

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



UNEP

**REPORT OF THE
PROCESS AGENTS TASK FORCE**

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Report of the
UNEP Technology and Economic Assessment Panel
PROCESS AGENTS TASK FORCE

October 2004

The text of this report is composed in Times New Roman.

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Reproduction: UNON Nairobi
Date: October 2004

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ISBN: 92-807-2512-2

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Acknowledgement

The Technology and Economic Assessment Panel, its Technical and Economic Options Committees and the Task Forces Co-chairs and members acknowledges with thanks the outstanding contributions from all of the individuals and organisations who provided support to Panel, Committees and Task Forces Co-chairs and members. The opinions expressed are those of the Panel, the Committees and Task Forces and do not necessarily reflect the reviews of any sponsoring or supporting organisation.

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Executive Summary

This study answers the request of Parties given in paragraph 3 of Decision XV/7: To review the new Process Agent uses that several Parties to the Montreal Protocol requested to be added to Table A, which is contained in Decision X/14 and was updated by Decision XV/6.

Process Agent applications were submitted to UNEP's Ozone Secretariat by Argentina (withdrawn in a later stage), the Democratic People's Republic of Korea, Romania, the United Kingdom and the USA. The list of these Process Agent applications is as follows:

- Bromochloromethane used in the manufacture of Losartan Potassium;
- CTC used for the synthesis of ascorbic acid, the antibiotics ciprofloxacin, norfloxacin, and the herbicides 2,4-D and DHEPC;
- CTC used for the removal of NCl_3 to produce the disinfectant sodium dichloroisocyanurate;
- CTC used for the preparation of radiolabelled Cyanocobalamin ^{57}Co diagnostic;
- CFC-113 used as extraction solvent of the spinning solvent used for the production of high modulus polyethylene fibre.

Process Agent uses of ODS were discussed in the 1995 Report of the Process Agents Working Group, in the 1997 and 2001 Reports of the Process Agents Task Force, and a final update can be found in Chapter 9 of the April 2002 TEAP Progress Report. The criteria set forth in those reports were used to determine whether the applications listed above qualify as new Process Agent uses.

It is the unanimous finding of the Task Force that all the processes reviewed in 2004 meet the criteria defined by the Process Agents Task Force in the 1997 Report. Parties may choose to add these Process Agent uses to Table A previously created by Decisions X/14 and XV/6.

The Task Force also notes that there are opportunities to switch to ODS free alternatives for all Process Agent uses, which have significant emissions of controlled substances and have been reviewed in this report.

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 all Process Agent uses.

1 Introduction

The Parties in Decision XV/7 decided as follows:

To request the Technology and Economic Assessment Panel:

- (a) To review, as mandated by Decision X/14, the list of Process Agent uses in Table A of that decision and to make appropriate recommendations for changes to that table;
- (b) To review requests for consideration of specific uses against Decision X/14 criteria for Process Agents, and make recommendations to the Parties annually on uses that could be added to or removed from Table A of Decision X/14;
- (c) To report to the Open-ended Working Group at its twenty fifth session, and every other year thereafter unless the Parties decide otherwise, on the progress made in reducing emissions of controlled substances from Process Agent uses and on the implementation and development of emissions-reduction techniques and alternative processes not using ozone-depleting substances (ODS).

These requests will ultimately fall under the expertise of the new Chemical Options Committee (CTOC). However, due to the fact that the new CTOC is still being organised, TEAP set up a Task Force that would review the requests for consideration of Process Agent uses submitted by Parties in 2003 and 2004. This report summarises the findings of the Task Force.

The Task Force consisted of the following members:

Nick Campbell, member CTOC, Atofina
Jose Pons, co-chair TEAP and co-chair ATOC
J.G.W. Porre, member CTOC, Teijin Twaron bv
Ian D. Rae, member TEAP and co-chair CTOC
Masaaki Yamabe, member TEAP and co-chair CTOC

Ms. Meg Seki from UNEP's Ozone Secretariat in Nairobi assisted the Task Force in providing the information sent by the Parties and by forwarding requests from the Task Force for more information to the relevant Parties.

The Task Force leaves to the CTOC the following tasks for its first meeting:

- (a) The review of the list of Process Agent uses in Table A of Decision XV/6;
- (b) The evaluation of progress made in reducing emissions of ODS from Process Agent uses, whether by emissions-reduction techniques or by the use of ODS free alternatives;

- (c) The review of data reported by Parties, in accordance with paragraph 4 of Decision X/14, regarding levels of emissions, containment technologies and alternative ODS free processes.

The structure of this report is as follows:

Chapter 2 presents the Decisions and Definitions relevant to Process Agents;

Chapter 3 lists the Process Agent uses submitted by Parties to UNEP and analyses whether the applications reviewed are Process Agent uses;

Chapter 4 presents some general remarks;

Chapter 5 contains the conclusions and recommendations of the Task Force;

Chapter 6 lists the references;

Annex I reproduces the definition of Feedstock and Process Agent given in the 1997 Report of the Process Agents Task Force;

Annex II reproduces the text of Decision X/14;

Annex III reproduces the text of Decision XV/6.

In its April 2002 Report TEAP /UNE02/ recommended that a distinction be made between Process Agent uses when emissions are negligible from those Process Agent uses with non-negligible emissions. The Task Force believes that the range of ODS emissions in the processes reviewed in 2004 (the upper limit being close to 100 MT CTC per year) is further proof of the need for this distinction.

The Task Force understands that, under Decision X/14, the availability of alternatives is an important consideration that affects the definition of Process Agent uses, depending on the location where the use is reported. Parties may wish to consider the advantage of having different tables listing Process Agent uses for Article 5(1) and non-Article 5(1) Parties.

Thus, if a non-Article 5(1) Party reports a Process Agent use for which an alternative has been established, the process could be removed from Table A and the use phased-out. However, if an Article 5(1) Party reports a Process Agent use for which an alternative is known, then the application, if still listed in Table A, could be eligible for funding by the Multilateral Fund. Examples of this dilemma are the use of CTC to manufacture either ascorbic acid or 2,4-D. Inclusion of these processes in Table A by a Decision of the Parties would allow the DPR of Korea and Romania to request funding, in accordance with the rules and guidelines of the Executive Committee of the Multilateral Fund, to adopt the well known ODS free alternative processes, but need not be justification to use the ODS based process in a non-Article 5(1) Party.

2 Relevant Decisions and Definitions

2.1 Decisions

Besides Decision XV/7, the following Decisions are important to understand the concept, complexity, and control of Process Agent uses:

- VI/10: Defines the concept of Process Agent and adopts an interim treatment similar to feedstock only for 1996.
- VII/10: Continues such treatment for 1997 and restricts ODS emissions in Process Agent applications for 1998 and beyond.
- X/14: Notes the differences in emissions between Process Agent uses in non-Article 5(1) Parties and emissions in Article 5(1) Parties. It defines Table A, which lists Process Agent uses and Table B with allowed emissions for those processes for non-Article 5(1) Parties. It continues to treat Process Agents in a manner similar to feedstock for 1998 and until 2001 only in non-Article 5(1) Parties, when emissions have been reduced to the insignificant levels set forth in Table B. For Article 5(1) Parties incremental costs of cost-effective measures to reduce emissions could be eligible for funding by the Multilateral Fund. The complete text of Decision X/14 is included in Annex II.
- XIII/13: Requests the TEAP to report to the Parties at the 22nd Meeting of the Open-ended Working Group.
- XV/6: Revises Table A of Decision X/14 to include 31 processes that use the controlled substances CTC, CFC-11, -12 and -113, and BCM (bromochloromethane). Decision XV/6 is included in Annex III.

2.2 Definitions

The detailed definition of a Process Agent was presented by the Process Agents Task Force in its 1997 Report /UNE97/ and it is reproduced in Annex I of this report. Other definitions commonly used in the chemical process industry that are relevant to understand Process Agent uses are discussed below.

- Make Up: When an ODS is used as a Process Agent, the supply of fresh material that is used to replenish process inventory of that ODS, may not necessarily be fully emitted to the atmosphere. Losses of ODS will include some transformation and /or destruction of the ODS besides emissions; some of which may be delayed because some ODS is present either in the final product or in waste streams.

Make up quantity was defined in the 2001 Process Agents Task Force Report /UNE01/ as “The quantity of controlled substance per year, needed to continue the manufacture of products in a plant, due to transformation, destruction and inadvertent losses (i.e. emissions and residual amounts in final product)”.

- Liquid-liquid extraction: “Is a process for separating components in solution by their distribution between two immiscible liquid phases”. “Since liquid-liquid extraction involves the transfer of mass from one liquid phase into a second immiscible liquid phase, the process can be carried out in many different ways. The simplest example involves the transfer of one component from a binary mixture into a second immiscible liquid phase” / Per97/. CTC, which is an excellent solvent, is immiscible with water and easily separated from water because of its high density; it therefore has found many uses as an extraction solvent. Removal of nitrogen trichloride (NCl_3) from liquid chlorine is an example of liquid-liquid extraction.
- Reaction media: An ODS can be used as the solvent in which a reaction is conducted. The solvent must be stable and non-reactive, it may sometimes stimulate some preferred reactions and therefore promote reaction yield and selectivity to the desired product.

3 Description and Analysis of the Process Agent Uses Submitted in 2003-2004

Table 3-1 on the following page summarises the Process Agent uses submitted by Parties for possible inclusion in Table A of Decision X/14. 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.

Answers providing more information were received from the DPR of Korea and the United States. A letter was also received from Argentina withdrawing its submission because the use of the ODS had been discontinued; however, discussion of the process is included in this report on technical grounds, as it is believed that the same process is used in other countries. Although not all the information requested was available to the Process Agents Task Force, and in one case the concerned Party considered the information on start up date, chemicals and installed capacity as confidential, the Task Force is confident that enough information was on hand for all processes to determine whether they meet the criteria of Process Agent for inclusion in Table A of Decision X/14. Detailed review of each process follows below.

<i>Country</i>	<i>Process Name</i>	<i>Application</i>	<i>Date Presented</i>	<i>ODS Used</i>	<i>Used as</i>	<i>Consumption (tonnes)</i>	<i>Emissions</i>	<i>Alternatives</i>	<i>Emission Abatement</i>	<i>Additional information</i>
<i>Argentina</i>	<i>Losartan Potassium</i>	<i>High blood pressure drug</i>	<i>16.10.03</i>	<i>Bromochloro-methane</i>	<i>Reaction media</i>	<i>20</i>	<i>Not given</i>		<i>75%recycle</i>	<i>Emissions and abatement</i>
<i>DPR Korea</i>	<i>Ascorbic Acid</i>	<i>Vitamin</i>	<i>19.12.03</i>	<i>CTC</i>	<i>Reaction media</i>	<i>75.3</i>	<i>Not given</i>	<i>L-sorbose fermentation</i>	<i>Not given</i>	<i>Emissions and abatement</i>
<i>DPR Korea</i>	<i>Ciprofloxacin</i>	<i>Antibiotic</i>	<i>19.12.03</i>	<i>CTC</i>	<i>Reaction media</i>	<i>16.3</i>	<i>Not given</i>	<i>Solventless chlorination</i>	<i>Not given</i>	<i>Emissions and abatement</i>
<i>DPR Korea</i>	<i>Norfloxacin</i>	<i>Antibiotic</i>	<i>19.12.03</i>	<i>CTC</i>	<i>Reaction media</i>	<i>60</i>	<i>Not given</i>	<i>Solventless chlorination</i>	<i>Not given</i>	<i>Emissions and abatement</i>
<i>DPR Korea</i>	<i>Sodium dichloro-isocyanurate</i>	<i>Disinfectant</i>	<i>19.12.03</i>	<i>CTC</i>	<i>NCl₃ removal</i>	<i>59.6</i>	<i>Not given</i>	<i>Reaction control</i>	<i>Not given</i>	<i>Emissions and abatement</i>
<i>Romania</i>	<i>2,4-D</i>	<i>Herbicide</i>	<i>14.01.04</i>	<i>CTC</i>	<i>Reaction media</i>	<i>99.7</i>	<i>Not given</i>	<i>Perchloro-ethylene</i>	<i>Not given</i>	<i>Emissions and abatement</i>
<i>Romania</i>	<i>DEHPC</i>	<i>Initiator</i>	<i>14.01.04</i>	<i>CTC</i>	<i>Reaction media</i>	<i>73.3</i>	<i>Not given</i>	<i>PVA dispersion</i>	<i>Not given</i>	<i>Emissions and abatement</i>
<i>United Kingdom</i>	<i>Cyanocobalamin ⁵⁷Co</i>	<i>Essay for vitamin B12</i>	<i>13.02.04</i>	<i>CTC</i>	<i>Extraction Solvent</i>	<i>0.008</i>	<i>Same</i>	<i>Needs approval</i>	<i>Currently none</i>	
<i>United States</i>	<i>High Modulus Polyethylene fibre</i>	<i>Ballistic armour</i>	<i>17.06.03</i>	<i>CFC113</i>	<i>Extraction Solvent</i>	<i>Not given</i>	<i>Less than 10</i>	<i>Flammable solvents</i>	<i>99.93% recycle</i>	<i>Provide emissions</i>

Table 3-1 List of Process Agents, which Parties have submitted and were considered by the Process Agents Task Force under TEAP

3.1 Losartan Potassium

Process Agent	Bromochloromethane
Application	Reaction media
Reason Used	Chemically inert, non-flammable, desirable physical properties
Product Use	High blood pressure treatment
Identified Alternatives	None
Submitting Country	Republic of Argentina
Reported Consumption	Typically 20 MT/ year

Losartan potassium is used in the form of tablets to control high blood pressure; it is marketed by Merck under the brand name Cozaar /FDA95/ and known as a generic drug under the name Hyzaar /Hyz04/. It is also manufactured in countries including China and India, although it is not known whether all manufacturing processes rely on the use of bromochloromethane /ZTP04, ZPP04/.

The information received from Argentina, where the chemical is manufactured by Maprimed S.A., was brief, but included two flow diagrams, in which the use of bromochloromethane as a reaction solvent is shown. The raw material mBTT is brominated with N-bromosuccinimide in the presence of catalyst VAZO88 (1,1- Azobis(cyclohexanecarbonitrile)). The reaction products are neutralised with an aqueous solution of sodium bicarbonate and the aqueous phase is further treated for disposal. Bromochloromethane is also used to wash solids present in the organic phase, recovered afterwards by distillation, and recycled to the reactor. A recovery of 75% bromochloromethane is reported.

From the process standpoint, this use of bromochloromethane to extract an organic compound from an aqueous solution could also be done with CTC, as this was one of the most common solvent uses for this chemical in the chemical industry. However, the role of bromochloromethane as reaction media in the bromination reactor is the main consideration to recommend to add this process to Table A.

3.2 Ascorbic Acid (Vitamin C)

Process Agent	CTC
Application	Reaction media
Reason Used	Chemically inert, non-flammable, desirable physical properties
Product Use	Vitamin C
Identified Alternatives	Alternative process by fermentation
Submitting Country	DPR of Korea
Reported Consumption	Average 75.3 MT/ year

The Democratic Republic of Korea reports that, since 1989, it has used a process that relies on technology imported from Romania.

This process comprises a sequence of chemical reactions by which D-glucose is transformed into ascorbic acid. It includes one step, the conversion of L-gulonic acid diketal to L-gulonic acid ethyl ester (removal of ketal protecting group with concomitant esterification of the carboxylic acid function), which is performed with hydrogen chloride (HCl) in a mixture of ethanol and CTC, which is needed for precise control of the acidity of the reaction media. After a reaction period, the ascorbic acid crystallises as the solution is cooled and is separated by centrifugation. 'The mother liquor containing water, ethanol, CTC and hydrogen chloride is discharged into the sewage'. Such discharge would not be permitted in most developed countries and its environmental impact could lead the regulatory authority in DPR-Korea to curtail or eliminate such discharge. A useful flow chart for the process was included with the request.

The request describes an alternative process for production of ascorbic acid from L-sorbose (a readily available starting material) by two stage fermentation with *acetobacter*. This fermentation type of process is used by most manufacturers of ascorbic acid world wide and provides a simple solution to phase-out emissions that are quite significant.

3.3 Ciprofloxacin

Process Agent	CTC
Application	Reaction media
Reason Used	Chemically inert, non-flammable, desirable physical properties
Product Use	Antibiotic
Identified Alternatives	Alternative ODS free processes
Submitting Country	DPR of Korea
Reported Consumption	Average 16.3 MT/ year

Ciprofloxacin is a broad spectrum antibiotic developed by Bayer /BAY04/, which is the main treatment for Anthrax infections. In 2001 the concern for terrorist attacks was a cause for interest in increased production capacity and disputes over compulsory licenses /CPT01/. Although under patent protection, this antibiotic is most likely also produced in Israel, India and maybe China by generic manufacturers. An internet search confirmed that Cipla, Dr. Reddy's Laboratories, Ranbaxy Pharmaceuticals in India and Teva Pharmaceuticals in Israel manufacture ciprofloxacin /Fro01, MSN04/. It is known that Bayer does not use CTC in its production, where the usual process to 1,2-dichloro-4-nitrobenzene is used, i.e., the nitration of 1,2-dichlorobenzene followed by the separation of the isomers.

Since 1992, Hungnam Pharmaceutical in DPR Korea uses CTC as a solvent for the reaction of 1-chloro-4-nitrobenzene with chlorine in the presence of FeCl₃ catalyst (1 hour at 50°C). After the reaction is completed, 'the solvent is removed partially by a distillation and returned to the production cycle'. Cooling the remaining solution causes the intermediate product, 1,2-dichloro-4-nitrobenzene, to crystallise and the solid is removed by centrifugation. Following this, 'the mother liquor', a solution of FeCl₃ and some chloronitrobenzenes, 'is disposed of'. No information is provided as to what this last phrase means. It might mean that CTC is released to the environment, in which case the quantity released may be taken as equal to the make-up quantity, 16.3 MT (metric tonne) average over three years. A useful flow chart for the process was included with the request. For ciprofloxacin and norfloxacin (see section 3.4), the CTC use occurs early in the chain of reactions to manufacture the same intermediate.

Reasons given for using CTC in the production of the intermediate 1,2-dichloro-4-nitrobenzene are:

- Higher selectivity resulting in 5% higher reaction yield, and

- Ease of separation of unreacted 1-chloro-4-nitrobenzene.

The request includes information about an alternative process in which the chlorination is conducted in a melt of 1-chloro-4-nitrobenzene, in the absence of a solvent. To avoid undesired consecutive reactions due to the high viscosity of the melt, precise dosage of reactants, efficient mixing, and improved process control will be required. This will be accomplished by use of a static mixer and computer control of reaction parameters. DPR of Korea expressed its preference to continue using the chlorination of 1-chloro-4-nitrobenzene as the preferred route to obtain 1,2 dichloro-4-nitrobenzene because this raw material is also used as an intermediate in the manufacture of an anti-malaria drug.

Chemical processes in which CTC plays an important role as reaction media as in this case have been granted Process Agent status in the past.

3.4 Norfloxacin

Process Agent	CTC
Application	Reaction media
Reason Used	Chemically inert, non-flammable, desirable physical properties
Product Use	Antibiotic
Identified Alternatives	Alternative ODS free processes
Submitting Country	DPR of Korea
Reported Consumption	Average 60 MT/ year

Norfloxacin is a fluoroquinolone type of broad spectrum antibiotic as is ciprofloxacin. Norfloxacin was developed by Merck and is now a generic product, which is marketed under the brand names Noroxin, Chibroxin, Floxacin and Oramor between other /MPI93, Phi04/. There is generic manufacture in India and China /NeI04, BuW02/. However, it is likely that most manufacturers prefer the nitration of 1,2-dichlorobenzene to produce the 1,2-dichloro-4-nitrobenzene intermediate as happens with ciprofloxacin.

However, in the case of the DPR of Korea, a similar process to that used in the manufacture of ciprofloxacin has been used in the synthesis of norfloxacin since 1991. The first step of the process is the same in each synthesis sequence, as it is shown in the flow chart provided by the Party. In this case, the make-up quantity averaged over three years is 60 MT.

The proposed solution by the Party is to conduct the chlorination reaction in the melt of 1-chloro-4 nitrobenzene under computer controlled conditions and mixing. A more common alternative is the previously mentioned nitration of 1,2-dichlorobenzene to produce the 1,2-dichloro-4-nitrobenzene intermediate.

3.5 Sodium dichloroisocyanurate (DCC-Na)

Process Agent	CTC
Application	Elimination of NCl_3
Reason Used	Safety and quality of product
Product Use	Antibiotic
Identified Alternatives	NCl_3 – free process, emissions control
Submitting Country	DPR of Korea
Reported Consumption	Average 59.6 MT/ year

This chemical is also known as sodium dichloro-s-triazinetriene is a white powder with a strong chlorine odour and is soluble in water. Its main uses are as a disinfectant, industrial deodorant and biocide in water and pool treatment, and it is used in detergents as a sanitiser and as a bleaching agent. This is a common chemical, which is also produced in China by the Hebei Jiheng Group Co., Ltd, although the Task Force does not know whether other processes exist /HJG04/.

DCC- Na has been produced in DPR of Korea since 1982. In one stage of the synthetic sequence leading to this substance, isocyanuric acid in solution in aqueous caustic soda is reacted with chlorine to form the sodium salt of the N, N'-dichloro product. The explosive substance nitrogen trichloride, NCl_3 , is produced as a by-product and is removed from the reaction mixture by extraction with CTC. The aqueous layer containing the desired product and the CTC layer containing the NCl_3 are separated, and the NCl_3 is chemically destroyed by reaction with aqueous sodium thiosulfate. The now-clean CTC is returned to the process.

Some CTC must be lost in the handling of solutions and solids, since a make-up quantity averaged over three years of 59.6 MT is required. A useful flow chart for the process was included with the request. The request mentions an improved process for chlorination of isocyanuric acid without formation of NCl_3 , which has been described in recent patent literature. This improved process relies on exact pH and temperature controls, which require a computerised operating system.

Process Agent status has been granted to similar applications for CTC used to remove nitrogen trichloride by-product formed during electrolytic generation of chlorine from brine. Although the nature of the industrial process being operated in DPR Korea is different, it concerns the same kind of use of CTC, and the Task Force only wishes to express concern about the emission quantity, which seems far too high, at a level of about 60 MT/year. Process improvements could be made to reduce these emissions.

3.6 2,4-Dichlorophenoxyacetic Acid (2,4-D)

Process Agent	CTC
Application	Reaction media and extraction solvent
Reason Used	Non reactive, non-flammable, physical properties
Product Use	Herbicide
Identified Alternatives	Use tetrachloroethene as alternative with improved control
Submitting Country	Romania
Reported Consumption	Average 99.7 MT/ year

2,4-D has been a well-known herbicide for many years, and was a component of the herbicide Agent Orange. 2,4-D belongs to the group of auxin mimics, substances that affect vegetable growth, particularly in broad leaved weeds. Patent protection for this chemical has expired and it can be manufactured freely /WIK04/. Known producers include Akzo Zout Chemie, Nufarm America, Inc., Dow Agrosiences and Aventis; it is almost certain that none of these producers use ODS in their processes. 2,4-D is also produced in Article 5(1) countries like China, where a manufacturer reports production of 2500 MT/year, but it is not known whether this producer uses CTC /LFF03/.

The process described for 2,4-D production in Romania is conducted in three steps that include chlorination of acetic acid in CTC, conversion of the intermediate product α -chloroacetic acid into phenoxyacetic acid, and a second chlorination in CTC to produce the end product 2,4-D.

The purification of the 2,4-D powder necessitates further CTC until the end-product has been washed to the desired purity. The CTC is recovered and recycled, although the flow diagram supplied shows that emissions of CTC to the environment take place in each of the process stages.

An alternative process based on the use of tetrachloroethene instead of CTC is mentioned. This solvent, which is better known as perchloroethylene, results in lower reactivity and selectivity. Therefore, tighter control of the reaction parameters is required to maintain plant production. Although alternatives are available, this specific process uses CTC both as a reaction media for improved yield and selectivity and as an extraction solvent for purification of the end product. This results in the largest emissions of all cases studied in this report.

3.7 Di (2-ethylhexyl) peroxydicarbonate (DEHPC)

Process Agent	CTC
Application	Reaction media and cleansing solvent
Reason Used	Non reactive, non-flammable, physical properties
Product Use	Free Radical Polymerization Initiator
Identified Alternatives	ODS-free synthesis with hydrolised PVA dispersant
Submitting Country	Romania
Reported Consumption	Average 78 MT/ year

The submission indicates that this chemical is an herbicide. However, this information neither fits with the text of the submission, nor matches reported uses. Romania never answered the letter sent by UNEP at the end of July on behalf of the Task Force, in which letter more information was requested.

DEHPC is a dangerous liquid, not soluble in water, which may explode if heated. DEHPC manufacturers are Degussa, Akzo Nobel Chemicals and Jin Hua Group. It is unlikely that the European producers use ODS in their processes /CBG04, ANC04, JCG04/.

This chemical is a free radical polymerisation initiator that is mixed with vinyl chloride monomer (VCM) to produce polyvinylchloride (PVC). Organic peroxides such as DEHPC are commonly used as the source of free radicals. Selection of the peroxide will help to control the polymerisation reaction and the final properties of the polymer /SCP04/.

The process described has two steps, first 2-ethylhexanol and phosgene react in CTC to form 2-ethylhexyl chloroformate. This substance then reacts with sodium peroxide in a CTC/water system to produce DEHPC. The organic and the water phases are separated. The organic phase contains DEHPC dissolved in CTC and this solution is used directly to polymerise PVC. The CTC remains unchanged in the polymer and is released into the environment through the plastic lifetime.

An alternative ODS-free process is mentioned that uses hydrolised polyvinyl acetate (PVA) dispersant in water for the synthesis of DEHPC from 2 ethylhexyl chloroformate. The addition of the sodium peroxide is conducted under a running homogeniser at 0-10⁰ C.

3.8 Radiolabelled cyanocobalamin

Process Agent	CTC
Application	Extraction and purification
Reason Used	Specific solvency, non-flammable, physical properties
Product Use	Diagnose causes of vitamin B ₁₂ deficiency
Identified Alternatives	Emission control
Submitting Country	United Kingdom
Reported Consumption	Around 8.5 kg

This was the most comprehensive submission presented to this Task Force, and it followed the format of an Essential Use Application. Amersham Health produces two diagnostic pharmaceutical products with CTC in small batches in a laboratory environment. The main difference between these products is their geographical end market.

About 8 batches of solution are manufactured every year to produce 28000 diagnostics world-wide. Alternative tests or combination of tests to diagnose vitamin B₁₂ deficiencies cannot completely replace these products, as they require more tests on the patient, with more visits to the clinic, and longer time to differentially diagnose the cause of the deficiency.

About 660 cm³ of CTC are used per batch for a total consumption of less than 8.5 kg per year; this consumption level is not expected to grow in the next 5 years. The company has in stock the CTC necessary to continue production during this period. Any change in the process will require validation to pharmaceutical standards including demonstration that unacceptable levels of residual solvents or other impurities are not present in the final capsule. Development, validation and submission to the relevant pharmaceutical authorities of such change will take a minimum of 2 years, the cost of which could not be justified by the product.

Radiolabelled cyanocobalamin is obtained from the fermentation product of actinomycete bacteria, which are grown in an aqueous media containing the radioactive tracer ⁵⁷Co. Once the fermentation is terminated, the product is extracted from the aqueous phase with a mixture of CTC and m-cresol. After multistage purification washes, the fermentation product is extracted for further processing from the organic mixture containing CTC, which is collected as waste.

Liquid waste from the process originates from the use of the solvents CTC, m-cresol and n-butanol. A small part of these solvents is lost by evaporation during the process, the remaining liquid has some cyanide and ⁵⁷Co trace contaminants. Up to now, disposal has been completed by evaporation of the solvents and adequate management of the solid residue.

A new waste disposal route is mentioned in the submission. The organic waste will be collected into a container, which can be securely sealed. After storage to allow decay of the radioactive contaminants, the sealed container will be transferred for incineration.

In July 2004 an Emergency Exception was provided to the European Community under Decision VIII/9 for the use of 8 litres of CTC for this application in 2004. The Ozone Secretariat will present this information to the Sixteenth Meeting of the Parties for review and appropriate action.

CTC acts as a liquid-liquid extraction solvent, like in the case of NCl₃ extraction from liquid chlorine. Selective solvency is important to transfer the fermentation product from the aqueous phase to the organic phase at different stages, and later to reverse the process and transfer the solute back to an aqueous layer. With the proposed incineration disposal emissions will be negligible.

3.9 High Modulus Polyethylene Fibre

Process Agent	CFC-113
Application	Extraction of spinning agent
Reason Used	Quality, safety, yield
Product Use	Ballistic armour for law enforcement and military personnel
Identified Alternatives	Emission control, flammable solvents
Submitting Country	United States
Reported Consumption	Less than 10 MT/ year

This is a high performance fibre sold under the trademark Spectra /SPE04/ whose properties depend upon the polymeric material used to create the fibre as the strands of long polymer chains can be stacked and packed with virtually no space in between. The submission mentions the following characteristics:

- High tensile strength (10 times stronger than steel per equivalent weight);
- Light weight;
- Outstanding energy absorption for ballistic resistance;
- Chemical and UV resistance;
- Hydrophobic nature that coupled with light weight makes it float.

As a result, high modulus polyethylene fibre is used in the production of ballistic armour for military and law enforcement personnel, ballistic armour for vehicles, high strength ropes and cordage, and cut resistant apparel. Military demand has been so strong that the U.S. Department of Commerce has been forced to allocate shipments. A line expansion was announced in 2001 and construction of a new facility is contemplated in the US in 2005-2006 /SPE04/. This new facility will also use ODS as an extraction solvent /Pji04/.

Although fibre properties may remind at first glance those of polyphenylene terephthalamide (position 8 in Table A), the two fibres are quite different, as are the reasons to use an ODS in the process. A gel spinning technology is used that requires a second solvent to extract the spinning solvent from the gel fibre. Manufacture takes place in a continuous process consisting of numerous unit operations in series. The polyethylene resin and spinning solvent are

mixed continuously to create a slurry, which is spun into a multifilament gel fibre.

The solvent on the fibre must be removed in a washing apparatus. CFC-113 is used counter-currently and assures good recovery of the spinning solvent. The extracted solvent and the CFC-113 are sent to a high-efficiency solvent recovery process for separation and recycle. Any CFC-113 that remains in the fibre is evaporated and the vapours condensed and/or absorbed. Recovery efficiency of captured CFC-113 is on average 99.93%. Emissions of CFC-113 are below 10 MT/year.

Although information on this submission was not as complete as the Task Force would desire, it is clear that the arguments for the use of CFC-113 are similar to those used to justify the use of CFC-11 for the manufacture of fine synthetic polyolefin fibre sheet (position 10 in Table A).

Reasons to consider this application as a process agent use are:

- Low toxicity;
- Non-flammability;
- Physico-chemical properties: boiling point;
- Critical temperature and pressure;
- Solvency power (capability to enter polymer matrix);
- Chemical stability;
- Non corrosiveness.

An undisclosed flammable solvent is mentioned as an alternative to the use of CFC-113. However, retrofitting the existing facility to safely accommodate the use of such a solvent is not feasible, not only for cost reasons, but also for the downtime that such a change would require.

Parties may wish to consider whether adding a new Process Agent to Table A should have any impact on Table B, which lists the maximum emissions allowed per region/country for Process Agents. With current emissions of around 10 MT/ year and an expected increase for 2005, total emissions for this process are significant when compared to the total of 181 MT/ year emissions approved for the US under table B of Decision X/14.

4 Other Remarks

Process Agents have proved to be a complex subject and merited a significant amount of attention from the Parties and TEAP. The review of the processes for addition to Table A of Decision XV/6 has again raised a number of issues that the Task Force wants to flag for attention by the Parties.

4.1 When is a use a Laboratory Use

The submission for radiolabelled cyanocobalamin is a case where the difference between industrial process and laboratory use cannot be easily distinguished. This is a case where the industrial process is carried out on such a small scale that it is done in a laboratory-like production facility, not a traditional factory. If venue or scale is the deciding factor, then this might be considered by the Parties as a laboratory use. If the nature of the activity - production, not research investigation or analytical measurement - is the deciding factor, then it might be considered by the Parties as an industrial process.

Assuming that in the future similar small applications may emerge, some rule or guideline would be useful, so that submitters can know the criteria on which their proposal would be judged. TEAP will welcome an assignment to provide definitions for consideration by the Parties.

4.2 Outdated technology

CTC was used widely in the chemical industry for many years, but concerns over its adverse effects on human health -which predated the discovery of its adverse environmental effects- caused its replacement and/or containment wherever modern technologies were used. Unfortunately, there are large variations in the degree of concern for health and safety issues world-wide, and even larger differences in the degree to which preventive measures are implemented.

Therefore, it is possible that a number of applications of old technologies are identified either in some Article 5(1) or in CEIT Parties. These technologies may in some cases be cheaper – at the expense of the integrity of workers and the environment – and are not protected by patents nor require sophisticated control of process conditions.

This is the situation with six of the eight processes reviewed in 2004 by the Process Agents Task Force. The Task Force recognises that these processes use the unique properties of CTC as a Process Agent despite the fact that in five of these processes there are either alternative processes (fermentation and nitration

as opposed to esterification and chlorination) or alternative reaction media (perchloroethylene, aqueous PVA).

The Task Force felt that, for a proper perspective with old technologies that in some cases may not need much initial investment, it was particularly important to request information from the submitting Parties on the date when the technology was installed and the actual production figures for the last three years.

4.3 Request by Israel to include its Process Agents use in the Table of Decision XV/7

Israel notified the Ozone Secretariat that its use of Process Agents is not included in the Table of Decision XV/7 with Brazil. The two countries use CTC for the removal of NCl_3 . Israel reports a make up of 6.5 MT/ year, but has not provided information on emissions.

5 Conclusions

- It is the unanimous opinion of the Task Force that all the processes reviewed in this 2004 Report of the Process Agents Task Force meet the criteria defined by the PATF in the 1997 Report. Therefore their inclusion by the Parties in Table A of Decisions X/14 and XV/6 is recommended.
- The Task Force also notes that there are opportunities to switch to ODS free alternatives for all Process Agent uses, which have significant emissions of controlled substances and have been reviewed in this 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 use for a non-Article 5(1) Party. This is the case when there are feasible non-ODS alternatives for the 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.

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Annex I - Definitions from the 1997 PATF Report

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

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

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

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

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

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

Annex II - Decision X/14. Process Agents

Noting with appreciation the report of the Technology and Economic Assessment Panel and the Process Agents Task Force in response to decision VII/10,

Noting the findings of the Technology and Economic Assessment Panel that emissions from the use of ozone-depleting substances as process agents in non-Article 5 Parties are comparable in quantity to the insignificant emissions of controlled substances from feedstock uses, and that yet further reductions in use and emissions are expected by 2000,

Noting also the Technology and Economic Assessment Panel's findings that emissions from the use of controlled substances as process agents in countries operating under Article 5, paragraph 1, are already significant and will continue to grow if no action is taken,

Recognizing the usefulness of having the controlled substances produced and used as process agents clearly delineated within the Montreal Protocol,

1. That, for the purposes of this decision, the term "process agents" should be understood to mean the use of controlled substances for the applications listed in table A below;
2. For non-Article 5 Parties, to treat process agents in a manner similar to feedstock for 1998 and until 31 December 2001;
3. That quantities of controlled substances produced or imported for the purpose of being used as process agents in plants and installations in operation before 1 January 1999, should not be taken into account in the calculation of production and consumption from 1 January 2002 onwards, provided that:
 - (a) In the case of non-Article 5 Parties, the emissions of controlled substances from these processes have been reduced to insignificant levels as defined for the purposes of this decision in table B below;
 - (b) In the case of Article 5 Parties, the emissions of controlled substances from process-agent use have been reduced to levels agreed by the Executive Committee to be reasonably achievable in a cost-effective manner without undue abandonment of infrastructure. In so deciding, the Executive Committee may consider a range of options as set out in paragraph 5 below;

4. That all Parties should:
 - (a) Report to the Secretariat by 30 September 2000 and each year thereafter on their use of controlled substances as process agents, the levels of emissions from those uses and the containment technologies used by them to minimize emissions of controlled substances. Those non-Article 5 Parties which have still not reported data for inclusion in tables A and B are urged to do so as soon as possible and in any case before the nineteenth meeting of the Open Ended Working Group;
 - (b) In reporting annual data to the Secretariat for 2000 and each year thereafter, provide information on the quantities of controlled substances produced or imported by them for process-agent applications;
5. That the incremental costs of a range of cost-effective measures, including, for example, process conversions, plant closures, emissions control technologies and industrial rationalization, to reduce emissions of controlled substances from process-agent uses in Article 5 Parties to the levels referred to in paragraph 3 (b) above should be eligible for funding in accordance with the rules and guidelines of the Executive Committee of the Multilateral Fund;
6. That the Executive Committee of the Multilateral Fund should, as a matter of priority, strive to develop funding guidelines and begin to consider initial project proposals during 1999;
7. 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;
8. To request the Technology and Economic Assessment Panel and the Executive Committee to report to the Meeting of the Parties in 2001 on the progress made in reducing emissions of controlled substances from process-agent uses and on the implementation and development of emissions-reduction techniques and alternative processes not using ozone-depleting substances and to review tables A and B of the present decision and make recommendations for any necessary changes;

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

No	Substance	Process agent application
1	CTC	Elimination of NCl_3 in the production of chlorine and caustic
2	CTC	Recovery of chlorine in tail gas from production of chlorine
3	CTC	Manufacture of chlorinated rubber
4	CTC	Manufacture of endosulphan (insecticide)
5	CTC	Manufacture of isobutyl acetophenone (ibuprofen analgesic)
6	CTC	Manufacture of 1-1, Bis (4-chlorophenyl) 2,2,2- trichloroethanol (dicofol insecticide)
7	CTC	Manufacture of chlorosulphonated polyolefin (CSM)
8	CTC	Manufacture of poly-phenylene-terephthal-amide
9	CFC 113	Manufacture of fluoropolymer resins
10	CFC 11	Manufacture of fine synthetic polyolefin fibre sheet
11	CTC	Manufacture of styrene butadiene rubber
12	CTC	Manufacture of chlorinated paraffin
13	CFC 113	Manufacture of vinorelbine (pharmaceutical product)
14	CFC 12	Photochemical synthesis of perfluoropolyetherpolyperoxide precursors of Z-perfluoropolyethers and difunctional derivatives
15	CFC 113	Reduction of perfluoropolyetherpolyperoxide intermediate for production of perfluoropolyether diesters
16	CFC 113	Preparation of perfluoropolyether diols with high functionality
17	CTC	Production of pharmaceuticals ketotifen, anticol and disulfiram
18	CTC	Production of tralomethrine (insecticide)
19	CTC	Bromohexine hydrochloride
20	CTC	Diclofenac sodium
21	CTC	Cloxacilin
22	CTC	Phenyl glycine
23	CTC	Isosorbid mononitrate
24	CTC	Omeprazol
25	CFC-12	Manufacture of vaccine bottles

Note: Parties may propose additions to this list by sending details to the Secretariat, which will forward them to the Technology and Economic Assessment Panel. The Panel will then investigate the proposed change and make a recommendation to the Meeting of Parties whether or not the proposed use should be added to the list by decision of the Parties.

Table B

Emission limits for Process Agent uses

(All figures are in metric tonnes per year)

Country/region	Make-up or consumption	Maximum emissions
European Community	1000	17
United States of America	2300	181
Canada	13	0
Japan	300	5
Hungary	15	0
Poland	68	0.5
Russian Federation	800	17
Australia	0	0
Czech Republic	0	0
Estonia	0	0
Lithuania	0	0
Slovakia	0	0
New Zealand	0	0
Norway	0	0
Iceland	0	0
Switzerland	5	0.4
TOTAL	4501	220.9 (4.9%)

Annex III - Decision XV/6. 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: List of uses of controlled substances as process agents

No.	Process agent application	Substance
1.	Elimination of NCl_3 in the production of chlorine and caustic	CTC
2.	Recovery of chlorine in tail gas from production of chlorine	CTC
3.	Manufacture of chlorinated rubber	CTC
4.	Manufacture of endosulphan (insecticide)	CTC
5.	Manufacture of isobutyl acetophenone (ibuprofen – analgesic)	CTC
6.	Manufacture of 1-1, bis (4-chlorophenyl) 2,2,2- trichloroethanol (dicofol insecticide)	CTC
7.	Manufacture of chlorosulphonated polyolefin (CSM)	CTC
8.	Manufacture of poly-phenylene-terephthal-amide	CTC
9.	Manufacture of fluoropolymer resins	CFC-113
10.	Manufacture of fine synthetic polyolefin fibre sheet	CFC-11
11.	Manufacture of styrene butadiene rubber	CTC
12.	Manufacture of chlorinated paraffin	CTC
13.	Photochemical synthesis of perfluoropolyetherpolyperoxide precursors of Z-perfluoropolyethers 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.	Bromohexine hydrochloride	CTC
17.	Diclofenac sodium	CTC
18.	Phenyl glycine	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-phenoxy benzaldehyde	CTC
24.	Production of 2-chloro-5-methylpyridine	CTC
25.	Production of Imidacloprid	CTC
26.	Production of Bupropfenzin	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 styrenic polymer	BCM (bromochloromethane)