Montreal Protocol

Report of the

Process Agents Task Force

April 2001

Notice

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Process Agents Task Force
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Report of the Process Agents Task Force
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Acknowledgements

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

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Summary and conclusions

In 1997 the PATF and the TEAP reported that it was technically feasible to further reduce the relatively small emissions from process agent use in non-Article 5(1) countries and that it was technically and economically feasible to substantially reduce the emissions of ODS process agents in CEIT and Article 5(1) countries. This 2001 PATF report has been prepared in response to the request of the TEAP contained in Decision X/14. The Multilateral Fund Secretariat is preparing a separate 2001 Report to Parties that describes the current process agent use in Article 5(1) countries and also reports progress in financing the incremental costs of reducing and eliminating those emissions.

1. ODS process agents are locally used but benefits are globally important

ODS process agents are reported to be used by fewer than 10 Parties to produce intermediate and final products that are globally marketed for uses important to health, safety, environmental protection and economic prosperity.

2. Process agents support health, safety, and economic prosperity

Products and processes depending on ODS process agents include human and animal drugs, pesticides, corrosion inhibitors, water purification, plastic armor used to protect humans and to contain ballistic debris from equipment failure, asbestos-free brake and clutch plates, and chlorine.

3. Most Parties have yet to report process agent use and emissions

Most Parties have yet to report process agent uses and emissions. Decision X/14 requested all Parties to 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. The Ozone Secretariat received only 17 reports, 4 from non-Article 5(1), 3 from CEIT, and 10 from Article 5(1). Most lacked sufficient detail to allow for meaningful evaluation.

The Ozone Secretariat has drawn our attention to paragraph 36 of the Report of the 25th meeting of the ImpCom, 9 December 2000, as follows:

"One representative expressed the view that the reporting requirement on process agents set out in decision X/14 was not sufficiently clear, leading to problems with the drafting of data form 6 and its eventual approval. It was agreed that the Secretariat would identify the Parties which would be affected by the reporting requirement and invite them to discuss which data should be provided and how the form should be designed. It would then report back to the Committee with a review to a recommendation being made to the Meeting of the Parties."

4. Precise accounting is difficult to achieve

Precise accounting of actual emissions is much more difficult than Parties may recognize because estimates are based on engineering calculations using process assumptions, because chemical process yields vary over time, and because equipment failure and leaks result in unmonitored emissions.

5. Unofficial reports confirm reduced emissions in non-Article 5(1) countries

The PATF estimates that 4000-5000 tonnes of ODSs are used annually in process agent applications in non-Article 5(1) countries. Plant specific annual emissions are estimated as less than 250 tonnes – less than 7% of make-up quantities. This has been achieved by capture and recycle or destruction, or chemical transformation of the ODS.

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

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

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

    - phase-out achieved or achievable
    - expected phase-out within the next few years subject to solution of final technical issues
    - a few processes facing extreme difficulty to find an alternative

- Realizing that these results have been achieved over a period of 5 to 6 years, together with measures to significantly reduce emissions where ODS process agents are still in use, there has been remarkable progress and further progress is expected.

- Care should be taken that ODS are not inadvertently produced in significant quantities by the substitution of an alternative process agent or by the use of an alternative process.

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

6. PATF recommendations for Necessary Changes to Table A and B (Decision X/14)

1) Table A:

In 1997, the PATF documented process agent uses numbered 1-12 and 19-24 found in Table A of Decision X/14. Despite efforts of the Ozone Secretariat, TEAP and the PATF, no documentation of uses 13, 17a, 17b, 17c and 25 has been received. Parties may wish to consider appropriate modifications to the list of authorized process agent uses found in Table A of Decision X/14. In addition one Party has supplied information to the Ozone Secretariat, the TEAP and the PATF regarding the use of CTC in the manufacture of Cyclodime. Parties may therefore wish to consider adding the use of CTC in the manufacture of Cyclodime to Table A.

As well, Parties may wish to consider those processes “Not Yet Submitted to the Ozone Secretariat” as shown in Table 2.1 of Chapter 2 of this report of the PATF. It appears that some Article 5(1) countries have been confused by the wording of Decision X/14 as to whether they should submit information to the Executive Committee of the Multilateral Fund or the Ozone Secretariat.

2) Table B:

i) Parties may wish to restructure Table B to require annual reporting of each ODS process agent use and estimated emissions but may not wish to prescribe limits to either use or emissions. The technical justification for this change is that society may require increases in the quantity of products depending on process agents, that business rationalization may shift the location of process agent use, and that emissions of process agents are a relatively insignificant contribution to ozone depletion.

ii) Parties may also wish to consider that “Make-Up” quantity include the total quantity of ODS from both stockpile and new production <u>plus</u> estimated ODS produced in-situ. Neglect of in-situ ODS production creates the false impression that a process has no impact on the ozone layer.

iii) Parties may wish to not require reporting of estimated emissions. The economic and administrative justification for CEIT and Article 5(1) countries is that accurate reporting of emissions for each process will require expensive training, equipment, and operating expenses that could better be spent in financing the incremental cost of phasing out ozone depleting substances. Reporting in non-Article 5(1) countries is an administrative burden that is increasingly difficult to justify as ozone staffs are down-sized. Periodic reporting by TEAP could be fully adequate.

iv) If Parties reject the option to not report emissions (iii above), then Parties may wish to estimate "Emissions" using procedures outlined in appropriate ISO Standards, using reporting guidelines established by some Parties (e.g. US-EPA), or other appropriate national instructions. The technical justification is that Parties need standardized instructions to report emissions.

Dissenting opinion

This report has been developed at meetings held in Washington and Beijing and by correspondence before, between and after these meetings. The report has been agreed upon by all members of the PATF, except one. One member, Mr. Arvind Kapoor has offered the following dissenting opinion to this report:

Dissenting opinion by Arvind Kapoor

1. At paragraph 5 of the Summary and Conclusions I differ with the conclusion: "Unofficial reports confirm reduced emissions in non-Article 5 (1) countries ".

No data on actual make up quantity and emissions of ODS in non-Article 5 countries was tabled, collated or discussed between the PATF members nor has any such data been published in this PATF report. The basis for PATF's estimate of 4000 – 5000 MT of ODS's as make up quantity per year for non-Article 5 countries is without any support. Further, in paragraph 4 of the Conclusions, it is stated that the ODS emissions in non-Article 5 countries are based only on engineering calculations and are not actuals.

Vide Decision X/14, Parties allowed non Article 5 countries a total ODS usage of 4501 MT per annum for process agents applications until 2001. In the TEAP April 1997 Report - Volume II at paragraph 2.2 on page 89, it was estimated that the make up quantity of ODS for process agent applications in 1995 in non-Article 5 (1) countries was 3498.5 MT and TEAP further projected that this would reduce to 1940 MT by the year 2000. Comparing these figures with that of the estimate of make up quantity of 4000-5000 MT of ODS per year mentioned in this PATF report does not signify a reduction in the use of ODS as process agents in non-Article 5 (1) countries.

Even the current ODS emissions of less than 250 MT per year in non-Article 5 countries as mentioned in this PATF report have not reduced as shown in the Table below. This table also compares the figures of ODS make up quantities for process agent applications in non - Article 5 countries.

TABLE: ESTIMATES OF MAKE UP QUANTITIES AND EMISSIONS OF ODS PROCESS AGENT USES IN NON-ARTICLE 5 COUNTRIES.

	Reference	**Year**	**Make up qty. (MT)**	**Emissions (MT)**	**Emissions, as percentage of make up qty. (%)**
1.	TEAP April 1997 Report, Vol. II, page 89	1995	3489.5	1087.9	31.1
2.	Table B, Decision X/14 of Meeting of Parties at Cairo (see page 7 of this report)	1998 to 2001	4501.0	220.9	4.9
3.	TEAP April 1997 Report, Vol. II , page 89.	2000	1940	79.4	4.1
4.	Estimates as per 2001 PATF Report at para 2.4 (see page 17 of this report)	2000	4000-5000	<250.0@	<7.0

@ Calculated as 7% of make-up quantity range of 4000-5000 MT, this figure should be 280 – 350 MT.

It is, thus, clear that both the ODS make up quantity as well as their emissions from process agent applications in non-Article 5 countries do not currently show any reduction.

2. With reference to following portions of the report:

(a) the last bullet on page viii under paragraph 5,
(b) paragraph 3 on page 42 under paragraph 4.4
(c) the bullet under Conclusions in paragraph 4.5 on page 43 and
(d) sub-item ii) on page ix of paragraph 6(2);

I see no justification in clubbing two entirely different scenarios emerging from the use of non - ODS alternative process agents and alternative aqueous chlorination processes of hydrocarbon substrates such as natural rubber, synthetic rubber, polyolefins or paraffins as done in the portions of this report cited above.

In the case of use of a chemical substance as a non-ODS process agent, there is possibility of such process agent itself transforming into its next ODS homologue, if reaction conditions are conducive for such a chemical conversion. The ODS production in such cases could be substantial and it cannot be termed as inadvertent production. During such chemical reactions, care needs to be exercised to prevent use of such a non-ODS chemical substitute which can result in production of the next ODS homologue in that chemical series, as recommended in this report.

However, the use of the alternative aqueous processes as a substitute of ODS as process agent is a totally different situation. In this case, any likely in situ and inadvertent ODS production in trace quantity can only occur if there are reaction conditions favorable for the same. No scientific evidence has been tabled to substantiate whether such inadvertent ODS production actually occurs in any or all such aqueous chlorination processes. Even in the event if such a minuscule inadvertent ODS production does take place during the use of aqueous process for the end product, then it is neither significant nor intentional. Further, such inadvertent ODS production is exempted under Decision IV/12 of the Protocol. The scenario utilizing aqueous process as an alternative process is, thus, quite different from the use of alternative non-ODS process agents.

Let us assume for the sake of argument, that the inadvertent and insitu CTC production does take place in Chlorinated rubber manufacture by an aqueous process which is of the order of a maximum of 150 ppm of the product. Even if this process were to be adopted by all countries, then for an assumed total production of about 10,000 MT per annum of Chlorinated Rubber (which could be about double the current chlorinated rubber production in Article 5(1) Countries), the insitu and inadvertent CTC production resulting from this process would be below 1.5 MT per annum which is insignificant. This report states at third paragraph under heading 4.4 on page 42 that:

"If the process is conducted on a very large scale, then even " slight" can result in substantial annual ODS emissions". This is by no means borne out by the above example.

In fact, in the case of Chlorinated Rubber production by an aqueous process recently developed in India, the inadvertent CTC production in that process is not measurable being miniscule.

In view of the foregoing any reference to need for care in adopting alternative processes through aqueous chlorination processes is not justified in any part of this report.

3. Mandate paragraph given to TEAP by the Parties vide paragraph 8 of Decision X/14.

This report does not fully deal with the mandate of the Parties in as much as that it does not cover the progress made in implementation and development of emission reduction techniques and alternative processes not using ODS's subsequent to the 1997 PATF report.

Due to TEAP's assumption as stated in the last paragraph on page 9 limited to non-Article 5(1) countries and does not update the situation in Article 5 (1) countries. However, some disjointed references concerning Article 5(1) countries are included in this report. This report, is therefore, not representative of the complete picture in Article 5(1) countries relating to identification of any additional process agent applications utilizing ODSs and progress made in developing alternative non-ODS processes for identified process agent applications since the 1997 PATF report.

As such, in my view, this report is not comprehensive and falls short of the mandate of the Parties.

Response by Gary Taylor, Co-chair PATF

Many of the points objected to by Mr. Kapoor were debated at length at the final meeting of the PATF held in Beijing. Mr. Kapoor was unable to attend the Beijing meeting because it took place at the same time as the ExCom meeting in Montreal. Mr. Kapoor is a principal of Rishiroop Rubber International and his company has requested assistance from the Multilateral Fund in conversion of their chlorinated rubber facility from a CTC based process to an aqueous process. It was his decision to attend the ExCom meeting in Montreal rather than the PATF meeting in Beijing.

With regard to the three specific points made by Mr. Kapoor in his dissent, the following are offered for consideration:

1. Since the last report of the PATF, Parties have identified several processes in addition to those found in the 1997 PATF report. However, the Ozone Secretariat has not been supplied with any data by Parties regarding make-up or emissions since Decision X/14. In the absence of "official" data, the PATF members reported on reductions in use of ODS process agents in processes reported in the 1997 PATF report that are employed by their respective companies in non-Article 5(1) countries. Significant reductions have occurred. Please refer to 4.2.9 and 4.2.10 of the report. In both cases significant production has now been switched to non-ODS processes, with only certain grades of product still being produced using ODS based technologies. The statement "Unofficial reports confirm reduced emissions in non-Article 5(1) countries" is a valid statement.

2. All members of the PATF, except Mr. Kapoor, have concluded that the possibility of small amounts of inadvertent production of CTC exists in the aqueous chlorination process. The report places this in context. Parties are especially referred to the final paragraph of 4.2.3. Parties may also wish to note that 1.5 MT of annual CTC emissions from the aqueous process, as estimated by Mr. Kapoor for a 10,000 MT/year of chlorinated rubber production, is over 150% of the annual CTC emissions from the German facility that actually produces 10,000 MT/year of chlorinated rubber.

3. The PATF would have preferred to eliminate Chapter 5 of the report, as a report on process agent use in Article 5(1) countries is being prepared by the Secretariat of the

Multilateral Fund. However, Chapter 5 provides the only reference to the processes identified in Chapters 2 and 4, as #27 to #38.

1 Introduction and definitions

1.1 Background

Pursuant to Decision X/14 of the Parties, the Technology and Economic Assessment Panel (TEAP) reconstituted the Process Agents Task Force (PATF). The PATF has endeavored to further develop and improve upon the previous work undertaken in 1997.

This report was developed during meetings held in Ouagadougou, Washington and Beijing. During the Beijing meeting a joint session was held with members of a Process Agents Task Group established by SEPA. The meeting was a useful opportunity for PATF members to gain insight into the typical issues facing Article 5(1) users of process agents and to share the new technologies that have been employed to significantly reduce emissions in the non-Article 5(1) countries.

1.2 Decisions

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

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

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

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

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

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

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

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

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

2. to urge Parties to take steps to minimize emissions of such substances, including such steps as avoidance of the creation of such emissions, reduction of emissions using practicable control technologies or process changes, containment or destruction;

3. to request the Technology and Economic Assessment Panel:

   (a) to give an estimate of the total emissions resulting from trace impurities, emission during product manufacture and handling losses;

   (b) to submit its findings to the Open-ended Working Group of the Parties to the Montreal Protocol not later than 31 March 1994.

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

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

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

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

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

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

1. To request the Technology and Economic Assessment Panel:

    (a) To identify uses of controlled substances as chemical process agents;

    (b) To estimate emissions of controlled substances when used as process agents and the ultimate fate of such emissions and to evaluate emissions associated with the different control technologies and other process conditions under which chemical process agents are used;

    (c) To evaluate alternative process agents or technologies or products available to replace controlled substances in such uses; and

    (d) To submit its findings to the Open-ended Working Group of the Parties to the Montreal Protocol not later than March 1995, and to request the Open-ended Working Group to formulate recommendations, if any, for the consideration of the Parties at their Seventh Meeting;

2. That Parties, for an interim period of 1996 only, treat chemical process agents in a manner similar to feedstock, as recommended by the Technology and Economic Assessment Panel, and take a final decision on such treatment at their Seventh Meeting.

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

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

1. To continue to treat process agents in a manner similar to feedstocks only for 1996 and 1997;

2. To decide in 1997, following recommendations by the Technology and Economic Assessment Panel and its relevant subgroups, on modalities and criteria for a continued use of controlled substances as process agents, and on restricting their emissions, for 1998 and beyond.

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

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

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

2. That the amount of controlled substances entirely used as feedstock in the manufacture of other chemicals should not be the subject of calculation of "consumption" in importing countries.

Decision X/14: Process agents

The *Tenth Meeting of the Parties* decided in *Dec. X/14:*

Noting with appreciation the report of the Technology and Economic Assessment Panel and the Process Agent 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	Carbon tetrachloride (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-terephtal-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%)

- end of Decisions -

1.3 Definitions

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

> **Feedstock:** A controlled substance that undergoes transformation in a process in which it is converted from its original composition except for insignificant trace emissions as allowed by Decision IV/12.
>
> **Process Agent:** A controlled substance, that because of its unique chemical and/or physical properties, facilitates an intended chemical reaction and/or inhibits an unintended chemical reaction.

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

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

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

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

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

The Montreal Protocol defines "consumption" as:

Consumption = production + imports - exports

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

In the case of ODS use as process agents, the supply is utilized to replenish process inventory lost as the result of transformation, destruction and emissions to the atmosphere from the process and/or trace quantities slowly emitted from the product. Therefore the supply required for replenishment of lost inventory is referred to as "make-up" and defined as follows:

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

1.4 Information required by the TEAP

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

> Report 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 Decision X/14 and make recommendations for any necessary changes.
>
> The TEAP assumes that the review by the PATF and the TEAP should be limited to non-Article 5(1) countries to avoid conflict with the instructions to the Executive Committee of the Multilateral Fund found in Decision X/14.

2 Process agent use and emissions

2.1 Summary of processes included in Decision X/14 or subsequently submitted to the Ozone Secretariat

Included in Decision X/14	Process	Process Agent	Case Study	Application	Reason used	Product use	Used in Article 5(1)	Used in non-Article 5(1)
1 - Yes	Chlor-alkali	CTC	CS-1*	Elimination of NCl_3	Safety and quality of product	Chlorine is a universal chemical used for more than 60 % of all chemical synthesis.	Unknown	Yes
2 - Yes	Chlor-alkali	CTC	CS-2*	Chlorine recovery by tail gas absorption	Safety, Yield	Chlorine is a universal chemical used for more than 60 % of all chemical synthesis.	Unknown	Yes
3 - Yes	Chlorinated Rubber	CTC	CS-3*	Chemical inert solvent for high quality product	Inert solvent	Heavy duty anti-corrosives and adhesives	Yes	Yes
4 - Yes	Endosulfan production	CTC	CS-4*	Solvent	Inert solvent	Biodegradable insecticide	Yes	Unlikely
5 - Yes	Ibuprofen production	CTC	CS-5*	Solvent for Friedel-Crafts synthesis	Inert solvent	Anti-inflammatory drug	Yes	Unlikely
6 - Yes	Dicofol	CTC	CS-6*	Solvent	Inert solvent	Broad spectrum acaracide	Yes	Unlikely
7 - Yes	Chlorosulfonated Polyolefin	CTC	CS-7a* & CS-7b*	Chlorination agent	Safety, yield		Yes	Yes

2.1 Summary of processes included in Decision X/14 or subsequently submitted to the Ozone Secretariat (cont.)

Included in Decision X/14	Process	Process Agent	Case Study	Application	Reason used	Product use	Used in Article 5(1)	Used in non-Article 5(1)
8 – Yes	Aramid Polymer PPTA	CTC	CS-8*	Chlorination specific solvent	Quality, safety, waste reduction	Asbestos replacement, public and military safety products	Unknown	Yes
9 – Yes	Fluoropolymer resins	CFC 113	CS-9*	Specific solvent	Specific dispersant, chemical inert	Extreme temperature electrical insulation, inert coatings	Unknown	Yes
10 – Yes	Synthetic fibre sheet	CFC 11	CS-10*	Spinning agent	Quality, safety, yield	Protective wrappings, very strong sheets	No	Yes
11 - Yes	SBR	CTC	No	Solvent	Chain transfer agent	Synthetic rubber, strong and resistant to extreme temperatures and climate	Yes	Unknown
12 - Yes	Chlorinated Parrafin	CTC	CS-12*	Solvent	Inert solvent	Lubricant additive, flame retardant for plastics, plasticizer in rubber paints	Yes	Unknown
13 - Yes	Manufacture of Vinobreline	CFC 113	No	Unknown	Unknown	Pharmaceutical	Unknown	Unknown

2.1 Summary of processes included in Decision X/14 or subsequently submitted to the Ozone Secretariat (cont.)

Included in Decision X/14	Process	Process Agent	Case Study	Application	Reason used	Product use	Used in Article 5(1)	Used in non-Article 5(1)
14 - Yes	Photochemical synthesis of perfluoropolyetherpolyperoxide precursors of Z-perfluoropolyethers and difunctional derivatives	CFC 12	CS-14*				Unknown	Yes
15 – Yes	Reduction of perfluoropolyetherpolyperoxide intermediate for production of perfluoropolyether diesters	CFC 113	CS-15*				Unknown	Yes
16 – Yes	Preparation of perfluoropolyether diols with high functionality	CFC 113	CS-16*				Unknown	Yes
17a - Yes	Production of ketotifen	CTC	No	Unknown	Unknown	Pharmaceutical	Likely	Likely
17b – Yes	Production of anticol	CTC	No	Unknown	Unknown	Pharmaceutical	Likely	Likely
17c - Yes	Production of disulfiram	CTC	No	Unknown	Unknown	Pharmaceutical	Likely	Likely
18 - Yes	Production of tralomethrine	CTC	No	Unknown	Unknown	Insecticide	Unknown	Unknown
19 - Yes	Bromohexine hydrochloride	CTC	CS-19*	Unknown	Unknown	Pharmaceutical	Yes	Unknown

2.1 Summary of processes included in Decision X/14 or subsequently submitted to the Ozone Secretariat (cont.)

Included in Decision X/14	Process	Process Agent	Case Study	Application	Reason used	Product use	Used in Article 5(1)	Used in non-Article 5(1)
20 - Yes	Diclofenac sodium	CTC	CS-20*	Solvent	Yield	Pharmaceutical	Yes	Unknown
21 - Yes	Cloxacillin	CTC	No – See Chapter 5a	Unknown	Unknown	Pharmaceutical	Yes	Unknown
22 - Yes	Phenyl glycine	CTC	CS-22*	Solvent	Unknown	Pharmaceutical	Yes	Unknown
23 - Yes	Isosorbid mononitrate	CTC	No – See Chapter 5a	Unknown	Unknown	Pharmaceutical	Yes	Unknown
24 - Yes	Omeprazol	CTC	No – See Chapter 5a	Unknown	Unknown	Pharmaceutical	Yes	Unknown
25 - Yes	Manufacture of vaccine bottles	CFC 12	No	Unknown	Unknown	Pharmaceutical	Unknown	Unknown
26 - Submitted to Ozone Secretariat	Manufacture of Cyclodime	CTC	CS-26*	Solvent	Inert solvent	Extreme and adverse temperatures in aeronautic hydraulic system components	Unknown	Yes

*** Case Studies can be found at: http://www.teap.org/html/process_agents_reports.html**

2.2 Summary of processes not yet included in Decision X/14 – information supplied to PATF

Included in Decision X/14	Process	Process Agent	Case Study	Application	Reason used	Product use	Used in Article 5(1)	Used in non-Article 5(1)
27 – Not yet submitted to Ozone Secretariat	Chlorophenesin	CTC	No – See Chapter 5a	Unknown	Unknown	Pharmaceutical	Yes	Unknown
28 - Not yet submitted to Ozone Secretariat	Manufacture of Chlorinated Polypropene	CTC	No – See Chapter 5b	Solvent	Yield, quality of product	Coating materials, adhesives, silk screen inks	Yes	Unknown
29 - Not yet submitted to Ozone Secretariat	Manufacture of Chlorinated EVA	CTC	No – See Chapter 5b	Solvent	Yield, quality of product	Coating materials, silk screen inks	Yes	Unknown
30 - Not yet submitted to Ozone Secretariat	Manufacture of methyl Isocyanate derivatives	CTC	No – See Chapter 5b	Solvent	Inert solvent, yield, quality, safety	Pesticide	Yes	Unknown
31 - Not yet submitted to Ozone Secretariat	Manufacture of 3-PhenoxyBenzyldehyde	CTC	No – See Chapter 5b	Solvent	Inert solvent, Yield, Quality, Safety	Pesticide	Yes	Unknown
32 - Not yet submitted to Ozone Secretariat	Manufacture of 2-chloro-5-methylpyridin	CTC	No – See Chapter 5b	Solvent	Inert solvent, Yield, Quality, Safety	Intermediate for Imidacloprid	Yes	Unknown
33 - Not yet submitted to Ozone Secretariat	Manufacture of Imidacloprid; 1-(6-chloro-3-pyridylmetyl)-N-nitroimidazolene amine-2	CTC	No – See Chapter 5b	Solvent	Inert solvent, Yield, Quality, Safety	Pesticide	Yes	Unknown

2.2 Summary of processes not yet included in Decision X/14 – information supplied to PATF (cont.)

Included in Decision X/14	Process	Process Agent	Case Study	Application	Reason used	Product use	Used in Article 5(1)	Used in non-Article 5(1)
34 - Not yet submitted to Ozone Secretariat	Manufacture of Buprofenzin; 2-tert-butylimino-3-isopropyl-5-phenylperhydro-1,3,5-thiodiazin-4-one	CTC	No – See Chapter 5b	Solvent	Inert solvent, Yield, Quality, Safety	Pesticide	Yes	Unknown
35 - Not yet submitted to Ozone Secretariat	Manufacture of Oxadiazon; 2-tert-butyl-4-(2,4-dichloro-5-iso-propoxyphenyl-1,3,4-oxadiazolan-5-one	CTC	No – See Chapter 5b	Solvent	Inert solvent, Yield, Quality, Safety	Herbicide	Yes	Unknown
36 - Not yet submitted to Ozone Secretariat	Manufacture of Chloridized N-methylaniline	CTC	No – See Chapter 5b	Solvent	Inert solvent, Yield, Quality, Safety	Intermediate for Buprofenzin	Yes	Unknown
37 - Not yet submitted to Ozone Secretariat	Manufacture of Mefenacet; D-(1,3-benzothiozole-2-oxy)-N-methylacetanilide	CTC	No – See Chapter 5b	Solvent	Inert solvent, Yield, Quality, Safety	Pesticide	Yes	Unknown
38 - Not yet submitted to Ozone Secretariat	Manufacture of 1,3-dichloro-benzothiazole	CTC	No – See Chapter 5b	Solvent	Inert solvent, Yield, Quality, Safety	Intermediate for Mefenacet	Yes	Unknown

2.3 ODS used as process agents

The preceding tables have shown that the most, common process agent used is CTC, one process used CFC-11, one uses CFC 12 and four use CFC-113. The widest use of CTC as a process agent is in the field of chlorine production. Other uses vary and consist of manufacture of polymers, chlorinated (intermediate) products, pharmaceuticals, pesticides and other agricultural chemicals.

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

2.4 Emissions of process agents in non-Article 5(1) countries

Precise accounting of emissions is not technically and administratively feasible because estimates are based on engineering calculations using process assumptions, because chemical process yields vary over time, and because equipment failure and leaks result in unmonitored emissions.

Most Parties have failed to report process agent uses and emissions. Decision X/14 requested all Parties to 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. The Ozone Secretariat received only 17 reports, 4 from non-Article 5(1), 3 from CEIT, and 10 from Article 5(1). Most lacked sufficient detail to allow for meaningful evaluation.

The Ozone Secretariat has drawn our attention to paragraph 36 of the Report of the 25th meeting of the ImpCom, 9 December 2000, as follows:

"One representative expressed the view that the reporting requirement on process agents set out in decision X/14 was not sufficiently clear, leading to problems with the drafting of data form 6 and its eventual approval. It was agreed that the Secretariat would identify the Parties which would be affected by the reporting requirement and invite them to discuss which data should be provided and how the form should be designed. It would then report back to the Committee with a review to a recommendation being made to the Meeting of the Parties."

The PATF received unofficial reports from industry association and process agent users and government authorities confirming that ODS emissions from process agent application in non-Article 5(1) countries have decreased since the 1997 TEAP report.

The PATF estimates that 4000-5000 tonnes of ODSs are used annually in process agent applications in non-Article 5(1) countries. Plant specific annual emissions are estimated as less than 250 tonnes – less than 7% of make-up quantities. This has been achieved by capture and recycle or destruction, or chemical transformation of the ODS.

3 Regulations and guidelines for minimizing and monitoring emissions

3.1 Introduction

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

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

3.2 Governmental approaches

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

3.2.1 Supra-national and regional approaches

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

3.2.2 National approaches

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

3.2.3 Sub-national approaches

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

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

3.3 Voluntary standards to reduce emissions

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

3.4. Regulatory review

3.4.1 Introduction

This section provides an overview of approaches currently in use in Article 5(1) and non Article 5(1) countries to monitor and minimize emissions of ozone-depleting substances in process agent applications. Differences in national, regional and local standards complicate efforts to compare standards or to estimate the overall burden placed on process agent facilities located in different countries or within a specific country. However, as indicated by the Case Studies that can be downloaded from http://www.teap.org/html/process_agents_reports.html, all non-Article 5(1) countries must currently meet specific regulations to minimize emissions of ODSs used in process agent applications. In the Article 5(1) countries emission standards for CTC and other ODS vary from stringent to non-existent. Similar to the non-Article 5(1) countries, widespread knowledge of the health and safety issues pertaining to CTC has resulted in some lowering of emissions, and thereby contributes to the goals of the Montreal

Protocol. The PATF also considered institutional/regulatory barriers to emission reductions.

3.4.2 Types of Standards

3.4.2.1 Regulatory

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

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

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

3.4.2.2 Voluntary and industry set standards to reduce emissions

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

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

3.4.3 Institutional/Regulatory impediments to emission reduction

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

4 Alternatives to the use of controlled substances as process agents

4.1 The nature of process agents

Alternatives for process agents can often be devised if the reasons for the use of the process agents are analysed carefully and due consideration is given to their chemical and physical properties, their toxicology, the environmental consequences of their release or emission, and the costs associated with their use or with modifications to plant or processes that might be needed to introduce alternatives.

No rigorous definition of process agent has been established by the Parties, but the PATF has provided an operational definition in section 1.3 of this report. In decision X/14, clause 1, the Parties agreed that process agents were those uses of controlled substances listed in table A of the decision . Table A of decision X/14 is shown in Section 1.2 of this report.

The process agent is generally present during the chemical reaction as a solvent, although examples are accepted in which the process agent participates in the chemical reaction but is recovered unchanged at the end of the reaction. This would be the case, for example, when a process agent is used as a chain transfer agent, in a polymerisation process, when the role of the process agent is to terminate a growing polymer chain and initiate the growth of a subsequent chain. The overall effect is to produce more short or intermediate-length polymer chains at the expense of fewer long chains.

The use of a process agent as a solvent is not necessarily a simple matter. The essential requirements are that one or more of the reactants, and possibly the products, should dissolve in the solvent, and that the solvent should remain unchanged while the chemical reaction takes place. These requirements are frequently in opposition: more polar substances have greater solvent power but they are more chemically reactive, too. For example, carbon tetrachloride (CTC) is not a particularly powerful solvent, but since it does not react with chlorine it is often the solvent of choice when chlorine chemistry is involved or when chlorine has to be absorbed from a gas stream. Chloroform, trichloromethane, is a more powerful solvent than carbon tetrachloride but it reacts with chlorine (as well as with many other chemical substances to which CTC is un-reactive) and so is less often employed in chemical industry.

Some specialised considerations of solvent properties may also apply, as when a re-crystallization needs to be performed. The product, in such a case, will need to dissolve in the hot solvent but be precipitated as the solution cools. The success of a subsequent materials handling step, for example filtration, will depend on the physical form of this precipitate, and this can often be optimised by choice of the appropriate solvent for re-crystallisation.

Examples are also known where the operation to be performed is not a chemical reaction but a physical one, such as fibre spinning, and here the viscosity of the solution will be an important factor. This will depend on the concentration of the solution that can be achieved (and thus on solvent power) as well as on specific solute-solvent interactions which determine viscosity.

In some cases, the preferred solvent is chosen over solvents with similar solvent power or chemical properties on the basis of its melting or boiling point. To take an example from outside the field of ODS, toluene (liquid range -95^o to 111^{o}C) may be preferred to the similar hydrocarbon, benzene (liquid range 6^o to 80^{o}C). By conducting the chemical reaction in solvent with appropriate boiling point, the reaction temperature may be maintained close to the boiling point of that solvent (in the case of CTC, 76^{o}C), although pressures higher than atmospheric may be required to maintain a low-boiling solvent in liquid state.

Finally, consideration in choice of a solvent would be given to the removal of the solvent from the product, especially where traces of retained solvent would constitute a hazard to human health or the environment. A well-known advantage of the use of carbon dioxide (used under high pressure to maintain the liquid or super-critical state) is that traces of residual "solvent" remaining in foodstuffs such as decaffeinated coffee do not constitute a hazard. Substantial efforts must be made, however, to remove the residues of solvents such as CTC from industrial products such as the aramid resins which are discussed below.

4.2. Alternatives to the use of ODS (Available Case Studies can be found at: http://www.teap.org/html/process_agents_reports.html

4.2.1 Chlor-Alkali production

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-1
Application	Elimination of NCl_3
Reason Used	Safety and quality of product
Product use	Chlorine is a universal chemical used for more than 60% of all chemical synthesis
Identified alternatives	No general alternatives. Some plant specific alternatives.

CTC is the traditional and efficient agent to extract nitrogen trichloride (NCl_3) from liquid chlorine. NCl_3 is a highly explosive substance inadvertently produced in chlor-alkali plants when the electrolysed salt contains nitrogenous impurities. Both sea salt and mined salt contain such impurities, although there is more in salt from the latter source. The nitrogen is at the ammonia (rather than nitrate) oxidation level, often in the form of protein material, and exposure to chlorine converts it to nitrogen trichloride. While some uses of chlorine can tolerate the presence of small proportions of nitrogen trichloride, when the focus of the operation is the production of liquid chlorine then NCl_3 can build up to a dangerous concentration.

The obvious ODS free solution is the use of very pure salt but this is an extremely rare commodity. Transportation of salt of required purity to an existing plant site is often not technically or economically feasible. Strategies for dealing with the NCl_3 problem must be taken on a case by case basis, as plant design and equipment, presence of nitrogen derivatives, and purity requirements for chlorine are very different from one facility to another. For a particular plant, one technique might be a suitable solution, only a partial one, or cannot be safely used at all.

The strategies available to the industry include:

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

The first of these has not been fruitful because no alternative process agent having the unique set of required properties has been identified by the industry. It has been suggested that chloroform might be a suitable replacement for CTC, since it is a good solvent for NCl_3, but it is converted to CTC by reaction with chlorine and so offers no advantage over starting with CTC itself. A complete set of technical requirements is not available to the PATF at this time, so the extent to which suitable alternative process agents have been sought cannot be evaluated.

Similarly, no method is available for economically removing nitrogenous impurities from the salt.

Nitrogen trichloride is rapidly destroyed by heating above approximately 50^{o}C, and this is the usual technique for destroying it either in the chlorine stream or in the CTC extract. The first method is employed where chlorine is used at the site of generation, with only minimal storage in liquid form. Re-vaporization of chlorine by heating the liquid, suffices to destroy the NCl_3. The second method is the one in which CTC is traditionally employed as solvent to extract NCl_3 from the chlorine.

As mentioned above, some uses can tolerate small proportions of NCl_3 in the chlorine gas, and it is presumably destroyed in subsequent processing or acts in the same way as chlorine to perform a chlorination reaction on some organic substrate.

4.2.2 Recovery of chlorine in gas from production of chlorine

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-2
Application	Chlorine recovery by gas absorption
Reason Used	Safety, yield
Product use	Chlorine is a universal chemical used for more than 60% of all chemical synthesis
Identified alternatives	Plant specific alternatives only

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

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

In addition to this technological approach, there are several chemical reactions that can be used to sequester chlorine from the tail gases. One is to absorb the chlorine in sodium hydroxide, leading to formation of the marketable product sodium hypochlorite. Another is to react the tail gas chlorine with hydrogen to form gaseous hydrogen chloride, which is then absorbed in water to form hydrochloric acid. This requires specialised equipment at a substantial cost, and also adds additional safety risk from the standpoint of explosion potential. Both of the “chemical” approaches involve the production of co-products, small in volume compared to the major product chlorine, but nonetheless requiring separate marketing or disposal.

4.2.3 Chlorinated Rubber

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-3
Application	Chemical inert solvent for high quality product
Reason Used	Inert solvent
Product use	Heavy duty anti-corrosives and adhesives
Identified alternatives	Aqueous process – see 4.4

Some details of the CTC based process used in Germany to produce chlorinated rubber (CR) are given in Case Study CS-3. These substances are used in surface coatings and solvent based inks. An important criterion which drives the choice of CTC is its role in determining the quality of the product, but a number of different processes are used for the production of chlorinated rubber so the search for alternatives has explored many possibilities. Two main lines of investigation can be distinguished:

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

The reduction of more than 99% of CTC emissions from CR production in the non-Article 5(1) countries, in less than 5 years, shows that CR can be produced in an environmentally responsible manner.

A Case Study (CS-3a) describing an aqueous process for the production of chlorinated rubber will be provided at: http://www.teap.org/html/process_agents_reports.html in the near future. The aqueous process does not require the use of CTC as a process agent, however there is some possibility of inadvertent production of CTC from the aqueous process. For a plant operating in an Article 5(1) country it is likely that the aqueous process would result in much lower emissions than the CTC based process. In an Article 5(1) country it would be very difficult to achieve the type of process control and facility maintenance achieved at the German plant or for an Article 5(1) government to provide the degree of compliance monitoring undertaken by the German government. These important factors have resulted in the extremely low emissions of CTC achieved by the German facility.

4.2.4 Endosulfan production

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-4
Application	Solvent
Reason Used	Inert solvent
Product use	Biodegradable insecticide
Identified alternatives	Yes – aromatic solvent

The insecticide Endosulfan, which is widely used by cotton growers, is produced in two stages, the second of which involves the reaction of thionyl chloride ($SOCl_2$) with the two $-CH_2OH$ groups of the initial adduct, forming a new seven-membered ring. The initial patent in this area does not describe the use of a solvent during this second stage, but while some plants operate in this way (probably using excess thionyl chloride as a solvent which is recovered when the reaction has taken place) others use CTC as solvent, recovering it at the conclusion of the reaction and recycling it in the process. There are few specific chemical requirements for such a solvent and so CTC should be easily replaced in this process and several companies have made such a substitution. Thus, one company uses ethylene dichloride (EDC) while another reports successful use of an aromatic solvent, but in the latter case flammability of the selected solvent may be an issue. The adoption of the alternatives requires only a small change in the production process (see Case Study CS-4.

4.2.5 Ibuprofen production

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-5
Application	Solvent for Friedel-Crafts synthesis
Reason Used	Inert solvent
Product use	Anti-inflammatory drug
Identified alternatives	Yes

The initial step in production of the anti-inflammatory drug Ibuprofen (see Case Study CS-5 available at: http://www.teap.org/html/process_agents_reports.html) involves the Friedel Crafts acylation of isobutyl benzene with acetyl chloride in the presence of aluminium chloride and a suitable solvent, and in the initial patent CTC was used for this purpose. As above, however, a range of solvents might be employed and it is reported that ethylenedichoride (EDC) is an acceptable substitute for CTC.

4.2.6 Dicofol production

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-6
Application	Solvent
Reason Used	Inert solvent
Product use	Broad spectrum acaracide
Identified alternatives	Yes

Mites and ticks are controlled with the acaricide Dicofol, the molecule of which is closely related to DDT and Dicofol is in fact prepared from that substance. CTC is used as a solvent in two of the three stages of that process. In the second stage, the reaction involves chlorination and so a non-reactive solvent is required, but in the third stage the CTC is used as a water-immiscible solvent to extract the Dicofol product. It is reported that dichloroethane (ethylene dichloride) is an acceptable substitute for CTC, although certain technical changes are required in both stages, see Case Study CS-6.

4.2.7 Chlorosulfonated Polyolefin (CSM)

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-7a and CS-7b
Application	Chlorination agents
Reason Used	Safety, yield
Product use	High tech coatings, protective materials
Identified alternatives	No viable alternative as yet for majority of products. Non-ODS for limited application.

These flexible materials find use mainly because of their oil and grease resistance and general durability. In North America, no viable alternative to the use of CTC has been found for the full range of products and processes of commercial significance. Of the many investigated possibilities chloroform seemed promising, but it leads to a 40% reduction of production capacity and to inadvertent formation of large quantities of CTC. The reaction conditions are particularly harsh, involving reaction of the polyolefin with chlorine and sulphur dioxide at moderately elevated temperature.

The processes employed are described in Case Studies CS-7a and CS-7b. In China, the possibility of using chlorobenzene as a process agent was investigated, but this option was abandoned for the following reasons:

- energy consumption is much higher than when using CTC due to the higher boiling point of chlorobenzene
- chemical stability of the solvent to chlorine and sulphur dioxide is lower than that of the CTC process
- plant safety was compromised by the flammability, explosivity and toxicity of chlorobenzene

4.2.8 Aramid polymer (PPTA)

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-8
Application	Chlorination specific solvent
Reason Used	Quality, safety, waste reduction
Product use	Asbestos replacement, public and military safety products
Identified alternatives	No viable alternative as yet

Fibres produced from these substances are light weight and have high tensile strength, good flame resistance and good chemical stability. They may be used in protective helmets, cladding for chemical storage and transport containers, non-asbestos brake linings, and bullet-proof vests. The polymer is formed by reaction of two monomers, paraphenylenediamine and terephthaloyl dichloride (TDC), as described in Case Study CS-8. The second of these monomers is formed in a preliminary stage which involves chlorination of p-xylene, in CTC, followed by fusion of the chlorination product, hexachloro-p-xylene with terephthalic acid.

A commercial non-ODS process for the production of the raw material TDC is known. This is however based on a different chemical reaction and the process is carried out with the use of phosgene as a raw material. Such use is only technically and commercially viable when phosgene is already available on the site or, where new plant is required, it may be used for more than one product. A research and development program to find an ODS free alternative to the existing production process is showing promising progress.

4.2.9 Fluoropolymer resins

Included in Decision X/14	Yes
Process agent	CFC-113
Case Study	CS-9
Application	Specific solvent
Reason Used	Specific dispersant, chemical inert
Product use	Extreme temperature electrical insulation, inert coatings
Identified alternatives	Alternative for portion of products. Continuing program.

This family of polymers are commonly used in non-stick cookware and high-performance electrical insulation, see Case Study CS-9. In North America, close to fifty potential process agents for use in polymer production have been explored over the past eight years as part of a research and development program. Much of the product line was converted away from CFC-113 (CF_3-CCl_3) during 1997 and 1998. However, there are still specific critical use applications for which non-ODS process agents have yet to be found. Efforts are continuing to find an acceptable process agent or suitable processing conditions for these products.

In Japan, a plant for manufacture of fluoropolymer resins has been converted to a non-ODS process utilizing a proprietary technology, but the facility does not produce the full range of products.

4.2.10 Fine synthetic fibre sheet

Included in Decision X/14	Yes
Process agent	CFC-11
Case Study	CS-10
Application	Spinning agent
Reason Used	Quality, safety, yield
Product use	Protective wrapping, very strong sheets
Identified alternatives	Conversion to non-ODS process agent underway.

Sheets derived from synthetic fibres such as high density polyethylene are widely used in protective clothing, sterilizable packaging, and air filtration. The fibres are formed by extrusion in a spin cell of solutions of the polymer in a low-boiling solvent which vaporizes as the fibrous mass is formed and may then be recovered for recycling, see Case Study CS-10. No simple, safe, drop-in candidate has been identified to replace CFC-11 in the existing facilities, despite a continuing (more than twelve years) program that has examined over one hundred and twenty possible process agents. A non-ODS process agent has been developed, but it requires completely new spinning and recovery facilities to use it. The first two new commercial facilities were started in 1995, and a third in 2000. Process safety management is key to the safe operation of these facilities. Continued safety analysis has shown that process safety can be significantly improved with the addition of new solution mixing technology. This technology will be retrofitted on the first two facilities at considerable expense and down time over the next three years. In addition, a new fourth generation facility is being constructed with operation scheduled for 2002. This fourth generation technology will form the basis for future capacity expansions. Confirmation of this fourth generation technology is needed to allow full conversion from CFC-11 operations.

4.2.11 SBR

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Chain transfer agent
Product use	High tech coatings, protective materials
Identified alternatives	Yes - mercaptans

CTC is used as a chain transfer agent in the manufacture of this type of synthetic rubber that is strong and resistant to extreme temperatures and climate. No CTC is used to manufacture this product in China.

4.2.12 Chlorinated paraffins

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-12
Application	Solvent
Reason Used	Inert solvent
Product use	Lubricant additive, flame retardant for plastics, plasticizer in rubber paints.
Identified alternatives	Yes

These substances, with chain lengths between 10 and 26 carbons and chlorine content of 28-70% are produced by chlorination of respective paraffin fractions derived from petroleum refining. They are used variously as high pressure lubricants, as plasticizers and as flame retardants, depending on their physical properties. The lower members of the family are bio-accumulative and are generally being phased-out in developed countries. Chlorination may be undertaken in the absence of a solvent provided the product is liquid at reaction temperatures, but the highly chlorinated materials are solids, making it necessary to use a solvent such as CTC to reduce the viscosity of the reaction mixture. Aqueous processes are probably available as well.

4.2.13 Vinorelbine

Included in Decision X/14	Yes
Process agent	CFC 113
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Pharmaceutical
Identified alternatives	Yes

This is an anticancer drug (antineoplastic) manufactured by modification of a natural product from the vinca alkaloid family and known as nor-5í-anhydrovinblastine. The original publications do not mention CFC 113, but instead report the use of m-chloroperbenzoic acid in dichloromethane followed by trifluoroacetic anhydride in the same solvent. It is possible that in manufacture CTC has been found to be more satisfactory from a chemical point of view than dichloromethane. Production quantities of such a drug are likely to be very small when compared to basic chemicals like chlorine or chlorinated rubbers.

4.2.14 Photochemical synthesis of perfluoropolyetherpolyperoxide precursors of Z-perfluoropolyethers and difunctional derivatives

Included in Decision X/14	Yes
Process agent	CFC 12
Case Study	CS-14
Application	
Reason Used	
Product use	
Identified alternatives	

4.2.15 Reduction of perfluoropolyetherpolyperoxide intermediate for production of perfluoropolyether diesters

Included in Decision X/14	Yes
Process agent	CFC 113
Case Study	CS-15
Application	
Reason Used	
Product use	
Identified alternatives	

4.2.16 Preparation of perfluoropolyether diols with high functionality

Included in Decision X/14	Yes
Process agent	CFC 113
Case Study	C-16
Application	
Reason Used	
Product use	
Identified alternatives	

4.2.17a Ketotifin

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Antihistamine
Identified alternatives	Likely

This substance is an antihistamine which is structurally similar to the tricyclic antidepressants. The first stage in its synthesis involves reaction of a CTC solution of an alkene (-CH=CH-) with N-bromosuccinimide and benzoyl peroxide, to form a dibromocompound (-CHBr-CHBr-) which is further modified in subsequent stages. None of these later stages involves the use of CTC. Investigations should easily identify a suitable replacement solvent.

4.2.17b Anticol

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Possible pharmaceutical
Identified alternatives	Unknown

No information was provided or located on this substance, which appears to be used as a pharmaceutical.

4.2.17c Disulfuram

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Pharmaceutical
Identified alternatives	Yes

This substance is taken to sensitise users against alcohol consumption. Nothing in the chemical literature suggests the use of CTC as reported to the PATF. In the first of two stages in its production, diethylamine is reacted with carbon disulphide in aqueous alkali, and then this product is oxidized with sodium hypochlorite, again in aqueous solution, in the second stage.

4.2.18 Tralomethrine

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Insecticide
Identified alternatives	Unknown

This substance is a synthetic pyrethrin, which like all members of this chemical family is an ester formed from a cyclopropane carboxylic acid and an aromatic alcohol. No further details are available.

4.2.19 Bromohexine hydrochloride

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-18
Application	No information provided
Reason Used	No information provided
Product use	Pharmaceutical - expectorant
Identified alternatives	Likely

The molecule of this substance, which is used as an expectorant, is constructed by joining two major portions at a central nitrogen atom. The original patent describes how one portion is elaborated through conversion of a $-CH_3$ group to $-CH_2Br$. This bromination is effected by a selective brominating agent and, although no solvent is mentioned in the patent, it is likely that CTC is involved since it is commonly employed in such reactions. As in other cases previously discussed, however, it should be easy to find a replacement solvent.

4.2.20 Diclofenac sodium

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-20
Application	Solvent
Reason Used	Yield
Product use	Pharmaceutical – anti-inflammatory
Identified alternatives	Yes

This anti-inflammatory drug has been synthesized in a number of ways, but the most elegant (and presumably commercially advantageous) method involves the use of oxalyl chloride (Cl-CO-CO-Cl) and a Friedel Crafts reaction catalysed by aluminium chloride. The original patent describes the use of “tetrachloroethane” as solvent for this stage of the synthesis, and it is possible that this is a misprint for tetrachloromethane - CTC. The reaction is conducted under mild conditions, so there would be no need to take advantage of the higher boiling point of the tetrachloroethane, but its greater solvent power may have been the reason for its use if indeed it was the solvent involved. In the scheme shown in Case Study CS-20, CTC is used (in conjunction with perchloroethylene) in the very first step, the chlorination of phenol. The choice of solvent affects the selectivity of the reaction so that 2,6-dichlorophenol is favoured over the alternative product, 2,4-dichlorophenol.

4.2.21 Cloxacillin

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Pharmaceutical - antibiotic
Identified alternatives	Likely

This is a semi-synthetic penicillin formed by reaction of the natural penicillanic acid and an acid chloride, which is turn formed from a synthetic acid. The formation of the acid chloride involves reaction of the acid with thionyl chloride ($SOCl_2$), and the original patent describes this reaction as being carried out in excess thionyl chloride, which thus plays the role of solvent as well as reactant. CTC could be used as solvent in this reaction, but finding a substitute for CTC should be possible.

4.2.22 Phenyl glycine

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	No information provided
Product use	Pharmaceutical
Identified alternatives	Unknown

The solvent CTC is known to be used in two successful chemical reactions which use this amino-acid (C-phenyl glycine). In the first reaction, HCl in dry CTC is used to form the hydrochloride salt, which is then reacted with thionyl chloride to convert the –COOH group to the acid chloride. This product, being similarly insoluble in CTC, is washed with CTC to effect purification.

4.2.23 Isosorbid mononitrate

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Pharmaceutical – vasodilator
Identified alternatives	Yes

This is a vasodilating drug, similar in its effects to the nitro-glycerine (glyceryl trinitrate) that is use by angina sufferers. The dinitrate, and presumably the mononitrate, may be prepared from sorbitol by reaction with a typical nitric-and-sulphuric acid nitrating mixture. The published chemistry provides no indication of the use of CTC.

4.2.24 Omeprazole

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	No information provided
Product use	Pharmaceutical – anti-ulcer drug
Identified alternatives	Likely

This anti-ulcer drug is produced by joining together two building blocks. One of these is primed for the coupling step by reacting it with thionyl chloride ($SOCl_2$) to convert a -CH_2OH group into a -CH_2Cl group. The literature descriptions of this step do not mention the use of a solvent, but CTC would be an appropriate choice, as it is for other reactions (see above) involving thionyl chloride. But, as before, suitable replacement solvents could be found at the expense of a little research and possibly minor adjustments to plant.

4.2.25 Manufacture of vaccine bottles

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Vaccine bottles
Identified alternatives	Likely

No information was provided or located that would justify the use of CTC for this purpose.

4.2.26 Manufacture of Cyclodime

Included in Decision X/14	Submitted to Ozone Secretariat
Process agent	CTC
Case Study	CS-26
Application	Inert solvent
Reason Used	Chemically and photochemically inert, product yield and quality
Product use	Formation of hydraulic components used in extreme and adverse temperatures including aeronautics and aerospace
Identified alternatives	

Cyclodime is a synthesis intermediate used for the manufacture of polymers raw materials. The polymers produced are used for technical applications (such as hydraulic systems) in the aerospace, aeronautics, automotive and appliance industries.

The materials are dissolved in CTC and then reacted under powerful light radiation in order to produce the crude Cyclodime by a photochemical reaction in CTC used as a solvent.

The use of CTC is at present essential in this process due to stability and as it is the only suitable solvent known to not decompose under the aggressive photochemical reaction. Evaluation of other solvents under process conditions, such as non-fully halogenated compounds has led to the resulting polymer raw material being unsatisfactory for the production of the final polymers, primarily due to the breakdown of the solvent during the photochemical reaction and the formation of free radicals.

4.2.27 Chlorophenesin

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5a Not yet submitted to Ozone Secretariat
Process agent	CTC
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Pharmaceutical
Identified alternatives	Unknown

4.2.28 Chlorinated polypropene

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b Not yet submitted to Ozone Secretariat
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Yield, quality of product
Product use	Coating materials, adhesives, paining inks
Identified alternatives	Unknown

4.2.29 Chlorinated EVA

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Yield, quality of product
Product use	Coating materials, painting inks
Identified alternatives	Unknown

4.2.30 Manufacture of methyl isocyanate derivatives

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Pesticide
Identified alternatives	Unknown

4.2.31 Manufacture of 3-phenoxy benzaldehyde

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Pesticide
Identified alternatives	Unknown

4.2.32 Manufacture of 2-chloro-5-metyhlpyridine

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Intermediate for Imidacloprid
Identified alternatives	Unknown

4.2.33 Imidacloprid

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Pesticide
Identified alternatives	Unknown

4.2.34 Buprofenzin

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b Not yet submitted to Ozone Secretariat
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Pesticide
Identified alternatives	Unknown

4.2.35 Oxadiazon

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b Not yet submitted to Ozone Secretariat
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Herbicide
Identified alternatives	Unknown

4.2.36 Chloradized N-methylaniline

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b Not yet submitted to Ozone Secretariat
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Intermediate for Buprofenzin
Identified alternatives	Unknown

4.2.37 Mefenacet

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b Not yet submitted to Ozone Secretariat
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Pesticide
Identified alternatives	Unknown

4.2.38 1,3-Dichlorobenzothiazole

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b Not yet submitted to Ozone Secretariat
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Intermediate for Mefenacet
Identified alternatives	Unknown

4.3 Submissions lacking documentation

Detailed process descriptions and explanations of why an ODS was used as a process agent were lacking for a number of the uses found in Table A of Decision X/14 or subsequently provided to the Ozone Secretariat and/or PATF. For many of the undocumented CTC uses, examination of the research and patent literature raised the possibility that CTC was being used as a result of developments in process chemistry, which pointed to advantages derived from CTC use, or from commercial considerations such as patent protection. However, the literature did not permit clarification of these matters.

4.4 Care in adopting alternatives

Care is required when changing an ODS based process to avoid changes that would result in the inadvertent production of the same or another ODS or a Persistent Organic Pollutant (POP).

In some cases the replacement process agent, although not itself an ODS might transform to an ODS during the chemical process. An example would be the substitution of chloroform for CTC in the production of chlorine. In this case it would be expected that the chloroform would be transformed to CTC. In such a case it is unclear what obligations or remedies would be provided by the Montreal Protocol to discourage emissions resulting from such emissions of "inadvertently produced" CTC.

Another situation that deserves consideration occurs when an ODS might be produced, albeit to only a slight extent, in the alternative process. If the process is conducted on a very large scale, then even "slight" can result in substantial annual ODS emissions. The most likely cases where there is a probability that this would occur are processes involving chlorination of hydrocarbon substrates, such as natural rubber, synthetic rubber, poly-olefins or paraffin. In such processes CTC is a likely minor by-product. Aqueous chlorination processes are not immune to this problem. Again, it is unclear what obligations or remedies would be provided by the Montreal Protocol to discourage emissions resulting from such emissions of "inadvertently produced" CTC.

4.5 Conclusions

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

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

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

    - phase-out achieved or achievable
    - expected phase-out within the next few years subject to solution of final technical issues
    - a few processes facing extreme difficulty to find an alternative

- Realizing that these results have been achieved over a period of 5 to 6 years, together with measures to significantly reduce emissions where ODS process agents are still in use, there has been remarkable progress and further progress is expected.

- Care should be taken that ODS are not inadvertently produced by the substitution of an alternative process agent or by the use of an alternative process.

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

5 Overview of ODS use in chemical processes in Article 5(1) countries

5.1 Emissions of ODS from chemical process industries in Article 5(1) countries

5.1.1 Use of controlled substances in chemical processes

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

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

5.1.2 Industries using CTC in chemical processes

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

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

The survey revealed that CTC is also being used as a chain transfer agent in the emulsion polymerisation process of SBR in South Korea. A more detailed investigation is needed, including that in other Article 5(1) countries, to further check possible use of CTC for this application.

5.1.3 CTC usage in chemical processes

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

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

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

In the pharmaceutical sector, CTC is being used in India for the following products:

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

Case Study CS-5 on the status of CTC usage in the production of Ibuprofen in India can be found at: http://www.teap.org/html/process_agents_reports.html. The manufacture of Ibuprofen is the largest amongst the above pharmaceutical products.

In the agricultural chemicals sector, CTC use in India is in the manufacture of the following products :

- Endosulfan (insecticide)
- Dicofol (an acaricide)

Case studies on the status of CTC usage in the production of Endosulfan and Dicofol in India, CS-4 and CS-6 are also available at :
http://www.teap.org/html/process_agents_reports.html.

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

At the time of preparation of the India Country Programme in 1993, the main source of emission of CTC was identified to be from the production of pharmaceutical product, Ibuprofen. There are, at least, 14 producers of Ibuprofen in India and a number of them have phased out use of CTC and converted their processes using non-ODS solvents. As a result, CTC emissions from Ibuprofen production has already been reduced .

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

5.3 ODS use in chemical processes in China

5.3.1 Background

China has recently completed its Country Program Update, which left phaseout of ODS process agent applications as a future action plan to be developed. However, there had been little study made of ODS process agent applications within China and detailed data on its consumption was not available. In order to make clear the main uses and the quantities of the ODS used as process agents in China to provide a sound basis for developing strategy for control, replacement and finally phase-out of the ODS process agents, a preliminary four-week survey was conducted in late December 1999 on a national basis.

Followed that, a project to develop the action plan for phasing out process agent applications in China was put into practice at the end of 2000 with financial supports from the MP Multilateral Funds. At the first stage of the work, a full field survey has been carried out to collect detailed information and conduct analysis on the consumption of ODS process agents and the development of emissions-reduction techniques and alternative process that does not use ozone-depleting substances. Currently the field survey is still going and expected to finish by April, 2001.

Therefore, the data and information presented in this report are essentially based on the results from:

1) The preliminary survey on the ODS process agent applications in China conducted in late December 1999.

2) The partly completed full survey currently carried out in China.

5.3.2 Review on the 25 Process Agent Applications

Process agent applications generally involve the use of ODS as a reaction or dissolving medium in the production of specified products. In China, carbon tetrachloride (CTC) is the main ODS which use in chemical processes as an inert solvent in carrying out chemical reactions. For the 25 applications of ODS process agents outlined in Decision X/14, review of the China's situation based on the 1999 preliminary survey is shown in Table 1. Of the applied processes, major uses of CTC are generally in the production of chlorinated rubber (CR), chlorosulphonated polyethylene (CSM) and chlorinated paraffin (70% solid grade, CP-70). For the question-marked processes, the situation is still unknown and need to be further verified.

Review on the 25 applications of ODS as process agents in China

ODS applications as process agents (as listed in Table A of Decision X/14)			China's situation	
No.	ODS	Process agent application	Status	Description
1	CTC	Elimination of NCl_3 in production of chlorine and caustic	Not applicable	No ODS used
2	CTC	Recovery of chlorine in tail gas from chlorine production	Not applicable	No ODS used
3	CTC	Manufacture of chlorinated rubber	Major use	
4	CTC	Manufacture of endosulphan (insecticide)	?	
5	CTC	Manufacture of isobutyl acetophenone (ibuprofen)	Not applicable	No ODS used
6	CTC	Manufacture of dicofol (insecticide)	Not applicable	No ODS used
7	CTC	Manufacture of chlorosulphonated polyolefin (CSM)	Major use	
8	CTC	Manufacture of poly-phenylene-terepthalamide	Not applicable	No production
9	CFC 113	Manufacture of fluoropolymer resins	Not applicable	No ODS used
10	CFC 11	Manufacture of fine synthetic polyolefin fibre sheet	?	
11	CTC	Manufacture of styrene butadiene rubber (SBR)	Not applicable	No ODS used
12	CTC	Manufacture of chlorinated paraffin	Major use	
13	CFC 113	Manufacture of vinorelbine (pharmaceutical product)	Not applicable	No ODS used
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	Not applicable	
16	CFC 113	Preparation of perfluoropolyether diols with high functionality	Not applicable	
17	CTC	Production of pharmaceuticals – ketotifen, anticol and disulfiram	?	
18	CTC	Production of tralomethrine (insecticide)	Not applicable	No production
19	CTC	Bromohexine hydrochloride	?	
20	CTC	Diclofenac sodium	Not applicable	No ODS used
21	CTC	Cloxacilin	Not applicable	No production
22	CTC	Phenyl glycine	?	
23	CTC	Isosorbid mononitrate	?	
24	CTC	Omeprazol	?	
25	CFC-12	Manufacture of vaccine bottles	?	

5.3.3 New Applications of CTC as a Process Agent

Based on the result from 1999 preliminary survey, a number of additional applications of CTC, which were not included in Decision X/14, might exist in China as follows:

- CTC application in manufacture of chlorinated polypropene.

- CTC application in manufacture of Methyl Isocyanate derivatives such as Furandan.

These new applications were verified in the current survey. Besides, some other new processes that use CTC as a process agent are also being found during this survey. The following Table summarizes the new applications of CTC that have been currently identified in China. Most of the new applications are concerned with the manufacture of agro-chemicals such as C3 to C11 processes.

Verified new applications of CTC as a process agent in China

Case No.	New applications of CTC as process agents	Product Use
C1	Manufacture of Chlorinated Polypropene (CPP)	Coating Materials, Adhesives, Painting Inks.
C2	Manufacture of Chlorinated Ethylene-Vinyl Acetate (CEVA)	Coating Materials, Painting Inks.
C3	Manufacture of 3-Phenoxybenzyldehyde	Agro-chemicals (Pesticide)
C4	Manufacture of 2-chloro-5-methylpyridin	Intermediate for Imidacloprid
C5	Manufacture of Imidacloprid; 1-(6-chloro-3-pyridylmetyl)-N-nitroimidazolene amine-2;	Agro-chemicals (Pesticide)
C6	Manufacture of Buprofenzin; 2-tert-butylimino-3-isopropyl-5-phenylperhydro-1,3,5-thiodiazin-4-one	Agro-chemicals (Pesticide)
C7	Manufacture of Oxadiazon; 2-tert-butyl-4-(2,4-dichloro-5-iso-propoxyphenyl-1,3,4-oxadiazolan-5-one	Agro-chemicals (Herbicide)
C8	Manufacture of Methyl Isocyanate derivatives (Furandan)	Pesticide
C9	Manufacture of Chloridized N-methylaniline	Intermediate for Buprofenzin
C10	Manufacture of Mefenacet; D-(1,3-benzothiazole-2-oxy)-N-methylacetanilide	Pesticide
C11	Manufacture of 1,3-dichloro-benzothiazole	Intermediate for Mefenacet

5.3.4 Progress on emission-reduction techniques in China

Since 1995, great efforts have been made in some manufactures to reduce CTC emissions in their production. The emission-reduction techniques or measures, which have been taken, are as follows:

- Modifying the production facilities;
- Changing the process technology to enhance CTC recovery;
- Exacting the technologic conditions and process operations;

Glossary

ATM	Atmospheric pressure
BAP	Best available technology
BEP	Best environmental practices
CAER	Community awareness and emergency response
CAS	Carbon adsorption system or carbon adsorption stripper
CCS	Compression and condensation system
CFC-11	Trichloromonofluoromethane
CFC-113	Trichlorotrifluoroethane
CR	Chlorinated rubber
CSM	Chlorosulphonated polyolefins
CTC	Carbon tetrachloride
DCS	Distributed control system
DCE	Dichloroethane
ECO	Ecological
ECTFE	Ethylenechlorotrifluoroethylene
EDC	Ethylenedichoride
eop	End of pipe
ETFE	Ethylenetetrafluoroethylene
EU	European Union
FMEA	Failure mode and effect analysis
H&V	Heating and ventillation
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
HP	High pressure
IR	Infrared
LEL	Lower explosive limit
LP	Low pressure
MACT	Maximum achievable control technology
MT	Metric tonne
NPDES	Non-point discharge elimination system
ODS	Ozone depleting substance
PA	Process agent
PATF	Process Agents Task Force
PAWG	Process Agents Working Group
PFC	Perfluorocarbon
ppb	Parts per billion
ppm	Parts per million
PPD	Para-phenylenediamine
PPTA	Polyparaphenyleneterephthalamide
R&D	Research and development

SBR	Styrene butadiene rubber
SS	Stainless steel
TEAP	Technology and Economic Assessment Panel
TCA	Trichloroethane
TDC	Terephthaloyl dichloride
TFE	Tetrafluoroethylene
TLV	Threshold limit value
UV	Ultraviolet