Transfer Register) regulation came into effect in 2002. The law requires reporting of release and transfer of 354 substances including all ODSs and chlorinated solvents.

The other new regulation which will have a major effect in controlling cleaning operation is the VOC regulation. It came into effect from April 2006. The VOC is defined as an organic compound which is a gas when emitted or dispersed into the atmosphere. Solvent cleaning facility having an area where the volatile organic compound contact the air (bath opening) larger than 5 square meter becomes subject to control. The VOCs emitted in industrial cleaning in 2002 was 141,000 tons. Of those VOCs emitted, 66% was chlorinated solvents.
such as methylene chloride (34%), trichloroethylene (23%) and perchloroethylene (9%). Their major emission sources are small and medium size industries. In order to achieve reduction in emission, various combinations of cleaning equipments, operating manuals and peripherals to suit the processes are needed and efforts are made to develop such systems.

In regards to the control of trichloroethylene and methylene chloride in the work area, their concentrations became 25ppm and 50ppm respectively.

7.6 Phase out of Ozone Depleting Substances in Article 5 Countries

The challenges that are facing the world are phase out of ozone depleting substances in Article 5 countries. CFC-113 (chlorofluorcarbon-113), TCA (1,1,1-trichloroethane or methyl chloroform), carbon tetrachloride (CTC) and HCFCs are the ozone depleting solvents which need to be phased out in the future. Substitutes and alternatives have been identified throughout the world and are generally readily available for incorporation into existing processes. The major drawbacks to the implementation are primarily access to information, and knowledge about what are the acceptable alternatives. A second major hurdle to be overcome is the economic considerations. However, the biggest problem is being able to identify the small and medium users.

Solvents account for a significant proportion of the ozone depleting emissions. Chemicals targeted for phase-out under the Montreal Protocol includes CFC-113, TCA, CTC and some HCFCs. Most of these solvents are used in the manufacture of the electronics products; for precision cleaning; to clean metal parts before further processing and as carriers for solvating agents, lubricants, adhesives and speciality coatings.

Progress in achieving the phase-out in Article 5 countries has been good, given the widespread use of ozone-depleting solvents and the variety and complexity of their applications. Of the various uses, the large-scale electronics industry has progressed furthest towards a complete phase-out, although this is not the case with smaller units. Full phase-out for metal cleaning applications is hampered by the large number of small users, many of whom are undercapitalised. In precision cleaning applications, users have been aggressively implementing alternatives. Yet, in some cases, they are still searching for solutions for cleaning precision parts that are especially vulnerable to residues or reactions, or that have unusually stringent cleanliness criteria.

One problem is due to inaccurate identification of solvents, often because of the use of a multitude of trade names which conceal the composition, many parallel commercial chains, undeclared transfrontier commerce and simple ignorance on the part of the small user.

Current Status and Tasks

Information on the status of the phase-out of OD solvents in South and South-east Asia is presented here. This may be a good barometer for some other Article 5 countries. The Montreal Protocol stipulates that a freeze should be implemented on the levels of consumption of CFCs during the period 1999 – 2004. This should be followed by a 50% reduction in consumption with reference to the baseline during the period 2005-2006. The target of 85% reduction with respect to the baseline is expected to be achieved by the year 2009 and a complete phase out is expected by 2010. With reference to the above, it is interesting to observe that a majority of countries have been able to fulfil the 2004 target
particularly in the case of Annex A Group 1: CFCs. Some of the countries are in a critical phase of compliance and are being guided to move away from a non-compliant status. The baseline range is as low as 4.6 ODP tonnes in the case of Maldives to about 58,000 ODP tonnes in the case of China. The former is only a consumer while the latter is a producer and a consumer of CFCs.

A reduction target of 85% with respect to CTC over the period 2005-2009 will be followed by the complete phase out scheduled for 2010. This aspect of ODS consumption appears to be a major challenge with a baseline stretching in quantities in the region from as low as 0.9 ODP tonnes to about 56,000 ODP tonnes in the case of China. Several countries in the region appear to need technical assistance to phase out the use of the significantly large quantities of CTC used as solvents.

TCA (Annex –B, Group-III) is targeted for complete phase out by the year 2015. While the situation with respect to non-compliance is not as severe as compared to CTC, technical assistance appears to be a critical imperative in some of the countries. Consumption is however much lower than that for CTC.

7.7 Choices of Technologies for Article 5 countries

The selection of the alternative should be based on five primary factors. The Alternative Solvent should:

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

The alternatives that should be considered for developing countries are:

- "No-clean", keep-clean
- Aqueous/hydrocarbon-surfactant cleaning
- Organic solvent cleaning (with solvents less toxic than non-ozone-depleting halogenated solvents)
- Non-ozone-depleting halogenated solvents (HFC, HFEs, TCE, PCE)
- Organic solvent cleaning (with solvents more toxic than non-ozone-depleting halogenated solvents)
- HCFC-225
- HCFC-141b
- PFCs

All applications to the Multilateral Fund that propose the use of aqueous or hydrocarbon surfactant cleaning should include funding for pollution prevention, recycling, waste water treatment, shower and eye-wash facilities and drying equipment, as appropriate. Applications that involve the use of organic and hydrogenated solvents should include containment equipment, adequate ventilation control, and/or low emission equipment. The guidelines for all processes should include requirements for personnel safety, for example, the use of eye guards and other personal protection equipment by workers who perform the cleaning operation and means for the measurement of operator exposure.
7.8 Essential Use Nomination

Decision XVIII/8 describes a nomination for Essential Use Exemption of CFC-113 for aerospace applications by the Russian Federation for the years 2007 to 2010. The additional information submitted by the Russian Federation discloses the selection measures and the major applications of CFC-113 as cleaning and degreasing solvent and unsuccessful results of research to find out alternatives to CFC-113 and to apply imported CFC-113 for this purpose.

The CTOC will make a detailed examination of the nomination and report in 2007 by collaborating with rocket and aerospace experts to provide technical support to the Russian Federation during the interim period.
8 Destruction and Other Issues

8.1 Introduction

The recovery and destruction of ODS have been focused and discussed since the discovery of ozone hole and enactment of the Montreal Protocol. The first report “Ad-Hoc Technical Advisory Committee on ODS Destruction Technologies” was reported in May, 1992, followed by the two reports “1993 ODS Destruction Technology Update” in February and “1995 ODS Disposal Technology Update” in June 1995.

TEAP was requested to establish a task force on collection, recovery and storage from all relevant use sectors. The Task Force studied (1) technical feasibility of collection, recovery and storage, (2) inventories and collection potential, (3) economic implication, (4) barrier to collection, recovery and storage. CFCs containing in refrigeration equipment are estimated to be between 350,000 and 400,000 ODP-tonnes in 2002. 1.25 million ODP-tonnes of CFC-11 still remain in installed foams in 2010. Halon 1301 and halon-1211 installed in firefighting equipment are 450,000 and 330,000 ODP-tonnes, respectively in 2002. The barriers to collection, recovery and storage are, for example, (1) lack of appropriate legislation and infrastructures, (2) financial resistance where manufacturer or owner has to pay, (3) ineffective collection of rigid construction foam within building structures, (4) restriction of trans-boundary movements of waste.

TEAP was also requested to establish a task force on destruction technologies to review criteria for approval of the destruction facilities and to assess their environmental and economic performance. In response to these request, the Task Force on Destruction Technologies co-chaired by Sukumar Devotta, Abe Finkelstein and Lambert Kuipers reported in April, 2002 that 16 ODS destruction technologies met the screening criteria among 45 considered. The criteria were destruction and removal efficiency (DRE), emissions of dioxins/furans, emissions of other pollutants (acid gases, particulate matter, and carbon monoxide), and technical capability (scale of destruction).

8.2 Progress Since 2002

Foam End-of-Life

TEAP established the Task Force on Foam End-of-Life Issues, in response to the request of the Parties to provide useful information on handling and destruction of insulation foams and to clarify the distinction between destruction efficiencies for re-concentrated sources and those for dilute sources (Decision XVII/10). The report was mainly focused on the description of the technical and economic aspects of blowing agent recovery and destruction from appliance and building insulation foams. The report in May, 2005 conclude firstly that a new parameter, recovery & destruction efficiency (RDE) which would be valuable to accommodate the whole recovery and destruction chain, and that currently practiced recovery and destruction process have the potential to reach an RDE of greater than 85%-90%. Secondly, the task force considered anaerobic degradation of ODS in case of landfilling (managed attenuation). Thirdly, the economics of recovery and destruction are greatly affected by segregation of foams from other components, infrastructure of transport, and so on. Mechanical separation followed by re-concentrated blowing agent (re-concentrated sources) and direct destruction of the foam including its blowing agent (dilute sources) work well with appliances and steel faced panels, and blowing agents can currently be recovered.
from appliances at a net cost of $25-40/kg. Finally, existing banks of CFCs and HCFCs are estimated to be 1.5 million and 0.75 million tones, respectively. These estimates from bottom-up analysis have confirmed broad agreement at country-level.

**IPCC/TEAP Special Report (Destruction of HFC-23)**

IPCC/TEAP special report was published in 2005. The report described the destruction of a by-product, HFC-23, which is produced in HCFC-22 production by 1.4% to 4.0% and has a GWP as high as 14,310. Global emissions of HFC-23 were estimated to be 15.2 kilo tonnes (218 MtCO2-eq) in 2005 and 23.2 kilo tonnes (332 MtCO2-eq) in 2015 in BAU case. The emissions of HFC-23 were less than 2,025 metric tonnes in EU for 1995 (EFCTC, 2001), 1,690 tonnes for 2002 in US (US EPA, 2004), and 1,124 tonnes for 2004 in Japan (METI, 2004). Emission reduction options are process optimization and capture/destruction. Usually thermal oxidation (incineration) test showed 99.996% of HFC-23 was destroyed. The by-product HFC-23 of 367 tonnes was destroyed in 2003. Assuming a technological life time of 15 year for thermal oxidation installation, specific abatement cost will be <0.2 US$/tCO2-eq.

**Article 5 Countries**

The expert meeting to assess the current and future requirements for the collection and disposition (emissions, export, reclamation and destruction) of non-reusable and unwanted ozone-depleting substances in Article 5 countries was organized by the Multilateral Fund Secretariat and was held in March 13 – 15, 2006 (Decision XVII/18, and decision 47/52 of the Executive Committee of MLF). The committee discussed on foam, halon and refrigerant banks on the basis of recoverable ODS. According to the quantitative results on CFC, halon and CTC regarding banks and annual flow, the total quantity of non-reusable CFCs from refrigeration has assessed as 3,500 metric tonnes. However, CFC blown insulation will be in use after the year 2015. Recovery and recycling from refrigeration would require a well coordinated effort in policy and subsequent infrastructure, since the recovery and recycling of them are viable applications. Recovery and recycling of halons are expected to function well since halons are used for decades and have the residual value due to high demand. There is likely to be an excess of CTC production in the near future, and the excess will need to be destroyed. However, in many cases, ODS recovery and destruction will not be achievable without any additional stimulation which may arise from other environmental agreement and economic imperatives.

**8.3 Synergy among Montreal Protocol, Basel Convention, Rotterdam Convention and Stockholm Convention**

Under the decision XVII/17(3), the TEAP has been requested to review possible synergies with other conventions, such as Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal, the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade and the Stockholm Convention on Persistent Organic Pollutants.

The Conventions included in the International Chemical Agenda as Basel, Stockholm and Rotterdam are related to Montreal Protocol in several issues as environmentally sound management of chemicals and wastes.
One of the main synergies between them exists in the implementation of best practices in order to reduce and eliminate the use of certain chemicals and their waste, also reducing the pollution to the environment.
### Co-chairs

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### Members

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