

Montreal Protocol



**Report of the
Process Agents Task Force**

April 1997

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Summary and Conclusions

Products

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

Example uses identified in this report are summarized in the following table:

Examples of Products Made Using Process Agents

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

Definitions

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

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

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

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

- 1.) Chemically inert during a chemical reaction
- 2.) Physical properties, 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 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:

$$\text{Consumption} = \text{production} + \text{imports} - \text{exports}$$

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

In the case of ODS used as process agents, the ODS consumption would be utilized to replenish process inventory losses resulting from transformation, destruction and emissions to the atmosphere from the process and/or trace quantities slowly emitted from the product.

However, the existing definition of consumption, when applied to process agent use of ODS, disregards transformation and destruction and could result in a disincentive to reduce emissions.

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

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

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

Identified uses of ODS as chemical process agents

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

Case Study	Application
1	Use of CTC in the elimination of NCl_3 in the production of chlorine and caustic soda
2	Use of CTC in the recovery of chlorine in tail gas from production of Chlorine
3	Use of CTC in the Chlorinated Rubber Process
4	Use of CTC in Endosulphan production
5	Usage of CTC in Ibuprofen production
6	Use of CTC in Dicofol production
7a	Use of CTC in Chlorosulphonated polyolefin (CSM) production in a non-Article 5(1) country
7b	Use of CTC in Chlorosulphonated polyolefin (CSM) production in an Article 5(1) country
8	Production of Poly-Phenylene-Terephtal-Amide with the aid of CTC in an intermediate raw product
9	Use of CFC 113 in manufacturing a family of fluoropolymer resins
10	Use of CFC 11 in manufacture of a fine synthetic fiber sheet structure
No Case Study	Use of CTC in Styrene Butadiene Rubber (SBR) production
No Case Study	Use of CTC in Chlorinated Paraffin production

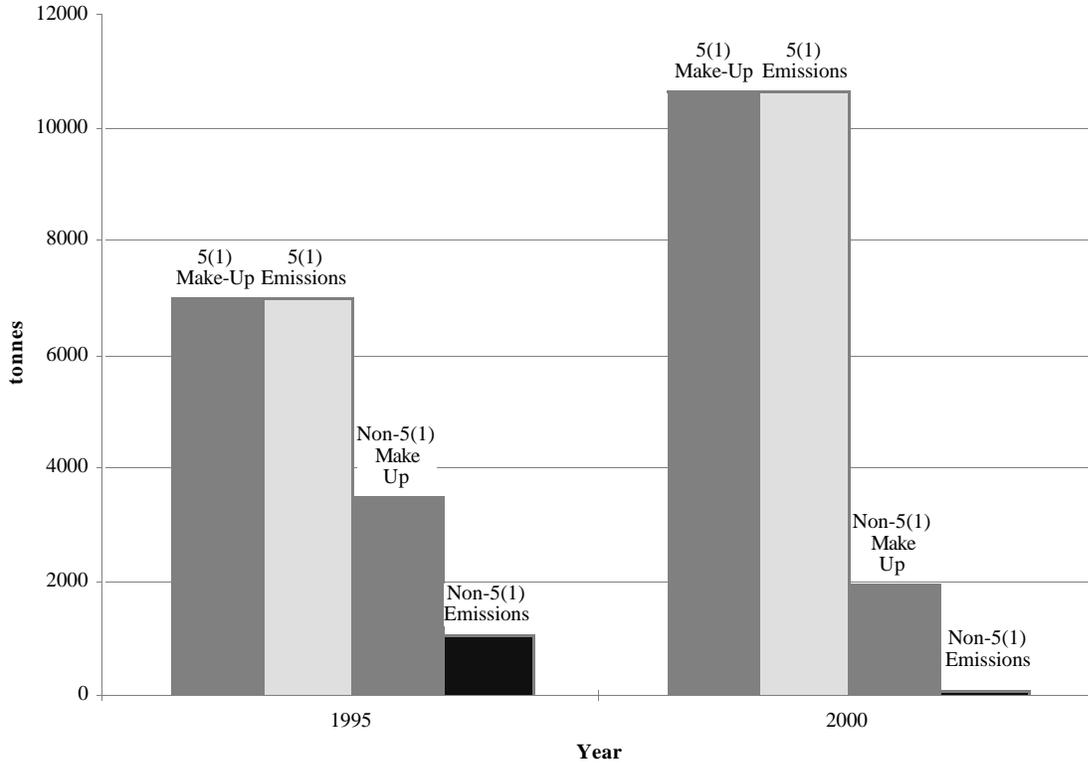
Feedstock applications

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

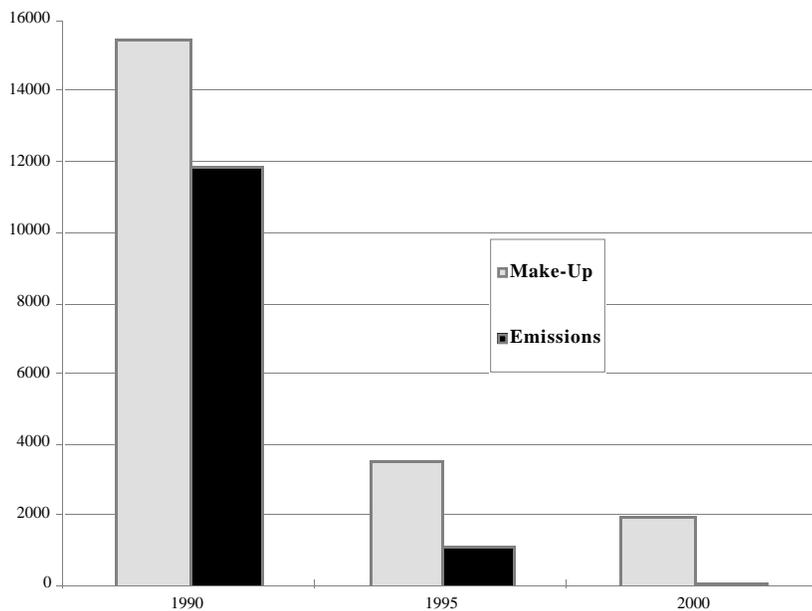
Case Study	Application
C-11	Use of Trichloroethane in the production of semiconductors
C-12	Use of CFC 12 in the purification of graphite

Estimates of emissions of ODS used as process agents

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



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



Emissions associated with the different control technologies and other process conditions under which chemical process agents are used

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

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

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

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

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

Alternative process agent technologies or products available to replace ODS in such uses.

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

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

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

General conclusions

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

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

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

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

Conclusions regarding non-Article 5(1) countries

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

Conclusions regarding Article 5(1) countries

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

Article 5(1) process agents by conversion of processes to the use of non ODS process agents or processes.

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

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

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

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

- (i) availability of skilled manpower and their appropriate training;
- (ii) access to technology; and
- (iii) adequate financing.

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

Conclusions regarding countries with economies in transition

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

1 Introduction and definitions

1.1 Background

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

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

1.2 Decisions

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

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

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

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

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

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

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

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

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

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

- end of Decisions -

1.3 Information required by the TEAP

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

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

1.4 Definitions

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

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

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

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

- 1.) Chemically inert during a chemical reaction
- 2.) Physical properties, eg.
 - boiling point
 - 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 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:

$$\text{Consumption} = \text{production} + \text{imports} - \text{exports}$$

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).

1.5 General considerations

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

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

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

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

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

Appendix B supplements information found in Chapter 3.

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

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

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

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

2 Process agent use and emissions

2.1 Identified processes

The following table summarizes major identified processes*:

Process (P.A.)	Application	Reason used	Product use
Chlor-alkali (CTC) (Case Study C-1)	Elimination of NCl_3	Safety and quality of product	Chlorine is a universal chemical used for more than 60 % of all chemical synthesis.
Chlor-alkali (CTC) (Case Study C-2)	Chlorine recovery by tail gas absorption	Safety, Yield	Chlorine is a universal chemical used for more than 60 % of all chemical synthesis.
Chlorinated Rubber (CTC) (Case Study C-3)	Chemical inert solvent for high quality product	Inert solvent	Heavy duty anti-corrosives and adhesives
Endosulfan production (CTC) (Case Study C-4)	Chlorination reaction	Inert solvent	Biodegradable insecticide
Ibuprofen production (CTC) (Case Study C-5)	Solvent for Friedel-Crafts synthesis	Inert solvent	Anti-inflammatory drug
Dicofol (Case Study C-6)	Solvent	Inert solvent	Broad spectrum acaricide
Chlorosulfonated Polyolefin (CTC) (Case Studies C-7a&b)	Chlorination solvent	Inert solvent, safety	High tech coatings, protective materials.
Aramid Polymer PPTA (CTC) (Case Study C-8)	Chlorination specific solvent	Quality, safety waste reduction	Asbestos replacement, public and military safety products
Fluoropolymer resins (CFC-113) (Case Study C-9)	Specific solvent	Specific dispersant, chemical inert	Extreme temperature electric insulation, inert coatings
Synthetic fiber sheet (CFC-11) (Case Study C-10)	Spinning solvent	Quality, safety yield	Protective wrappings, very strong sheets

* for more details see case studies in Appendix C

2.1 Identified processes (continued)

Process (P.A.)	Application	Reason used	Product use
SBR (CTC) (No Case Study)	Solvent	Chain transfer agent	Synthetic rubber, strong and resistant to extreme temperatures and climate
Chlorinated Paraffin (CTC) (No Case Study)	Solvent	Inert solvent	Lubricant additive, flame retardant for plastics, plasticizer in rubber paints

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

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

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

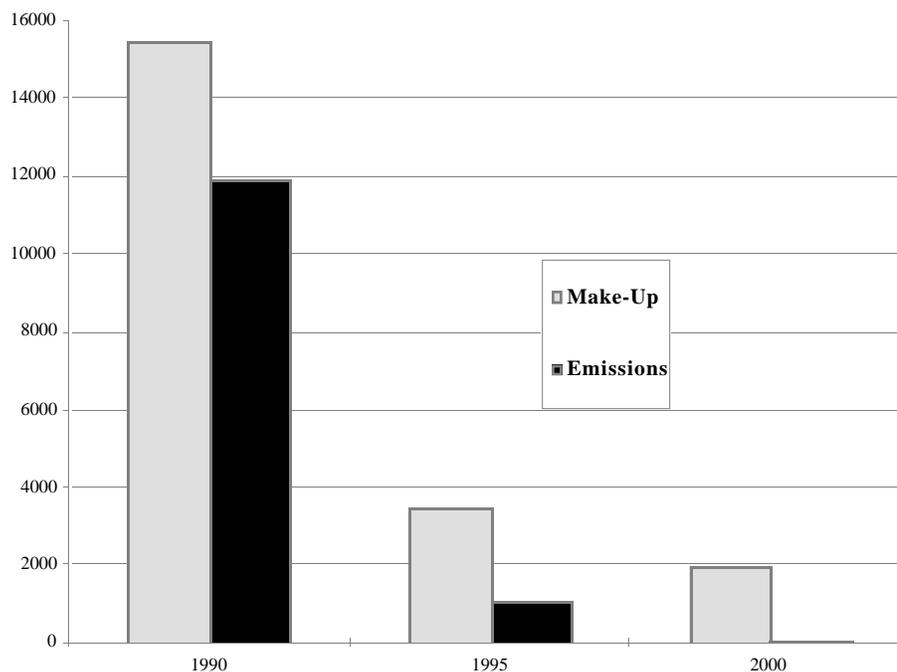
To show the development of "make up" and emissions of the identified manufacturing processes for Europe, North America and Japan the data are condensed in the following table for the relevant years 1990, 1995 and predictions for 2000.

Make up and emissions of ODS used as process agents for Western Europe, North America and Japan (tonnes/year)

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

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

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



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

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

2.3 Make up and emissions in Article 5(1) countries

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

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

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

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

** Emissions were previously higher.

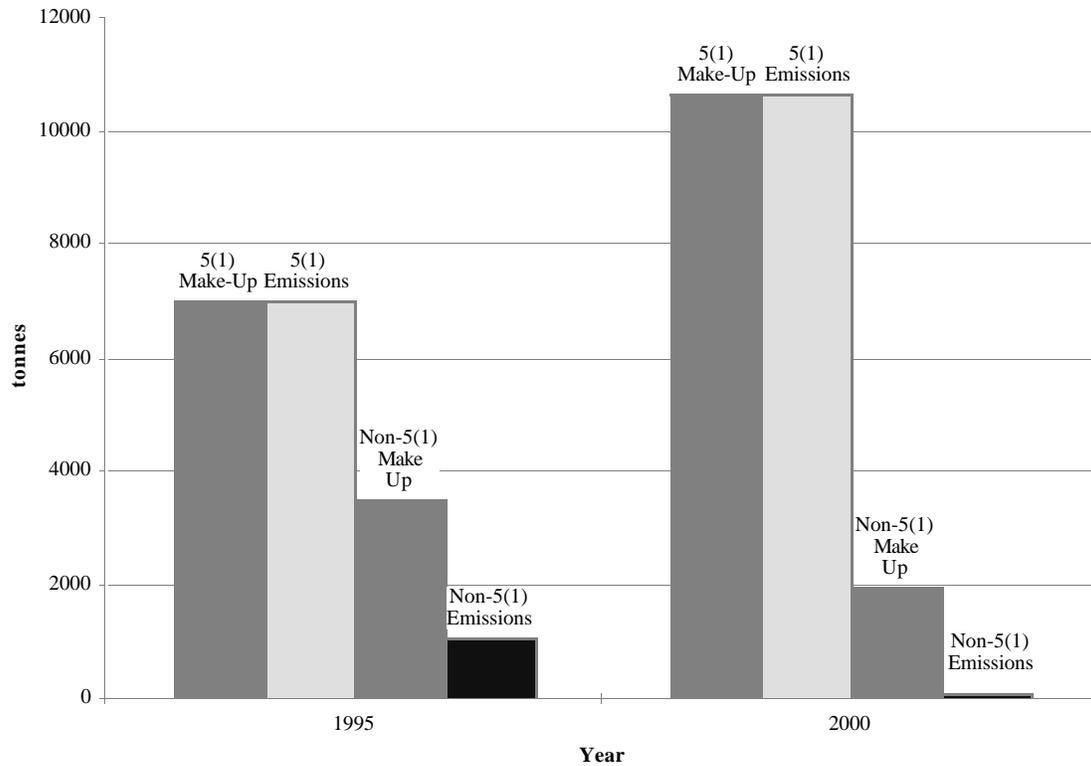
*** Figures for China are estimates provided by Dr. Zhang Zhiqun. It was not possible to provide definitive figures for China as a full investigation could not be carried out in the time available.

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

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

2.4 Global estimates

Global estimate of emission of ODS used as process agents (tonnes/year)



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

3 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 ODS 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.

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

4 Substitutes and alternatives

Identified alternatives to the use of ODS*

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

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

* for more details see case studies in Appendix C

4.1 Chlor-Alkali production

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

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

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

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

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

4.2 Recovery of chlorine in tail gas from production of chlorine

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

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

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

4.3 Chlorinated Rubber

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

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

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

4.4 Endosulfan production

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

4.5 Ibuprofen production

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

4.6 Dicofol production

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

4.7 Chlorosulfonated Polyolefin (CSM)

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

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

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

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

4.8 Aramid Polymer PPTA

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

4.9 Fluoropolymer resins

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

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

4.10 Fine synthetic fiber sheet

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

4.11 Conclusions

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

- In most cases emissions from use of ODS as process agents in non-Article 5(1) countries are similar to the insignificant quantities emitted from feedstock uses.
- For all of the identified processes, programs are underway to find and/or develop alternatives to the use of ODS as process agents.

- Depending on the difficulties of the process under investigation there is a diversity of progress ranging as follows:
 - phaseout achieved or achievable
 - expected phaseout within the next few years subject to solution of final technical issues
 - those processes with extreme difficulty to find an alternative.
- Realising that these results have been achieved over a period of 5 to 6 years, together with measures to significantly reduce emissions, there has been remarkable progress and further progress is expected.

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

5 Article 5(1) countries

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

5.1.1 Use of controlled substances in chemical processes

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

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

5.1.2 Survey of CTC usage

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

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

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

5.1.3 Industries using CTC in chemical processes

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

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

The survey revealed for the first time that CTC is also being used as a chain transfer agent in the emulsion polymerization process of SBR in South Korea. Reported CTC consumption for SBR production in South Korea in one industrial unit of 600 MT is quite high and it has been

taken into account. A more detailed investigation is needed, including that in other Article 5(1) countries, to further check possible use of CTC for this application.

5.1.4. CTC usage in chemical processes

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

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

Table 1
CTC Process Inventory in Chemical
Process Industries in Article 5(1) countries
(in metric tonnes)

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

* unconstrained cycle use

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

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

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

The survey shows that in 1995 in Article 5(1) countries, the emissions of CTC from the industries listed under 5.1.3. were about 7,001 MT as given in Table 2. However, as further information becomes available, the actual quantities of usage and of emissions of CTC in Article 5(1) countries may be higher.

Table 2
Make-up and emissions of CTC as a Process Agent
in Article 5(1) countries for 1995 and 2000*
(in metric tonnes)

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

* Make up and emissions are virtually the same.

* * Unconstrained use

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

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

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

Table 3
Application-wise emissions of CTC in
chemical processes in Article 5(1) countries in 1995
(in metric tonnes)

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

** Consumption was higher in the earlier period (see Table 5)

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

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

In the pharmaceutical sector, CTC is being used in India for the following products and its estimates of consumption(emissions) for each product are shown in Table 4.

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

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

In the agricultural chemicals sector, CTC use in India is in the manufacture of the following products and estimates of consumption(emissions) of CTC in each case are given in Table 4.

- Endosulfan (insecticide)
- Dicofol (an acaricide)

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

Table 4
Application-wise usage and emissions of CTC in India
(in metric tonnes)

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

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

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

Table 4 shows that in India, an estimated quantity of 27,660 MT of CTC was used in the production cycle in 1995 and an estimated quantities of 2,084 MT of CTC emissions resulted from such use.

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

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

For the year 2000, the projected unconstrained CTC use is 44,015 MT and the corresponding emissions are projected at 3,354 MT. The profile of the changing pattern of CTC use and emissions in India is given in Table 5.

Table 5
Changing pattern of CTC emissions in
chemical process applications in India
(in metric tonnes)

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

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

5.2. Plan for restricting use and emissions of CTC in Article 5(1) countries

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

Table 2 summarizes CTC emissions in Article 5(1) countries, in the identified chemical processes. Use is large and is increasing.

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

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

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

- (i) The plants and facilities of the user industries in Article 5(1) countries are generally simple batch operations. The effective implementation of emission

minimization strategies to significantly lower down the emissions of CTC is not attainable without carrying out major modification of plants/facilities and installation of new equipment for monitoring, control systems and destruction technologies.

- (ii) There is residual CTC entrapped in the end-products of some processes.

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

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

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

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

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

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

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

5.2.4. Availability of alternatives

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

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

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

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

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

5.2.6. Phaseout cost

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

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

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

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

5.3 Acknowledgments

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

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

A **Emission abatement techniques**

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

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

A.1 Developing a program

A.1.1 Organization

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

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

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

A.1.2 The situation at the starting point

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

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

A.1.3 Establish an action plan

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

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

At this stage a skilled engineer should begin to look for first step in-house measures based on proven techniques and process conditions and using the concepts of recycling and pollution

source elimination. These measures have a good chance to pay for themselves and they help to reduce the magnitude of end of pipe treatments.

A.1.4 Final goals

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

A.1.5 Emissions

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

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

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

A.1.6 Types of abatement techniques

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

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

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

A.1.7 What reductions are possible?

- Air purification: 90 - 99 %
- Water purification: 90 - 99 %
- Product purification: (Product specific)
- Waste destruction: 99.9 %
- Good maintenance: up to 90 %
- Good housekeeping: No incidents

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

A.1.8 Essentials for achieving emission reduction

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

A.1.9 Types of constraints

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

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

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

Organizational: space, facilities, integrated or stand alone.

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

Environmental: are the standards met?

A.1.10 How to deal with the constraints

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

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

A.1.11 Engineering characteristics

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

A.1.12 Assistance

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

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

A.2 Practical guide to emission abatement techniques

A.2.1. Losses and loss control

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

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

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

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

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

A.2.2 Sources of emissions

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

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

A.2.2.1 Emissions to the atmosphere.

A chemical plant normally has:

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

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

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

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

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

A.2.2.2 Emissions to water

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

A.2.2.3 Losses in products

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

A.2.2.4 Losses in soil

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

A.2.2.5 Losses in waste

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

A.2.3 Purification techniques and constraints

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

Table 1
Purification techniques
(not exhaustive)

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

Table 2
Constraints

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

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

A.2.3.1 Conditions for successful application of purification techniques.

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

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

A.2.4 The quality of knowledge

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

A.2.5 Looking into the future

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

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

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

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

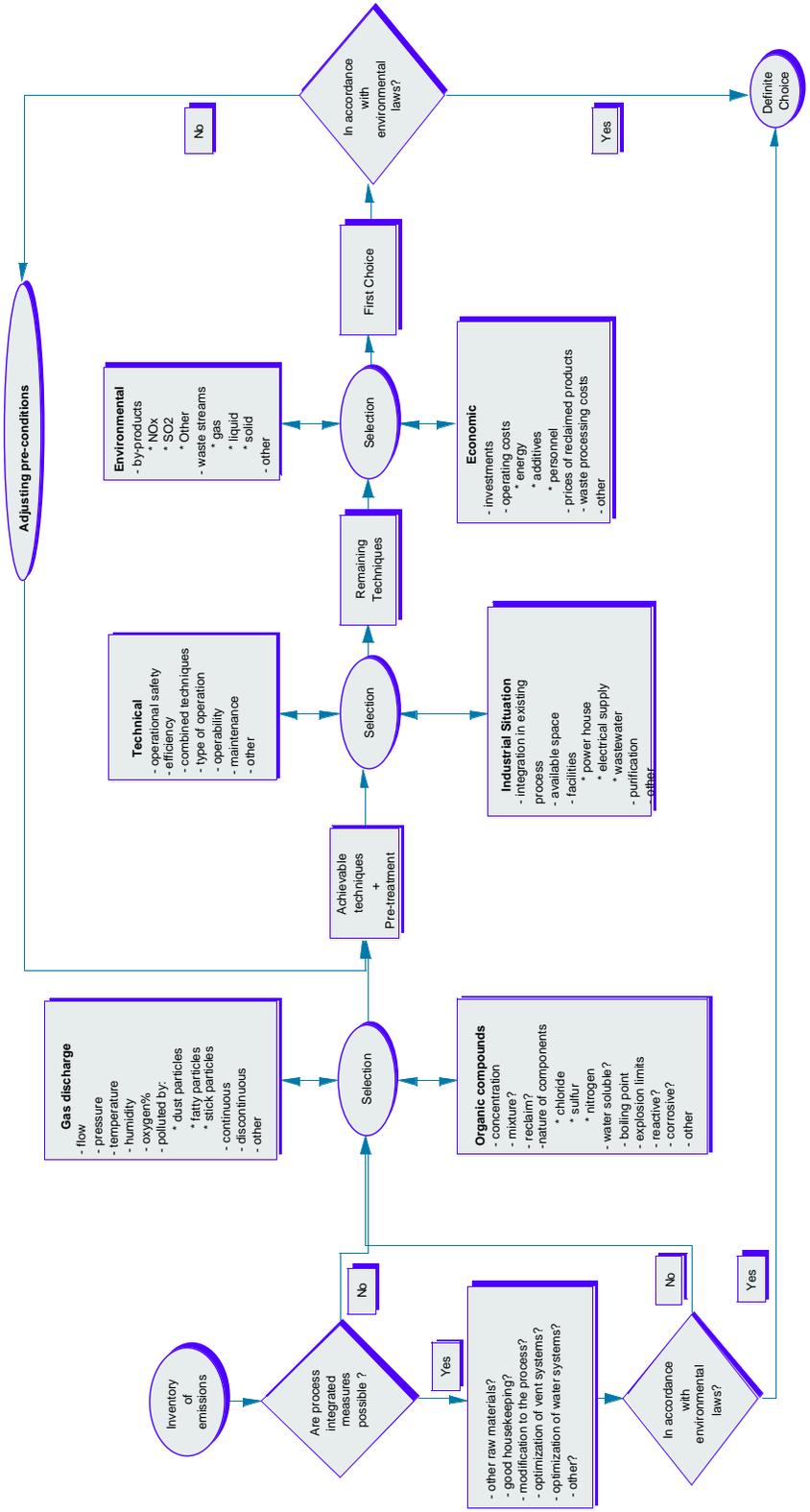
A.2.6 Human factors

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

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

"The craftsmanship lies in handling the tool smartly."

A.2.7 Scheme of consecutive steps as a guide



A.2.8 Survey of purification techniques for gases

We will differentiate between:

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

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

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

A.2.8.1 Without "end of pipe" techniques

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

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

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

Examples are:

Selection of flows:	avoid mixing concentrated flows with other flows and look for recycling or cooling and condensing possibilities.
Reduction of flows:	Look for conditions to minimize the flow by proper design of the flow conditions.
Recycling:	Recirculation of a part of an outlet reduces the end stream with that amount.
Vaporization retarding :	one can have to do with time sequences in bath processes, temperature and pressure changes. There may be some free or acceptable choices to suppress or prevent vaporization.
Low temperature sources:	can be used for condensing ODS from gas streams or can be used to get a more favorable temperature for scrubbing etc. The use of the low temperature of liquid

Nitrogen, already installed for inerting purposes, is an example.

Collecting systems:

that contain fluids with volatile ODS should be closed to avoid direct vaporization into the atmosphere prior to treatment.

Scrubbing:

If ODS is used in a mixture of compounds, scrubbing the outlet gas with a less volatile compound of the mixture, followed by recycling, can lower the loss.

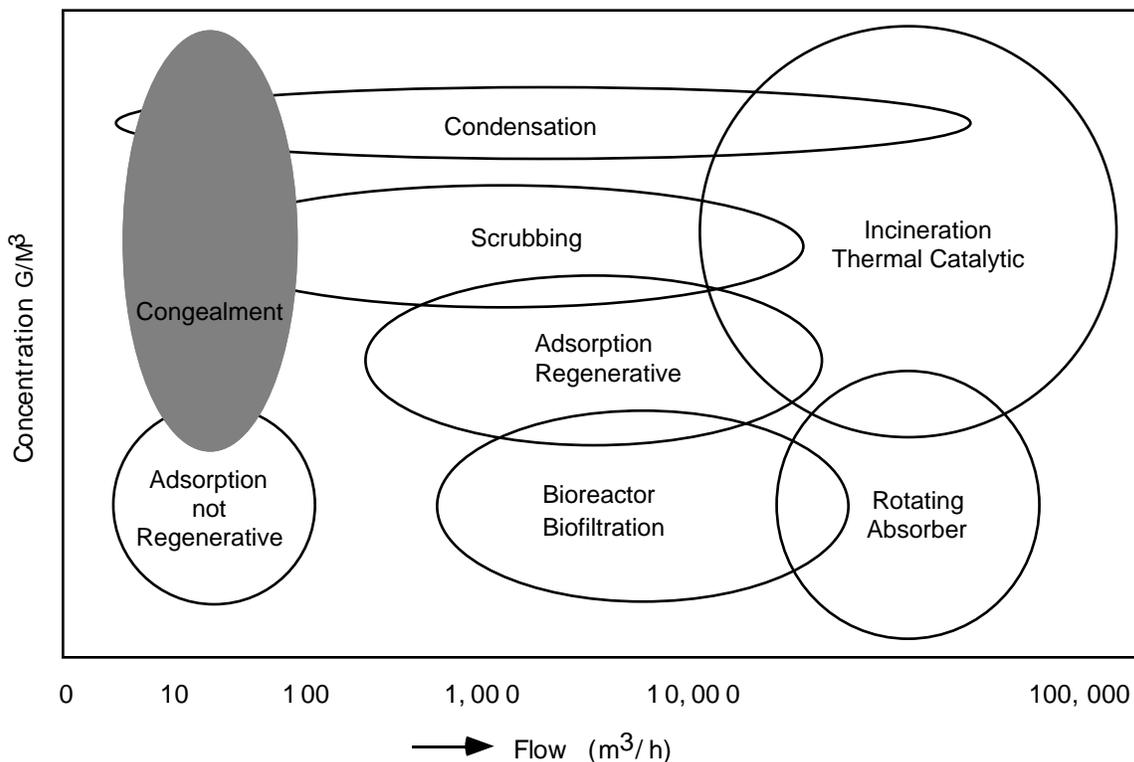
A.2.8.2 End of pipe techniques

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

These techniques are:

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

Global areas in which these techniques normally are applied



A.2.9 Gas purification

A short description of the gas purification techniques:

A.2.9.1 Adsorption by activated carbon

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

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

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

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

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

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

A.2.9.2 Scrubbing

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

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

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

A.2.9.3 Aftercooling and deepcooling

There are two types of condensation apparatus's:

- with direct condensation
- with indirect condensation

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

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

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

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

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

A.2.9.4 Incineration.

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

A.2.9.5 Bioreaction/biofiltration

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

A.2.10 General aspects on wastewater purification in plants.

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

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

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

A.2.10.1 Wastewater purifying techniques.

The unit operations that are common for this purpose are:

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

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

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

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

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

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

A.2.11 Rough guidance for choice

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

A.2.11.1 Gas purification

If the concentration of the polluting component rises from 1 g/m³ to 10 g/m³ the cost is roughly doubled. The same holds for a rise in capacity from 5000 m³/h to ca 30,000 m³/h.

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

A.2.11.2 Wastewater purification

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

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

B Regulatory review

B.1 Introduction

This Appendix provides an overview of approaches currently in use in Article 5(1) and non Article 5(1) countries to monitor and 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, all non-Article 5(1) countries must currently meet specific regulations to minimize emissions of ODS used in process agent applications. In the Article 5(1) countries emission standards for CTC and other ODS vary from stringent to non-existent. Similar to the non-Article 5(1) countries, widespread knowledge of the health and safety issues pertaining to CTC has resulted in some lowering of emissions, and thereby contributing to the goals of the Montreal Protocol. The PATF also considered institutional/regulatory barriers to emission reductions.

B.2 Types of Standards

B.2.1 Regulatory

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

In addition to ambient emission controls, some countries regulate equipment leaks or mandate leak detection and repair 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.

B.2.2 Voluntary and industry set standards to reduce emissions

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

Some non-article 5(1) governments have developed ordinances or guidelines in lieu of or to supplement regulatory requirements. One country reported negotiated but non-binding agreements with process agent sources in order to identify specific control commitments. One

country also reported the use economic incentives such as grants or tax concessions to reduce the burden of environmental regulation and encourage environmentally friendly actions.

B.3 Institutional/Regulatory impediments to emission reduction

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

C-1 Use of CTC in the elimination of NCl_3 in the production of chlorine and caustic soda

C-1.1 Introduction

The products made by electrolysis of sodium chloride are:

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

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

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

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

C-1.2 Description of overall manufacturing process

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

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

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

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

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

C-1.3 Why CTC is used as a process agent

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

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

C-1.3.1 Quality of final product

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

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

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

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

Many severe accidents, including fatalities, resulting from NCl_3 explosions have been recorded. To avoid any risk of concentration higher than 1%, Euro Chlor specifically recommends that maximum levels of NCl_3 in liquid chlorine must be maintained below 20 ppm during chlorine production and not exceed 2 ppm for large storage tanks and transport containers of liquid chlorine.

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

C-1.3.3 Unique properties of CTC required for this application

Carbon tetrachloride :

- is an excellent solvent of chlorine and NCl_3 ;
- has a boiling point (+77°C) much higher than chlorine (-34 °C), but near the boiling point of NCl_3 (+ 71°C), which is important to keep NCl_3 in solution with CTC and separate chlorine;
- is stable in the presence of chlorine;
- is inert and not corrosive.

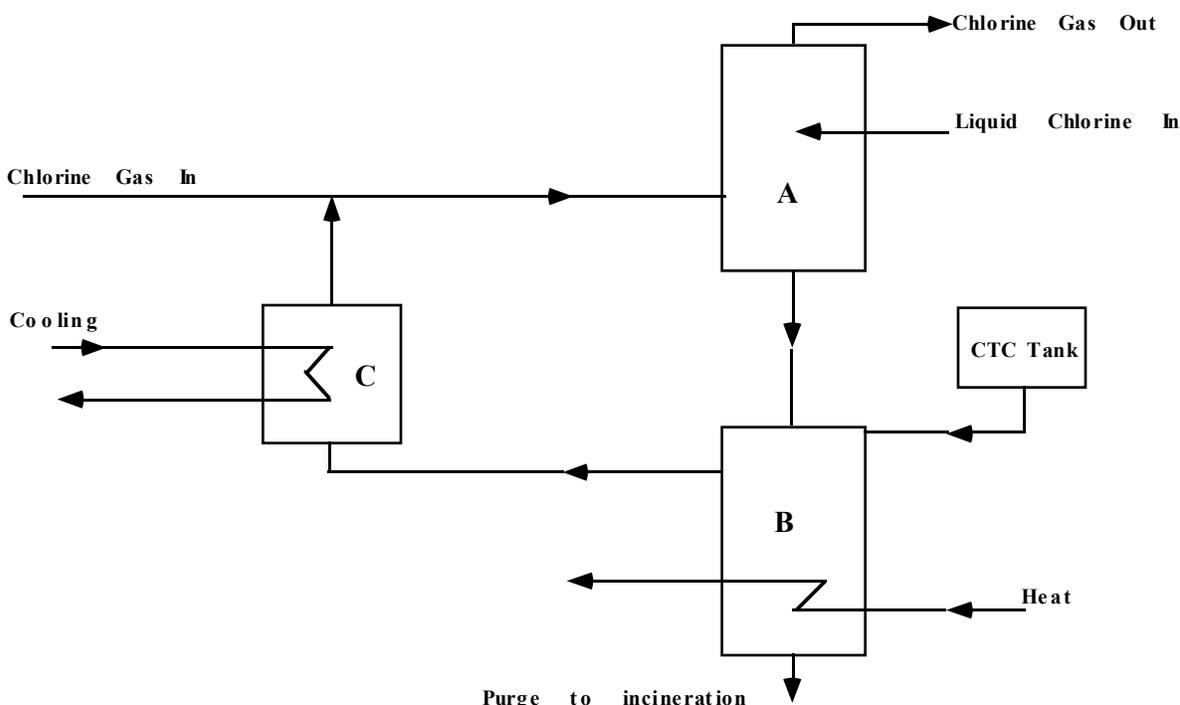
C-1.4 How CTC is used as a process agent

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

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

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

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



C-1.5 Quantity of CTC required for make up

In 1990, the yearly make up of CTC to compensate for the quantity destroyed when used for eliminating NCl_3 was 810 tonne for 21 plants using this process. In 1995, the make up quantity fell to 650 tonne: 550 tonne in non-Article 5(1) countries and 100 tonne in Article 5(1) countries. A further decrease is expected in the near future.

C-1.6 Pollution abatement

C-1.6.1 Emissions

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

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

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

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

C-1.6.3 Regulations affecting operations

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

For example, in the United States of America, these regulations include the National Emissions Standard for Hazardous Air Pollutants established under the Clean Air Act and incineration standards established under the Resource Conservation and Recovery Act. The US EPA requires that permits be granted to operate such facilities. The permits require emission control technology for all facilities and set maximum allowable CTC emissions.

C-1.7 Opportunities for substitutes without CTC and limitations

C-1.7.1 Identical products produced without the use of CTC

C-1.7.1.1 Elimination of nitrogen compounds from the brine

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

C-1.7.1.2 Elimination of NCl_3 by destruction

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

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

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

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

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

C-1.7.1.4 Supply of very pure salt

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

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

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

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

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

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

C-2 Use of CTC in the recovery of chlorine in tail gas from production of Chlorine

C-2.1 Introduction of process

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

C-2.2 Products made, use of the products

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

C-2.3 Description of overall manufacturing process

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

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

C-2.4 Why CTC is used as a process agent

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

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

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

C-2.4.1 Quality of final product

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

C-2.4.2 Safety with in-plant production

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

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

The CTC process is also more dependable than a substitute technology of combusting the tail gas with hydrogen. The flame safety control systems required to prevent the explosion of the CL_2/H_2 combustion equipment also result in less reliable operation. The combustion substitute also cannot be used for depressurizing and evacuation of equipment under repair.

C-2.4.3 Cost of use

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

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

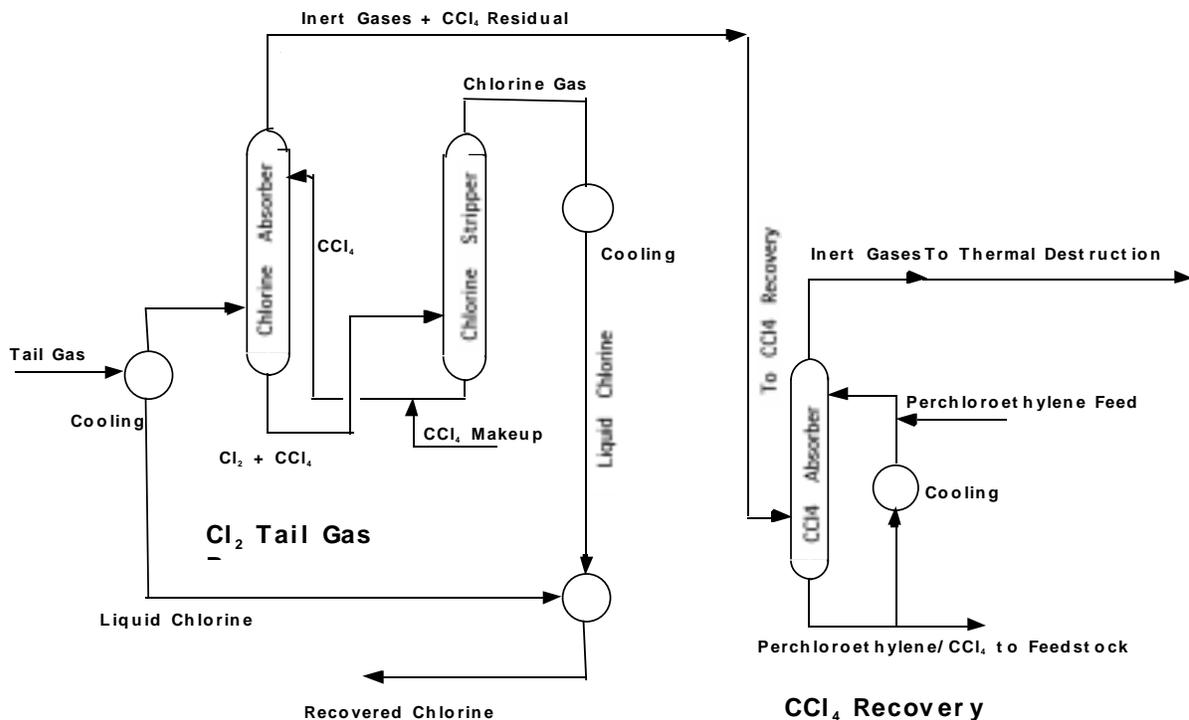
C-2.5 How CTC is used as a process agent

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

C-2.6 Flow diagrams

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

Chlorine Tail Gas and CTC Recovery



C-2.7 Pollution Abatement

C-2.7.1 Efficiency of recovery of the CTC after use

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

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

C-2.7.2 Final Disposal of CTC

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

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

C-2.7.3 Quantity required for make-up

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

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

C-2.8 Opportunities for substitutes without CTC and limitations

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

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

Another substitute technology is to install additional liquefaction equipment as a partial alternative to the CTC tail gas process. Additional drying steps using sulphuric acid may be necessary to prevent excessive corrosion in this case. Equipment to perform a 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 neutralisation step must then be disposed of in an appropriate manner.

C-2.8.1 Cost comparison

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

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

C-3 Use of CTC in the Chlorinated Rubber Process

C-3.1 General

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

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

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

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

C-3.2 Why CTC is used as a process agent

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

C-3.3 CTC Emissions

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

Chlorinated Rubber production with CTC

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

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

C-3.4 Bayer Chlorinated Rubber Process

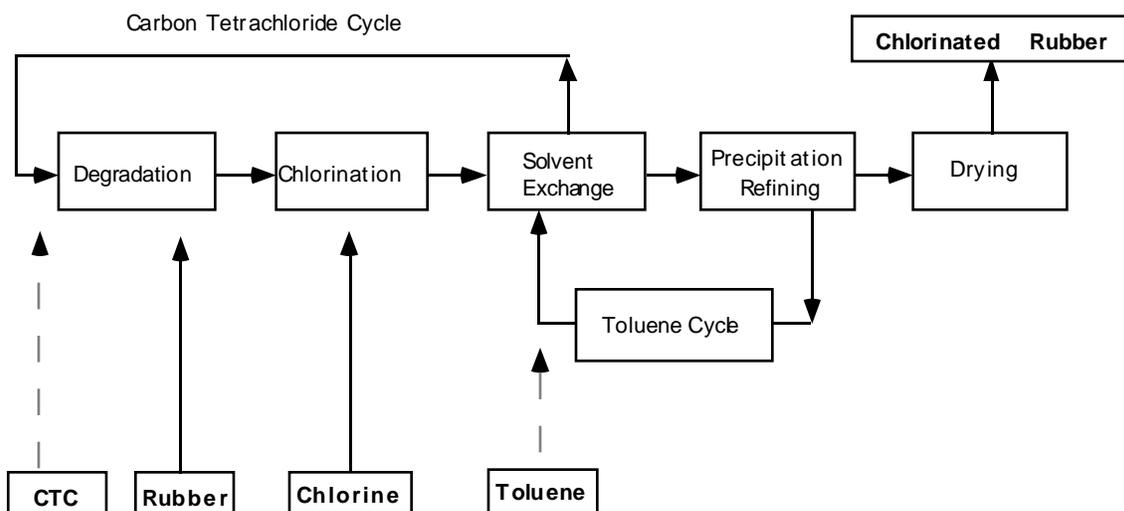
C-3.4.1 Process

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

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

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

C-3.4.2 Flow chart



C-3.5 Pollution abatement

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

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

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

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

chlorination of rubber would increase substantially and its feedstock use would be more evident.

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

C-3.6 Substitutes and Alternatives

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

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

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

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

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

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

- Plants with a replacement value in excess of US \$150 million were shut down.
- The installation of closed systems and solvent exchange and the change to the aqueous process together cost some US \$100 million.
- Formulations had to be revised and customers for 50,000 to 100,000 tonnes of end product had to switch to alternative products such as polyurethanes, epoxides or acrylates.

C-4 Use of CTC in Endosulfan production

C-4.1 Introduction

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

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

C-4.2 Endosulfan manufacturing process

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

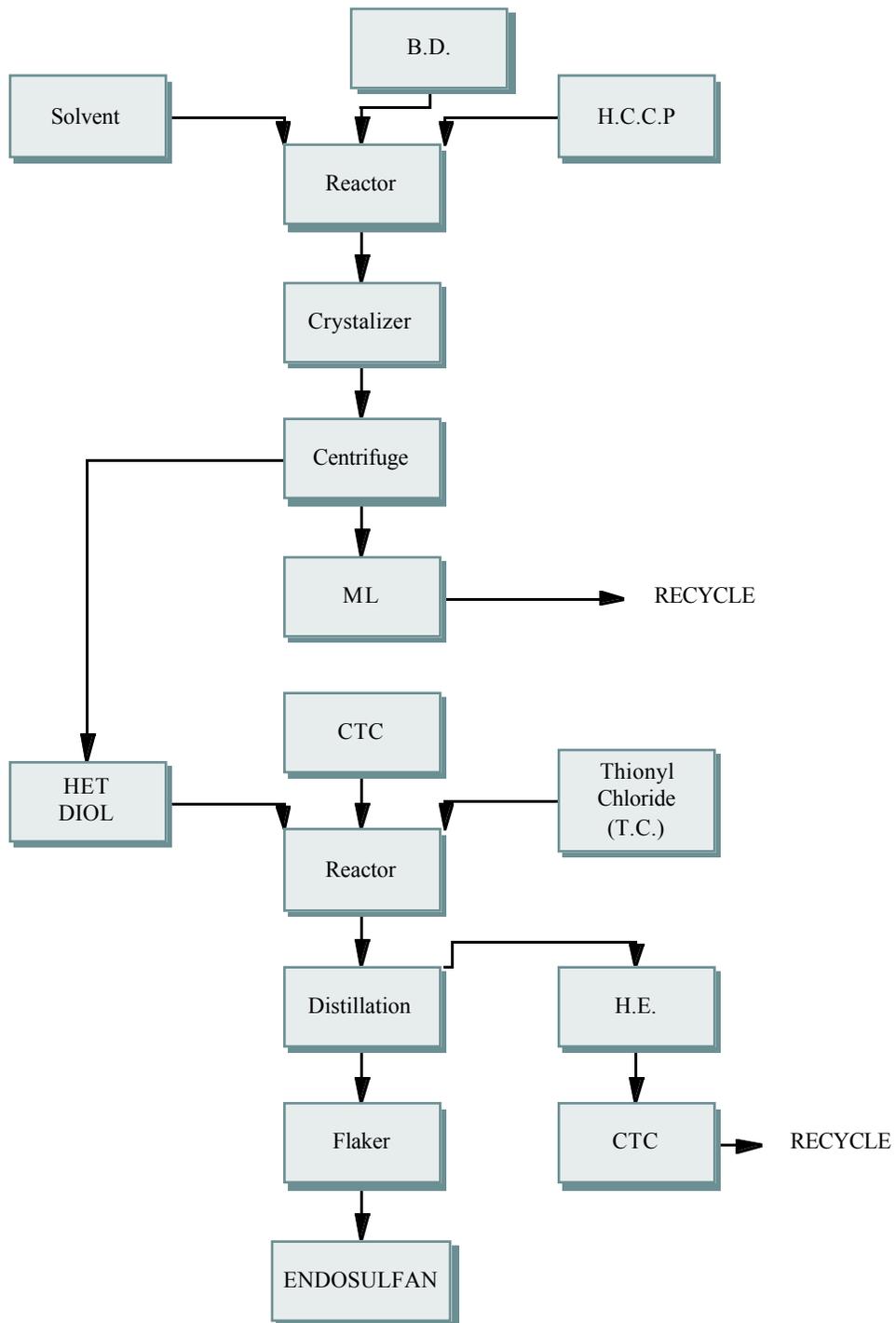
C-4.3 CTC consumption and emission

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

C-4.4 Conversion to use of non-ODS solvent

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

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

C-4.5 Endosulpan production process

C-4.5.2 Material balance

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

C-5 Use of CTC in Ibuprofen production

C-5.1 Introduction

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

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

C-5.2 Ibuprofen manufacturing process

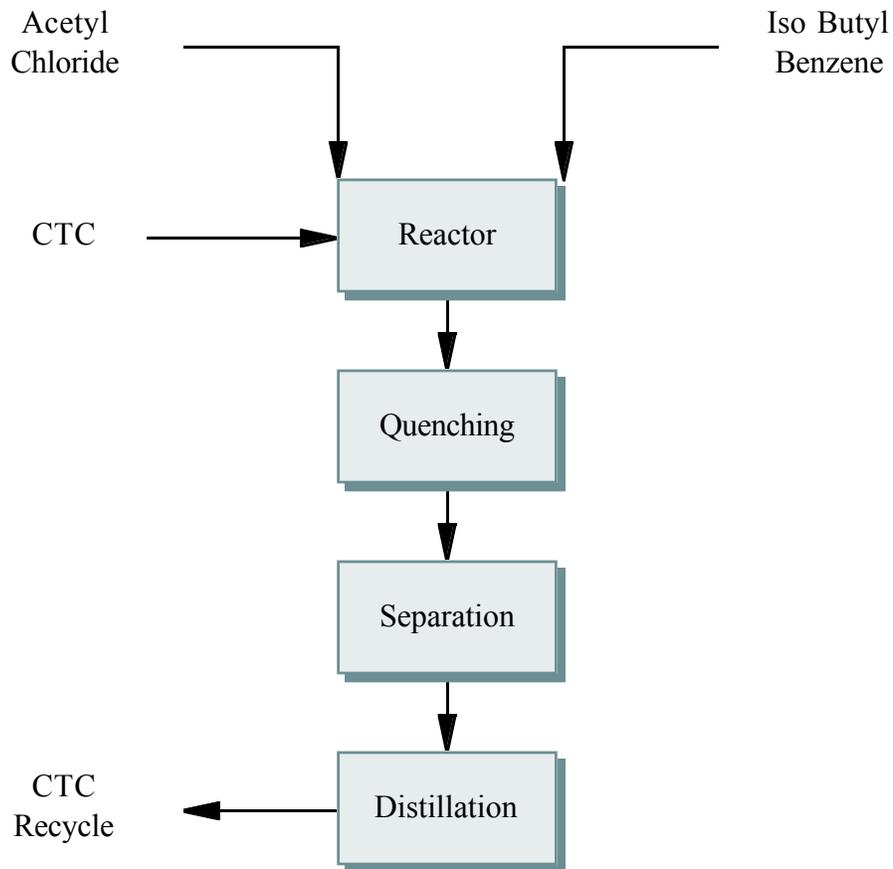
Iso Butyl Benzene is reacted with acetyl chloride in presence of aluminium chloride catalyst with CTC as an inert solvent. By-product hydrochloric acid gas generated is scrubbed with water. The unreacted components like aluminium chloride are dissolved in water by quenching process and Iso Butyl Acetophenone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

C-5.3 CTC consumption and emission

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

C-5.4 Conversion to use of non-ODS solvent

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

C-5.5 Flow chart and material balance of Ibuprofen production process**C-5.5.1 Shasun Iso-Butyl Aceto Phenone Process**

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

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

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

C-6 Use of CTC in Dicofol production

C-6.1 Introduction

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

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

The technical grade is brown viscous liquid (82% pure) and has density 1.45. It is primarily a mixture of 1-1, Bis (4-chlorophenyl) - 2,2,2 - trichloro ethanol and 1-1 (4-chlorophenyl, 2-chlorophenyl) - 2,2,2 - trichloro ethanol in the ratio of 4 : 1

Technical Dicofol is practically insoluble in water but soluble in most aliphatic and aromatic solvents. The product is compatible with all but highly alkaline pesticides. Its wettable powder (wp) formulations are sensitive to solvents and surfactants and these may affect acaricidal activity and phytotoxicity.

The various formulations of Dicofol are:

- a) 35% wettable powder (wp)
- b) 18.5% and 42% emulsifiable concentrates (EC)
- c) and as 41% flowable

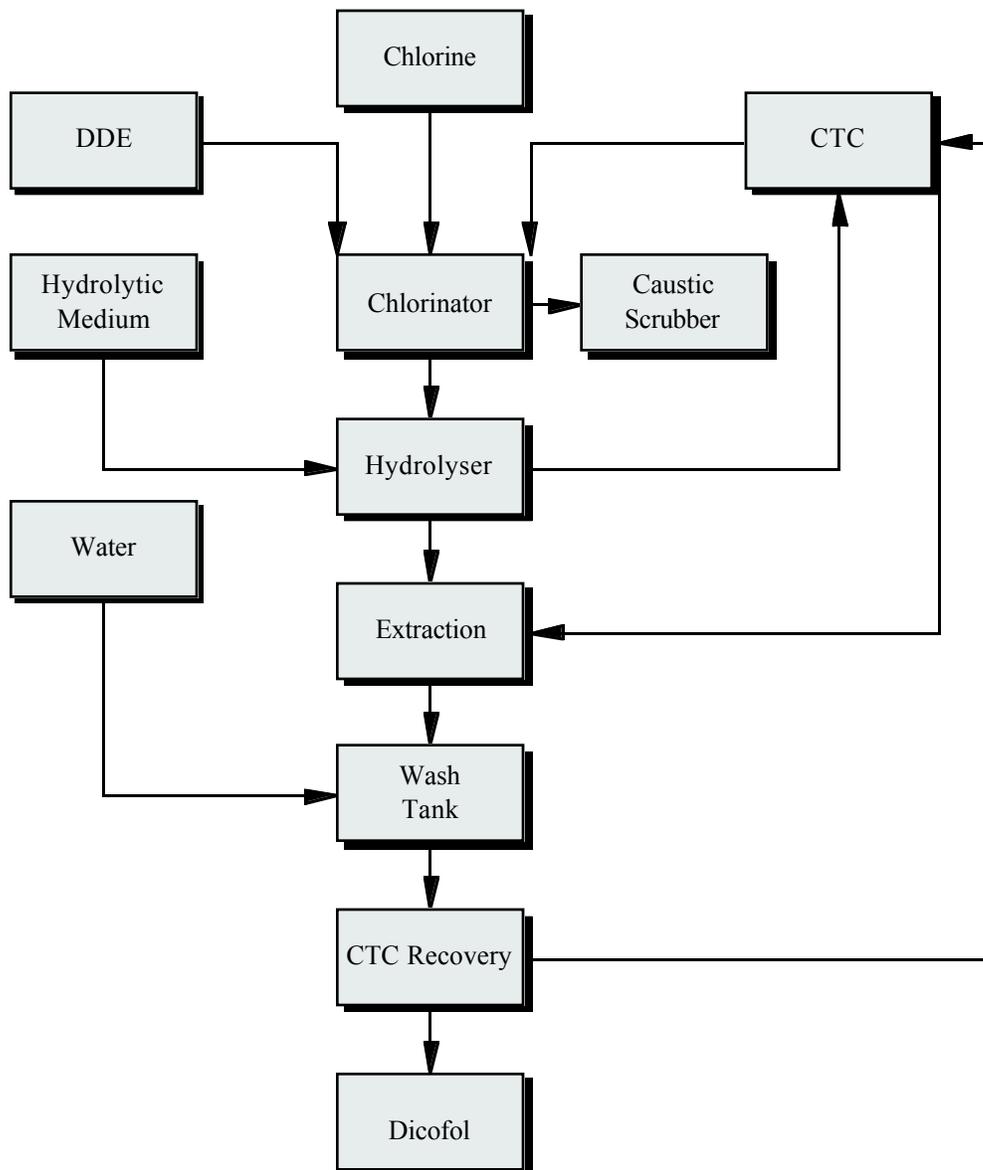
Of the above formulations, generally 18.5% (EC) is widely used in India

C-6.2 Manufacturing process

The current capacity of the plant in India is 150 tonnes/annum. The product is manufactured by converting tech-DDT, which is mainly a mixture of 1,1 Bis (4-chlorophenyl) - 2,2,2 trichloro ethane and 1,1 (4-chlorophenyl, 2 chlorophenyl), 2,2,2 trichloro ethane to tech-DDE which is also a mixture of 1,1 Bis (4-chlorophenyl) 2,2 - dichloro ethene and 1,1 - (4-chlorophenyl; 2 - chlorophenyl) 2,2 dichloro ethene.

After the conversion of tech-DDT to tech-DDE, carbon tetrachloride (CTC) (4.5 kg for 1 kgh of DDE) is added. The CTC solution containing DDE is then taken to special chlorinators and then chlorinated with chlorine till the intermediate tetrachloro, 1-chloro, 1,1 Bis (4-chlorophenyl), 2,2,2 trichloro ethane and 1-chloro, 1,1 (4-chlorophenyl, 2-chlorophenyl) - 2,2,2-trichloro ethane are formed. The chlorinating solvent CTC is then removed and is recycled.

The product is then hydrolyzed by an acidic hydrolytic medium. After the complete conversion of tetrachloro to tech Dicofol, CTC is added to the reaction mixture to extract tech Dicofol from the reaction mixture. The CTC layer which contains Dicofol is separated and then taken to wash tank and washed till product is neutral. CTC is then removed from the product by simple distillation, followed by vacuum distillation to get tech Dicofol.



C-6.3 Conversion to a non-ODS process agent

This process presently produces 150 tonnes/year of Dicofol and uses 960 tonnes of CTC in the production cycle. Due to increasing demands and good potential of the product the company envisages a 20% annual production increase. Although most of the CTC used during chlorination and as a Dicofol extractor after tetrachloro DDT hydrolysis is recycled, 48 tonnes is emitted annually, including residual trace amounts in the product. These emissions will likely increase as production increases.

There is a limited choice of solvents, as only Chlorinated aliphatic solvents can be used as a replacement process agent. Work at the laboratory level has already been initiated to replace CTC using 1,2 dichloro ethane (DCE). The initial results are quite optimistic and it is hoped that this process agent will be a suitable replacement for CTC in this process. However, laboratory experiments so far indicate that if dichloro ethane (DCE) is used as a replacement for

CTC, some process modifications will be required to meet the needs of the present and future production schedules, which would have a bearing upon productivity and cost economics of the product.

In order to carry out this change from CTC to DCE more studies in pilot plant at 5 kg level are to be undertaken. Moreover, before marketing technical Dicofol, as per C.I.B. guidelines, phytotoxicity studies of the product must be carried out on the alternatively produced product.

Although there is not much change in the solvent ratio in the change from CTC to DCE at the chlorination stage, it has been observed that the chlorination time is 15 to 20% longer, as chlorine has more residence time in CTC compared to DCE. Hence to maintain the present production schedule a complete chlorination unit consisting of a 3 Kl, all glass lined, jacketed vessel, along with two scavengers of the same capacity and kind having proper condenser and other requisite accessories will have to be installed.

The extraction of technical Dicofol after hydrolysis of tetra chloro DDT with CTC is easier as CTC is heavier (density 1.6), compared to DCE (density 1.24) and thus CTC containing the Dicofol remains in the lower layer. However when DCE is used there is no separation of the layer for DCE, either at the top or at the bottom, and much more DCE and water is required to get DCE containing technical Dicofol in the lower layer. Due to the larger volume of DCE and water, the size of the vessel has to be increased substantially. Simultaneously, the present wash tank for washing technical Dicofol in DCE also has to be replaced with a larger one. Therefore to maintain the present production level of technical Dicofol, a 5 Kl MSGL hydrolyser and another 5 Kl MSGL wash tank with necessary accessories must be installed.

C-6.4 Material balance

Item Description	Quantity	Tonnes
Annual Dicofol (tech) production	t/a	150
Annual CTC recycle	t/a	960
CTC recycle per production	t/t	3.2
Annual CTC make-up	t/t	48
CTC consumed per production	t/t	0.16
Annual CTC transformed or destroyed	t/a	0.00
CTC transformed or destroyed	%	0.00
Annual CTC used as CPA	t/a	960
Annual CTC emission	t/a	48
to atmosphere	t/a	47.52
to water	t/a	0.00
to product	t/a	0.48
CTC emission per production	t/t	0.16
to atmosphere	t/t	0.1584
to water	t/t	0.00
to product	t/t	0.0016
CTC emission per recycle	t/t	0.05

C-7a Use of CTC in Chlorosulphonated Polyolefin (CSM) production in a non-Article 5(1) country

C-7a.1 Introduction to CSM

Following invention of CSM and introduction in 1952, this product has developed a small, but very important, niche in the global synthetic elastomers market. CSM is a specialty elastomer with properties far superior to general purpose elastomers such as styrene-butadiene rubber, polyisoprene, polychloroprene, and nitrile rubber. The properties of CSM may be summarized as:

- Ability to be brightly or permanently colored,
- Superb ozone and weather resistance,
- Heat resistance to 125-135 degrees Celsius,
- Low temperature flexibility down to -18 to -23 degrees Celsius,
- Resistance to a wide range of oxidizing agents and chemicals,
- Oil, grease, and solvent resistance,
- Good electrical insulating properties, and
- Excellent resistance to abrasion and wear.

In many instances, such as automotive, appliance, military and recreational applications (i.e., white water rafting), general purpose elastomers cannot adequately replace CSM elastomer. The following applications have specifications where CSM is the preferred product:

C-7a.1.1 Coatings

Coatings of CSM are used to provide resistance to gas or moisture vapor permeability, weather, chemicals, oils and solvents while maintaining an attractive color. Applications include coatings for inflated fabric structures, inflatable boats, diaphragms, tarpaulins, rain wear and protective garments, roof coatings for chemical tanks and liners for secondary containment.

C-7a.1.2 Automotive

Specialty grades are used for vital automotive components because of its proven resistance to heat, oil, grease and ozone. Applications include power steering pressure hoses, fuel hose covers, brake hose and filler neck hose (connected to the gas tank). New grades of this elastomer are being used in the manufacture of high performance timing belts and accessory drive belts which will operate for the life of the vehicle without replacement.

C-7a.1.3 Wire and cable

CSM is widely used as a sheathing material for cable constructions. Its higher thermal rating combined with its low water absorption rate, and resistance to weathering, sunlight, ozone, corona and radiation make it a valuable jacketing material for control cable, nuclear power station cable, and mine trailing cable.

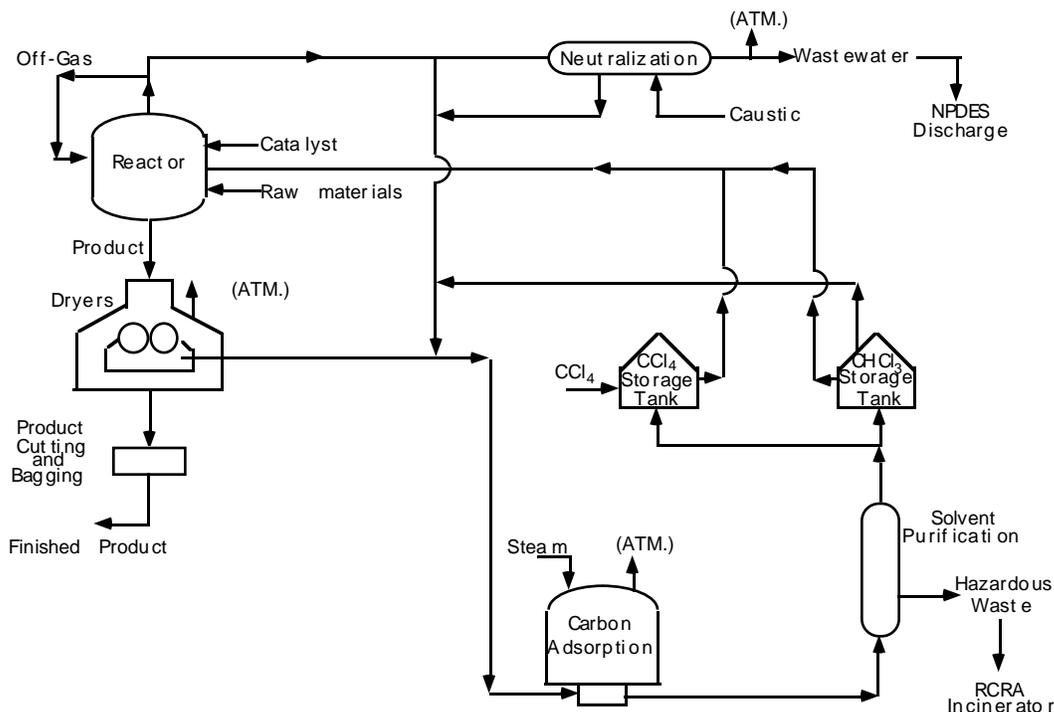
C-7a.1.4 Industrial

CSM has wide spread application in roll covers and acid hoses because of its resistance to a large variety of chemicals and solvents over a wide range of temperatures. Unique binder properties make it the preferred elastomer for magnetic applications which include refrigerator and microwave door enclosures.

C-7a.1.5 Construction

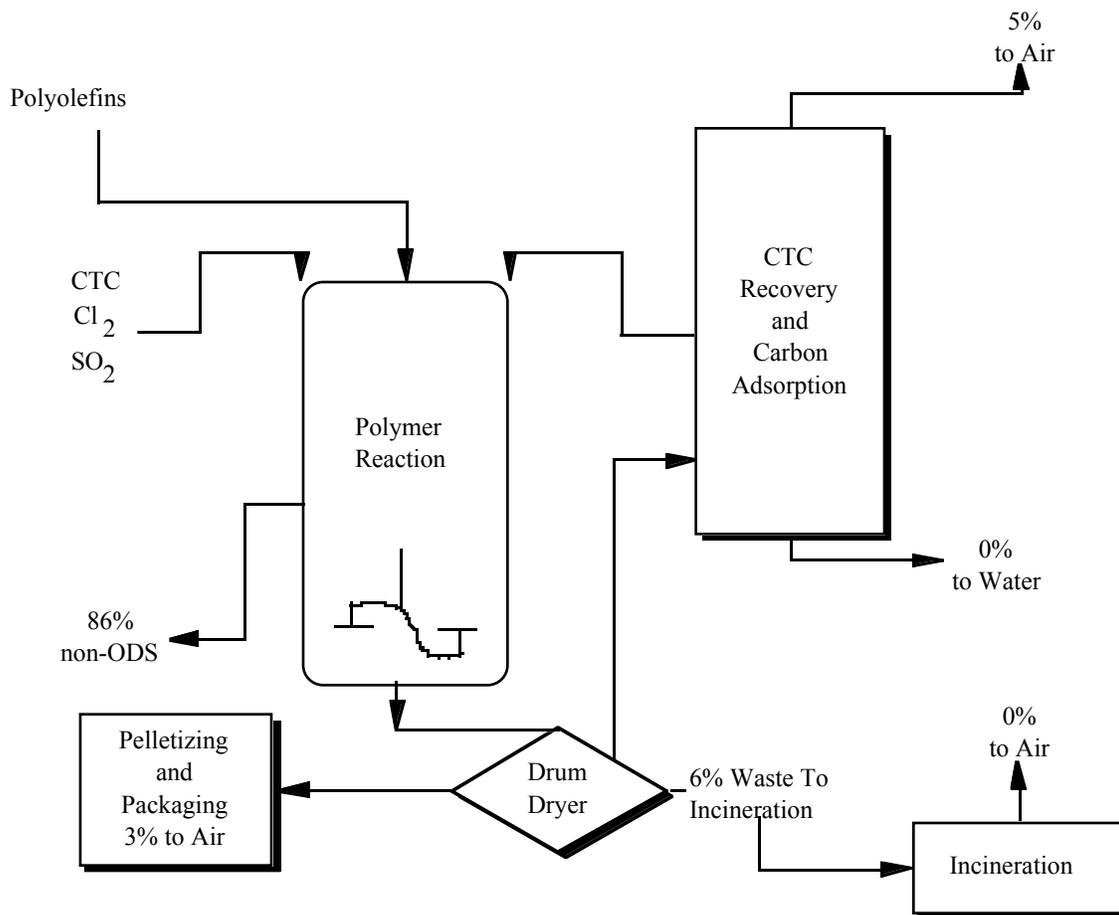
A particular type of CSM is used to produce single ply roofing membranes. The roofing membrane is white in color for heat reflectance and remains thermoplastic during installation on the roof, enabling heat welding of the seams. The roofing then slowly vulcanizes during use. No other elastomer possesses this combination of properties. This type of CSM is used to produce fabric reinforced sheets which are heat welded into liners for reservoirs and effluent ponds.

C-7a.2 Description of the North American CSM Process



The polyolefin “base resin” (typically polyethylene or ethylene copolymer) is first dissolved in hot carbon tetrachloride (CTC) in batch reactors. Chlorine and sulfur dioxide are introduced into the reactor which, in combination with CTC and polyolefin, yield the chlorosulphonated product. Unreacted chlorine and CTC are removed through the off-gas condenser system which condenses and cools CTC prior to recycle to the reactor. Any remaining off-gases from the reactor are either combined and recycled to the reactor or neutralized. The reactor solution is blended, continuously filtered, and dried on enclosed drum dryers. CTC emissions from these enclosed operations are condensed and recovered for reuse in the process. Dilute emissions that are not recovered by condensation are collected in a carbon adsorption system. After steam regeneration of the carbon beds, the remaining CTC is purified and recycled to the process. The finished product is packaged in the form of chips and stored in bags.

CTC Balance for the North American CSM process



Annual Make-up	Converted to non-ODS	Incinerated	Emitted to Air (direct)	Emitted to Air (from Product)
100%	86%	6%	5%	3%

C-7a.3 Why CTC is Used In the North American CSM Process

The ideal solvent for the CSM Process must have the following characteristics:

- Non-flammable
- Inert to Chlorine
- Proper Vapor Pressure
- Low Solubility in Water

CTC is used in the CSM Process for the following reasons:

1. CTC is a non-flammable solvent that allows safe operation and meets the stringent process safety concerns for large chemical production facilities. The North American

CSM Process has been designed for use of non-flammable solvents and cannot use flammable solvents without major changes to the process design and equipment.

2. CTC is fully-chlorinated and, therefore, inert to further chlorination. The reaction step in the CSM Process involves chlorination and sulphonation of polyolefins that have been dissolved in CTC. Side reactions with the solvent during this process step must be minimized to prevent unwanted by-products.
3. CTC has the proper vapor pressure to allow for stripping and condensation to recover and recycle solvent. The CTC vapor pressure is also in the right range for the CSM reaction and storage equipment.
4. CTC is practically immiscible with water which allows for unreacted solvent to be washed and neutralized along with other reactants with minimum solvent losses to the neutralization systems. CTC is compatible with the CSM caustic system and minimizes side reactions in this process step.

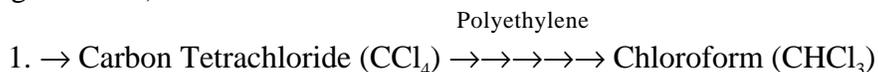
Given the numerous unit operations needed to effectively contain and recover CTC and the large capital investment required, it is necessary to use a solvent that will meet the above criteria.

In addition to the impact on process operations, the properties of specific CSM grades are significantly improved when the reaction is carried out with CTC. Several studies in 1993 demonstrated the impact of CTC versus other solvents on the properties of specific CSM products. Property improvements included oil resistance, low temperature flexibility, dielectric constant and dissipation factor, optimum sulfur levels, heat resistance, water swell, and compression set.

These differences were attributed to the evenly spaced distribution of chlorine atoms along the polymer chain when using CTC. The reason for the more even distribution of chlorine and sulfur atoms was that CTC surrounds each polymer segment in the chain with an envelope of solvating molecules, preventing contact with other segments and chains. This allows the individual chain to remain elongated allowing better exposure to chlorine and sulfur reaction of all polymer segments, and thus more even spacing. Other solvents allow the polymer chains to be irregularly folded into tight coils reducing exposure of the entangled segments to chlorine and sulfur atoms.

C-7a.4 How CTC is used in the North American CSM Process

In addition to the recycle and reuse of CTC in the North American CSM process, 86% of the CTC is transformed into chloroform during the chlorination reaction. As shown below, CTC gives up a chlorine radical in the reaction, ultimately forming chloroform (a non-ozone depleting chemical).



The chloroform is then consumed in the neutralization step of the process to form carbon monoxide and sodium formate.



This consumption of chloroform occurs in many locations within the CSM Process. Testing of the North American CSM Process has confirmed that this reaction occurs at high rates.

All the CTC in the North American CSM process is recycled, transformed to chloroform and consumed, or incinerated. All waste streams containing CTC are shipped off-site for incineration. The incinerators operate with a destruction efficiency of 99.99 percent which meets the control requirements of the Montreal Protocol (Decision IV/12). Based on an overall CTC balance for this CSM process, 99.95 percent of the CTC used in the process is recycled, converted (transformed), or incinerated (destroyed). The remaining losses (trace emissions) to the environment (0.05 percent) are largely from product handling.

Table 1 provides the chronology showing how CTC use per tonne of CSM declined from 142 kilograms (kg) to 2.9 kg. of CTC per tonne of CSM. Table 2 is a comparison of the emissions from the CSM Process in North America versus the CSM Process in China (see Case Study C-7b). Emissions of CTC are two orders of magnitude lower in the CSM Process in North America, per tonne of product, versus the CSM Process in China.

Table 1
Chronology of CSM process emissions
North American CSM process

Time Period	Process Changes/ Improvements	Emissions (kg CTC/ tonne CSM)
1957 to 1963	Start-up facility; Reactor upgrade; Solvent Recovery improvements	No emission data.
1964 to 1970	Expansion of capacity; Blend Tank for product uniformity; Off-gas system for recycle of SO ₂ ; Caustic Scrubber for emergency releases; Solvent Recovery improvements; Storage Tank condensers	142
1971 to 1977	Expansion of capacity; Reactor improvements; Solvent Recovery improvements; Carbon Adsorption System and Solvent Purification System installed (1977)	129
1978 to 1983	Expansion of capacity; Process Computer controls; Carbon Adsorption System improvements	8.3
1984 to 1988	Carbon Adsorption System improvements; Chlorine Stripper improvements; Wastewater Effluent Stripper to Carbon Adsorption System (1988)	4.3
1989 to 1994	Carbon Adsorption System improvements (Storage Tanks and Drying Column vents)	4.1
1995	Process control improvements; Continuous Emission Monitoring System improvements; Leak Detection and Repair program for fugitive emissions	2.9

Notes:

CSM process emissions from the North American facility are for carbon tetrachloride (CTC) only. These estimates include CTC emissions from process vents, storage tanks, wastewater, equipment leaks, building ventilation and products.

Table 2
Comparison of CSM process emissions
1995 emission estimates

Comparison of CSM Process Emissions	CSM Process China (1)	CSM Process North America (2)
Production (tonnes/ year)	3,000	23,000
CTC recovered, recycled (tonnes/ year)	28,906	135,049
CTC recycled per usage (%)	97	99.4
CTC annual requirement (tonnes/ year)	8 9 4	781
CTC transformed/ destroyed (tonnes/ year)	0	717
CTC recycled/ transformed/ destroyed (%)	97	99.95
CTC used in process (tonnes/ year)	29,800	135,830
CTC emissions (tonnes/ year)	894	64
CTC emissions (kg CTC/ tonne CSM)	298	2.9
CTC emission (%)	3	0.05

Notes:

- (1) Information based on the Case Study entitled "Use of CTC in Chlorosulphinated Polyolefin (CSM) Production in China" prepared by Professor Zhang Zhiqun of Beijing University of Chemical Technology for the Report of the UNEP Process Agents Task Force (see C-7b).
- (2) Information based on a paper presented by Mr. Tony Vogelsberg to the UNEP Process Agents Task Force on October 21, 1996.

C-7a.5 Pollution Abatement in the North American CSM Process

The North American CSM Process employs several systems to recover and recycle CTC. These operations include the Reactor, Off-gas, Isolation, Neutralization, Spent Caustic, Solvent Recovery, Carbon Adsorption, and Wastewater Treatment systems. Although all these systems contribute to the recovery and recycle of CTC, only the Carbon Adsorption and Wastewater Treatment systems are considered pollution abatement operations. Other operations such as a leak detection and repair program and the waste management program also contribute to the reduction and recovery of CTC emissions.

CTC emissions that are too dilute for recovery by condensation in one of the other systems are collected in a single header and sent through a bank of carbon adsorber beds. Normally, all but one bed are adsorbing at any given time; the one being regenerated by steam or on stand-by. Each bed contains 40,000 pounds of carbon and can treat 140,000 scfm of air during normal operations. Based on performance data, the carbon adsorption system has a recovery efficiency of greater than 99 percent.

During regeneration of the carbon beds, steam is passed through each bed (effectively removing the CTC from the carbon) and condensed with the recovered solvent in a water-cooled condenser. The recovered solvent is decanted from the water and sent to the Solvent Purification Column which separates the CTC from the solvent by batch distillation. The CTC is recycled to the Neutralization system and then to the process. Trace compounds and

miscellaneous catalyst fragments are left as residual from the column reboiler. This residual waste material is removed and shipped to an off-site incinerator for destruction of the CTC. The incinerator is required to operate at a destruction efficiency of 99.99 percent.

Monitoring systems in the North American CSM process continuously sample all CTC emissions from process vents to the atmosphere. These systems monitor CTC concentrations at various points throughout the process. The monitoring system data is reported quarterly as a condition of a state air permit and must meet the permit emission limitations. In addition to the continuous emissions monitoring systems, fugitive emissions from valves, pump seals, connectors, etc. are monitored monthly, quarterly and annually. Leaks are repaired within 5 to 15 days of detection.

The results of this program are reported to the federal and state agencies semi-annually under the National Emission Standards for Hazardous Air Pollutants (NESHAP) regulations. New NESHAP regulations issued on September 4, 1996 (specifically for the North American CSM processes) will also require record keeping and reporting of emissions from storage tanks, process vents, wastewater and equipment leaks.

Water from the Solvent Purification Column is stripped with air to recover and recycle CTC prior to being pumped to the Wastewater Treatment system. Other wastewater streams including any process spills and rainwater are collected in a series of sumps and sent to a holding tank prior to being pumped through filters and a coalescer separator and then air stripped for CTC removal. The stripping air is routed to the Carbon Adsorption system for CTC recovery. The water from the process ditch stripper is discharged to a diversion sump which also collects any overflow from the process ditch sumps. This water is pumped through a residence tank which overflows to an outfall which is permitted by the state and federal environmental agencies under the National Pollutant Discharge Elimination System (NPDES).

A continuous sample is taken from the diversion sump and analyzed for CTC, as well as, other hydrocarbons, pH, temperature, and total suspended solids. A high signal automatically starts the diversion pump and sends the water stream to the diversion tank for treatment in the process ditch stripper or the pH control systems. Periodic sampling of wastewater discharges for various pollutants (including CTC) is conducted at the NPDES outfall and reported monthly to the state and federal environmental agencies.

Solid wastes (including hazardous wastes) from the reboiler of the Solvent Purification column and drummed wastes are sent off-site for incineration. The shipments are manifested and sent to government-approved facilities for proper handling and treatment. These facilities are required to meet an incinerator destruction efficiency of 99.99 percent. Monthly and quarterly reports of all shipments must be made by the generator, shipper, and incinerator of the wastes to state and federal agencies under the Resource Conservation and Recovery Act (RCRA) regulations.

All monitoring systems and environmental programs are audited annually by representatives of the state agencies compliance with state and federal regulations. In addition, several internal audits are conducted by corporate and business unit teams annually to ensure all systems and programs are in place and functioning properly.

C-7b Use of CTC in Chlorosulphonated Polyolefin (CSM) production in an Article 5(1) country

C-7b.1 Introduction

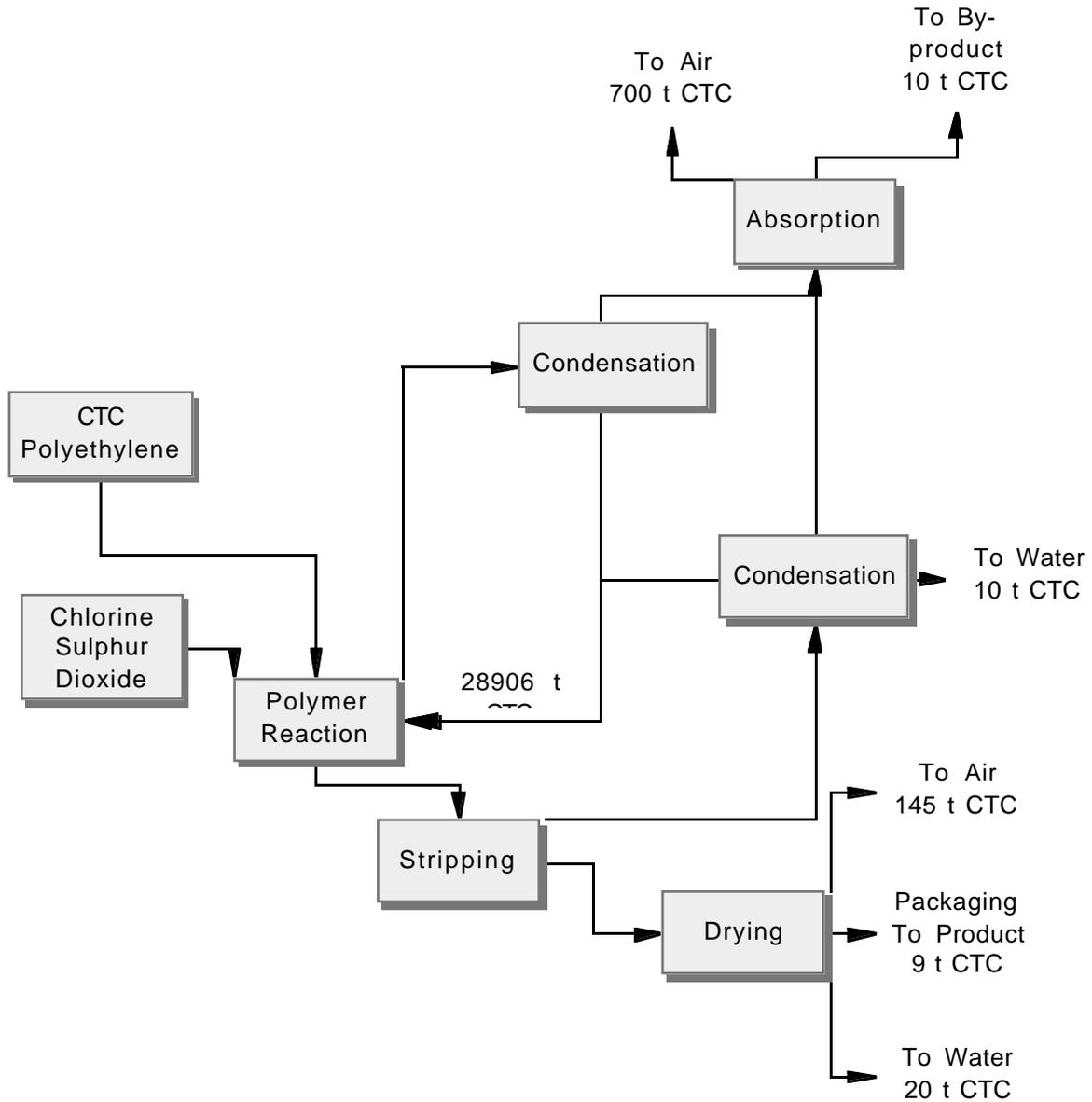
Chlorosulphonated Polyethylene (CSM) is a specialty elastomer with superior properties in resistance to weather, heat, oil, chemicals and abrasion, combined with excellent flexibility and color stability. China began to produce this product in the late 1970's and currently production capacity and output has reached over 3,000 tonnes per year.

Jilin Chemical Industrial Company Limited (JCICL) is the largest producer of CSM in China. Other CSM producers in China are comparatively small producers and their statistical data are not available as yet. Therefore, only the elaborated JCICL CSM process and its update CTC balance are presented in this case study.

C-7b.2 Description of the process

The JCICL CSM process was a CTC based process, which was developed and improved by JCICL.

Polyethylene is first dissolved in hot CTC and then, together with chlorine and sulphur dioxide, introduced into the reactor, in which the chlorosulphonated product is yielded. The finished product is further isolated by stripping and drying operations and then packaged in the form of chips. The released CTC from the reactor and rear operations is recovered, purified and recycled by condensation and absorption.

CTC balance for JCICL process

C-7b.3 CTC consumption and emissions in the JCICL process

Item Description	JCICL CSM Process
Annual CSM production (t/a)	3,000
Annual CTC recycle (t/a)	28,906
CTC recycled per production (t/t)	9.635
Annual CTC consumption (t/a)	894
CTC consumption per production (t/t)	0.298
Annual CTC transformed/destroyed	0
CTC transformed/destroyed (%)	0
Annual CTC used as PA (t/a)	894
Annual CTC emissions (t/a)	894
to air (t/a)	845 (94.52%)
to water (t/a)	40 (4.47%)
to product (t/a)	9 (1.01%)
Annual CTC emissions (%)	100
CTC emissions per production (t/t)	0.298
to air (t/t)	0.282
to water (t/t)	0.013
to product (t/t)	0.003
CTC emissions per recycle (t/t)	0.03

C-7b.4 CTC alternative process

In the 1970's JCICL had explored the feasibility of using chlorobenzene instead of CTC as a process agent for CSM production. After years of research, this option was abandoned for the following reasons:

1. Energy consumption is much higher than that of using CTC due to higher boiling point of chlorobenzene.
2. Chemical stability to chlorine and sulphur dioxide is not as good as use of CTC in the process
3. In-plant safety is not as good as that of using CTC due to flammability, explosivity and toxicity of chlorobenzene.

C-8 Production of Poly-Phenylene-Terephthal-Amide with the aid of CTC in an intermediate raw product

C-8.1 Introduction

The aromatic polymer PPTA (**Poly-Phenylene-Terephthal-Amide**), is produced in the Netherlands. Carbon tetrachloride (CTC) is used as a process agent in the production of an intermediate raw material.

C-8.1.1 Products

The main products are fibers with a wide field of high tech application based on the extreme strength (5 times as strong as steel) combined with a series of other outstanding properties including: high tensile modulus, good chemical stability, very low creep rate, good dielectric properties, flame resistant, self extinguishing and others.

C-8.1.2 Application

The perfect manufacture of complex products which exceed design specifications are enabled. The applications are in composites with rubber and synthetic materials and in composed textures. Composites are often combined with existing materials to improve properties.

In combination with steel, the fiber is used for impact shields to give protection for equipment and vehicles. This means that police and civilian vehicles can be armored and yet be light and maneuverable. Similarly tanks and military vehicles become lighter and safer. Weight savings amount between 30 and 60%. The material is also used to provide light weight body protection in the manufacture of helmets for motor cycling, police and military (a 100% better ballistic performance than a steel helmet) as well as flexible, bullet and fragment resistant vests which are easy to wear. As an impact resistant composite material, it is used as an anti piercing shield for the protection of railway and road tank cars transporting dangerous goods.

Reinforced refrigerator trailers are some 25% less in weight, are better insulated and less sensitive to damage. Savings result from a lighter weight, smaller refrigerator with greater payload.

Optical fiber cables can be made lighter in weight and rodent resistant.

In the field of rubber goods better performance is achieved for transmission belts, hydraulic hoses, automotive hoses, conveyor belts and ultra light weight automobile tires, the latter also leading to savings in fuel consumption.

Wood laminates can replace hardwood applications without loss of strength (for instance large warehouses).

The PPTA fiber plays an important role in replacement of asbestos for brake linings, brake blocs and disk brake pads; for chemical resistant gaskets; for heat resistant workwear and fire blankets.

There is a growing market for these applications.

C-8.2 The manufacturing process

The polymer is produced from the raw materials PPD (para-phenylenediamine) and TDC (terephthaloyldichloride). The raw materials PPD and TDC are produced at the same facility. The plant has a permitted capacity of 18,000 tons of polymer.

The only use of CTC is in the production of TDC. TDC is produced by side chain chlorination of p-Xylene in CTC followed by fusion with terephthalic acid. Purification is by distillation; hydrochloric acid (muriatic acid) is produced as a byproduct. CTC is separated from product streams and recycled constantly in the process. It is regenerated for reuse by distillation. The CTC distiller waste is incinerated. All waste streams (gas and liquid) are purified. Wastewater and vent gases are purified in an integrated system by air stripping and active carbon adsorption. Active carbon is regenerated with steam; the condensed CTC is recycled. The Hydrochloric acid (HCl) is purified by steam stripping and the recovered CTC is recycled, see flow chart. The entire process is contained.

C-8.3 Why CTC is used

CTC is used for the following reasons:

1. Quality by avoiding side reactions during chlorination. The quality is crucial for the polymerization.
2. Safety by avoiding explosion risks during chlorination.
3. A carrier for recycling of incomplete chlorination products which results in less waste and a high yield.
4. A cleaning agent for the HCl emerging from the reactors. The cleaning solution is recycled.

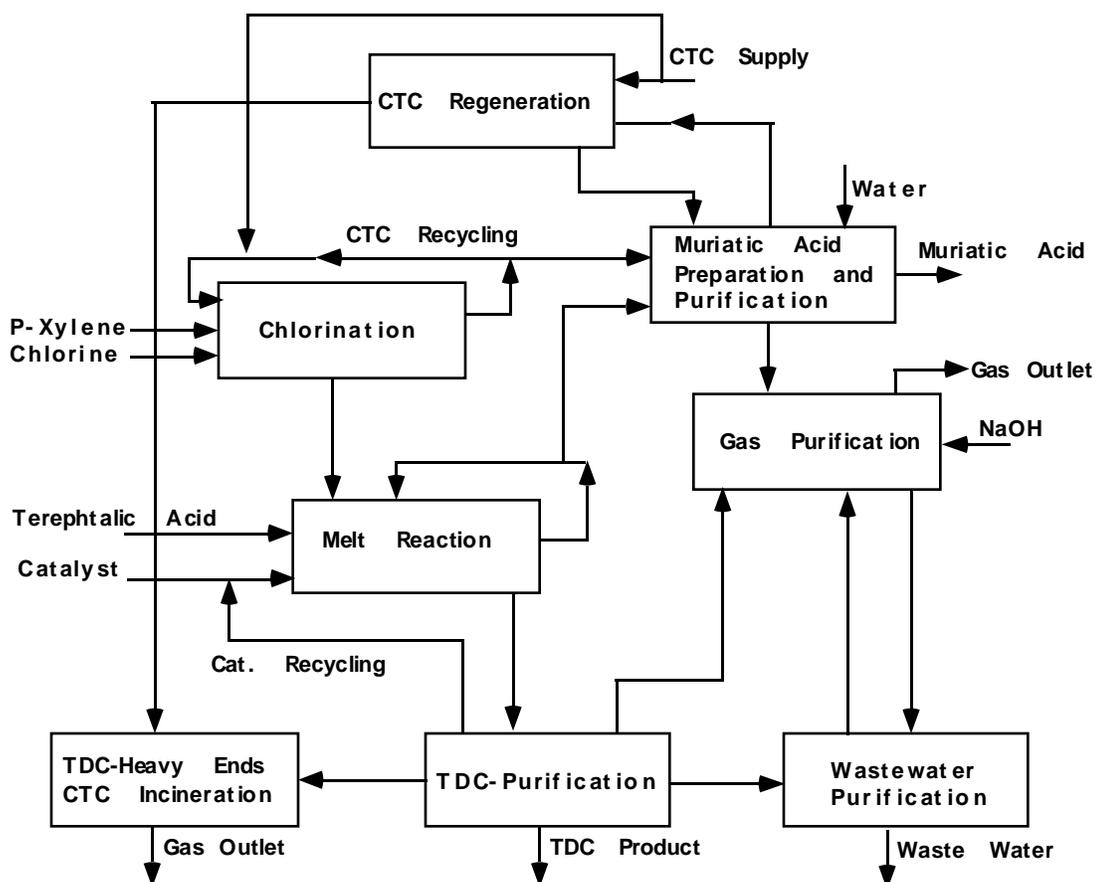
Combination of all these purposes, under the various conditions of the process, can, according to current knowledge and practical experience, only be fulfilled with CTC. There is no single chemical that can replace CTC in this process.

It is unique:

- 1 it is inert in all process steps;
- 2 prevents side reactions to take place in the reactor;
- 3 has the right vapor pressure to prevent explosive reactions in the gas cap of the reactor;
- 4 is easy to recover;
- 5 has a low solubility in HCl.

As a consequence the use of CTC from the start of the TDC-plant has been fully integrated in the process.

TDC Process for Aramid polymer Production



C-8.4 How CTC is used

The “make-up” quantity (1995) is 72.5 tons per year, mainly arising from the destruction of CTC distillers waste (the unusable bottom fraction that remains in distilling the recycled CTC).

Source	Name	Discharge of CTC ton/year	Remarks
Product	TDC	0	
Product	30% HCl	max. 0.240	
Wastewater	after treatment	max. 0.060	
Vent gas	after treatment	ca. 2	improvement foreseen
Diffuse	losses in collecting system	pm	project for total containment in execution
Leakage	losses	0.030	measured and calc. EPA
Incidental	losses	0.200	fixed entry for maintenance
Waste	incineration	70	
Required	Make-up	72.5	year 1995

C-8.5 Pollution abatement

In August 1989 at Nairobi carbon tetrachloride (CTC) was placed on the list of ozone depleting chemicals. From that time efforts have continued to replace CTC.

These efforts have been made up in 2 areas:

- Reducing emissions in the existing TDC-plant;
- Research for substitutes for CTC or other processes.

C-8.5.1 The emission reduction has led to the following results:

- The CTC discharge in wastewater was reduced by 99% by redesign and installing more separators for CTC.
- The CTC discharge in waste gas was reduced over 90% by investigation and redesign.
- Liquid and gas flow systems were simplified to facilitate recycling.
- All waste streams are monitored.
- Wastes containing CTC are incinerated by an UNEP accepted technique.
- The CTC content of HCl was reduced with the aid of monitoring.
- Diffuse losses were measured and reduced to some 30 kg/year (according to correlated emission factors).
- The inadvertent losses relative to the total circulation rate amounts ca. 0.01%.
- The environmental management system has been certified under British Standard 7750.

Emissions for 1990 and 1995 in tons of CTC/year:

Source	Name	1990	1995
Product	30% HCl	0.45	0.12
Wastewater	after treatment	1.680	0.06
Vent gas	after treatment	35	1.62
Diffuse	losses	0.54	0.03
Incidental	losses	0.20	0.20
Total emission		37.87	2.03

C-8.5.2 Research activities have led to:

- Substitution of CTC in a coolant system for reactor lamps.
- The understanding that there is no single substitute for CTC for all the purposes to be served. Every other substitute for a single purpose suffers from degradation or contamination by chlorination and possible origination of CTC thereby complicating the process to an unknown degree in relation to the desired quality of the product.
- A commercial alternative process for the production of TDC is known, however this process belongs to the only competitor. In addition the cost of buying and building a complete new TDC plant next to the operating one is prohibitive. A rough cost estimate is US \$150 million (reducing the CTC emission by 2 tonnes per year).

C-8.5.3 Regulatory

The environmental regulations together with the decisions of the Montreal Protocol have had their influence on the restrictions of emissions in a direct and indirect way as the following table shows.

Legislative aspects versus measures and results:

#	Type of law ¹⁾	Conditions	Applied technique	Results ²⁾
1	Restriction of water pollution	Reduce existing pollution 50 -90%	Separators followed by air stripper	99% reduction
2	Restriction on air pollution	Reduce existing pollution to standard	Active carbon adsorbers, containment	1995: 90% reduction; ongoing program
3	Unpolluted products	max. 10 mg/kg	steam stripper	Well below 10 mg/kg
4	Waste destruction to standard	According to Dec IV/11	Incinerator	Destruction more than 99,9%
5	Unpolluted soil	No polluted soil	impenetrable slabs with water collecting provisions	No pollution

1 There is a voluntary convention between government and the chemical industry to restrict emissions as low as is feasible.

2 Monitoring has added a lot to good and reliable results.

C-8.6 Future aspects

In the near future:

- The vent gas purification will be improved on the basis of the data of the monitoring.

- A project for a fully closed CTC wastewater collecting system will be carried out to achieve complete containment of the plant.

After these improvements which will give a further reduction of emissions the best available techniques and the best environmental practice for this production have been applied. This is confirmed in the environmental permits (Dutch Air pollution act and water pollution act) which are based on the figures given in the table. The monitoring of the waste streams have to be reported on a quarterly basis for wastewater and for waste gases on a yearly basis.

Further extensions are expected in the future. Therefore efforts are being made to gather knowledge about modifications in the existing process without the use of CTC. The objective is worth pursuing and the efforts are appreciable but the chance on success can't be predicted. However adoption of this course is seen as the best there is, given the circumstances that growth of sales and sales potentials must make further extensions possible. As of 1996 this knowledge has not been developed adequately to eliminate use of CTC for future expansion of the production facility.

C-8.7 Substitutes without ODS application

As already mentioned there is one commercial process to produce PPTA without the use of CTC in producing one of the raw materials: TDC. However the possibility of using this process is limited while licensing meets considerable constraints in terms of competitiveness and introduction of other environmental problems. The process is based on a different chemical reaction and it is carried out with phosgene as a raw material. Such use is only technical and commercial viable when phosgene is already present or is used for more than one product (which is not the case). Moreover the cost of adopting this process is estimated 150 million US dollars which is not feasible. Research is done to find a better corresponding ODS free alternative. The progress of this program looks promising.

The possibility of using alternate products is more or less contradicted by the market that consumes the product on the base of exploiting the outstanding properties of the polymer as there are:

- replacement of asbestos in brake applications, heat resistant workwear and fire blankets,
- impact protection properties of hitherto unknown quality,
- composites of hitherto unknown strength.

In these fields there are only alternatives if one abandons the progress in quality of the products or safety.

C-9 Use of CFC 113 for manufacturing a family of fluoropolymer resins

C-9.1 Introduction

Fluoropolymer resins that have traditionally used an ODS processing agent are manufactured by a small number of multinationals in Europe, North America, and Japan. One North American-based multinational chemical, plastics, and fiber company manufactures three basic product lines of fluoropolymers that have traditionally used CFC-113 as a process agent. Its manufacturing facilities are located only in non-Article 5(1) countries. The generic types of fluoroproducts are typically:

- Ethylenetetrafluoroethylene or ETFE
- Ethylenechlorotrifluoroethylene or ECTFE
- Perfluoroalkoxy, fully fluorinated resins or PFA
- Perfluorovinylethers

C-9.1.1 Process description

These products are typically produced in batch operations where resins, process agents (solvents), and other reactants are batch charged into reaction vessels followed by product isolation, product purification, and solvent recovery.

The operations described in this case study are unique to the industry due to their much higher volume and use of some continuous instead of batch technology for much of the production.

C-9.2 Unique product properties

The products are all high value resins used primarily in industrial applications where lower cost resins are unable to meet demanding performance criteria typically characterized by:

- Ultra-high purity and chemical inertness for chemical processing operations.
- Mechanical toughness and chemical inertness for containers dedicated to handling hazardous or toxic materials in a safe, environmentally sound manner.
- Predetermined electrical conductivity for extended use high temperature components.

Specific uses for these fluoropolymer resins include:

- Electrical and control wiring for commercial and military aircraft because of excellent electrical insulation properties, inertness to atmospheric pollutants, and retention of properties over very extreme temperatures.
- Non-stick coatings on high value cookware.
- Computer wiring.

C-9.3 Why and how is CFC-113 used as a process agent?

	Purpose
Quality of final product	XX
Safety	X
Necessary for reaction	
Yield	X
Cost	X
Other	

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

CFC-113 was originally selected as a process agent for this family of fluorinated resins because it exhibited several key properties:

- Low toxicity.
- Provides excellent dispersions.
- Suitable solvency for several polymer structures that are insoluble and a wide range of solvents.
- Inhibits explosion of tetrafluoroethylene (TFE) (backbone of these products).
- Chemical stability to temperatures and pressure.
- Non-flammable.

Since the four world scale manufacturing facilities exist and represent a combined investment of several tens of millions of dollars, it is economically impractical to convert to a flammable solvent without complete redesign of all process equipment and building to a flammable hazard classification.

The unique properties for several critical customer applications are very dependent upon the specific solvent and process conditions. Hence, finding a suitable solvent replacement requires not only that it provide similar process operability, safety, and cost, but its specific products must be rigorously proven in every unique customer application.

Another process safety concern is to suppress the explosion tendency of the main feedstock, TFE. Experience has demonstrated that hydrocarbon solvents that may exhibit suitable solvent properties will not suppress TFE explosions. The only practical solvents have proven to be fully halogenated materials like CFCs, perfluorocarbons (PFCs), hydrofluorocarbons (HFCs), and marginal hydrofluorocarbons (HCFCs).

Documented CFC-113 use for the global fluoropolymer plants are not accurate prior to the late 1980s since CFCs were not recognized as harmful to the environment and their use and emissions were not under any special control. Undocumented memory indicates that just one of four sites used about 400/tonnes/yr. of CFC-113. Documented use by 1988 was in the range of 250 metric tonnes per year for the four plants. By taking steps described in the following text, emissions have been cut by more than two-thirds of the 1988 documented experience; while product output has risen.

C-9.3.1 Efficiency of ODS recovery

Emphasis has been placed on developing technology to displace CFC-113 as opposed to expenditure of large R&D plus capital to achieve 99.9+% recovery. The short term process improvements and handling practices have generally resulted in a 90+% efficiency in CFC-113 use. See Section C-8.4. for details.

C-9.4 ODS abatement and containment

Overall process agent emissions are one-third of what they were in the late 1980s due to several capital and procedure steps taken at all four plant sites globally. It is important to note that one plant anticipated shutting down rather than spend the large amount of capital to convert to a non-ODS process agent; however sharply increased global demand necessitated continued operation of this facility. It is now planned to convert this facility to a non-ODS process agent if global market conditions support this activity.

All sites use similar technology to minimize ODS loss or to abate emissions. Vent collection and recovery systems capture and recycle 99% of CFC-113 in the primary vents. Losses previously experienced during plant maintenance are now recovered in a maintenance vent recovery system. Product dryer modifications reduce CFC-113 emission by greater than 90% of prior experience during dryer regeneration. A fugitive emission program aimed at leak detection and repair has been instituted. Special emphasis has been devoted to mechanical seal designs, maintenance techniques, and use of a non-ODS seal flush. CFC-113 detectors have been installed on equipment pressure relief vents to ensure rapid correction of a relief device failure or activation. Finally, a rigorous solvent record keeping and emission tracking program pinpoints sources for future CFC-113 reductions as well as focusing attention on current emissions.

Since the ultimate objective is to convert all plants and their respective products to non-ODS process agents, there has been a balance of scarce development resources and capital between minimizing current CFC-113 losses and completion of the transition to non-ODS process agents.

Since the total makeup for the four plants is a rather modest amount, inventory at each site was established prior to the end of 1995 with the expectation that future ODS purchases would be unnecessary, assuming successful conversion to non-ODS process techniques.

C-9.4.1 Regulatory requirements

All four plant sites are in countries where chemical production facilities are permitted by national, state, or local authorities. CFC-113 is regulated in some states as a ground water pollutant, so any non-volatile waste is disposed of in environmentally secure landfills.

C-9.5 Non-ODS technology options

Efforts to identify potential alternate process agents that would work in the four different global plants and for the full range of fluoropolymer products got underway in 1987, following U.S. CFC industry recognition and support for an international regime to stabilize or reduce CFC emissions globally.

Any suitable replacement solvent(s) (process agent(s)) would have to deal with a host of process and product issues that were all cost effectively managed with a single solvent,

CFC-113. Safety was of foremost concern since tetrafluoroethylene (TFE), the backbone of much of the product line has a tendency towards severe deflagration (explosion). A key property of the process agent of choice suppresses the deflagration tendency of TFE. Hydrocarbons will not suppress TFE deflagration but fully halogenated solvents will. With CFCs, carbon tetrachloride, and halons already set for phaseout, and HCFCs scheduled for near term phaseout, the options were significantly limited; primarily PFCs and HFCs.

Close to fifty potential process agents have been explored over the past eight years as part of a multimillion dollar research and development program.

It is expected that much of the product line will be converted away from CFC-113 during 1997 and 1998. However, there are still specific critical customer applications that have not yet been able to accept the non-ODS products. Effort is continuing to find an acceptable process agent or suitable processing conditions for these products.

After eight years of extensive research and development, there are still unresolved challenges to a 100% ODS use phaseout and some continued use could occur past 1998.

A Japanese, manufacture of fluoropolymer resins has converted to a non-ODS process utilizing a proprietary technology, however the facility does not produce the full range of fluoropolymer products.

C-10 Use of CFC 11 in manufacturing a fine synthetic fiber sheet structure

C-10.1 Introduction of process

C-10.1.1 Products made, use of the products:

Fine synthetic fibers are formed into strong sheet structures used for a variety of important applications including:

- Air infiltration barriers in buildings to reduce heating and air conditioning costs and to extend the useful economic life of wooden building material (by excluding water rot)
- Medical device packaging that allows sterilization after packaging and providing long, safe, shelf life
- Protective clothing for workers handling toxic or dangerous chemicals (i.e. asbestos removal)
- Packaging for important products and information in tear resistant light-weight envelopes that save shipping costs and assure intact long distance delivery
- graphic applications that ensure long life of maps, banners, tags, under severe climate or service conditions
- special purpose clothing, packaging, padding, and insulating applications

C-10.2 Description of overall manufacturing process:

Fine synthetic polyolefin fibers are manufactured using CFC-11 as a process agent. CFC-11 is contacted with high density polyethylene pellets in a slurry mix tank, pumped with high pressure pumps through a heat exchanger and stirred tank mixers to form a spinnable polymer solution.

Using a manifold, the polymer solution is fed to spin packs mounted on top of a 'spincell'. Filaments are flash spun inside the spincell onto a belt to form a sheet structure which is consolidated, extracted from the spincell through seals rolls, devolatilized inside an air enclosure before being wound-up. The process agent, in vapor form inside the spincell, is entirely recovered, neutralized and returned to storage.

C-10.3 Why is the ODS used as process agent ?

QUALITY OF FINAL PRODUCT	PURPOSE XX
SAFETY NECESSARY FOR CHEM. REACTION	X
YIELD	X
COST	X
OTHER	

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

C-10.3.1 Unique process agent properties:

- low toxicity
- non flammable
- physico-chemical properties: boiling point, critical temp. / pressure
- solvency power (capability to enter polymer matrix)
- controls solution viscosity and process operating pressures
- chemical stability to high temperature and pressure
- non corrosive

C-10.4.4 Process Agent Losses: past and future changes for total global capacity:

Year	Locations/Lines	Losses [Tonnes]	Losses as % of '86 base
1986	U.S./2	2323	100
1987	U.S./2	1626	70
1988	U.S./2	1211	52
1989	U.S./EU/3	813	35
*			
1995	U.S./EU/3	131	< 6

It must be noted that approx. 10 % of the process agent losses are the result of ODS transformation or destruction, not from a diffuse or point source emission. In fact chloride salts measured in the active carbon adsorption system steam condensate neutralization station confirm the ODS transformation and destruction mechanism.

C-10.5 Pollution abatement

General description of control technology (EU plant data presented for case study consistency). The CFC-11 Recovery process essentially distinguishes between:

C-10.5.1 Primary Recovery (CCS)

The main process agent flow (approx. 24,000 kg/h) from the spincell (volume \approx 1000 m³) is recovered in a 'compression and condensation system' (CCS) utilising a spraycooler, compressor, condenser and vent condenser. Recovered liquid is neutralized with caustic water injection, decanted before being pumped back to storage. Non-condensables vent to CAS.

C-10.5.2 Carbon Adsorption System (CAS)

Process agent vapors from the sheet devolatilization process inside the air enclosure and other small quantities or dilute sources of process agent from process equipments are conveyed to the Carbon Adsorption System. Roughly 3 % of the main process agent flow is recovered in CAS.

Steam condensate from CAS containing trace amounts of process agent is recovered using an air stripper.

The Carbon Adsorption System presents two 'point' emission sources: process agent from the continuous air exhaust and drying cycles.

Recovery Systems in place during upset conditions:

Following devices recover the process agent during process upset conditions:

- a) all vessels presenting a vapor space with potential vapor pressure build-up are protected with a rupture disc connected to a containment tank. In case of spincell overpressurization due to recovery compressor failure, process agent vapors are also

collected in this containment tank. Recovery of containment tank vapors takes place via CCS and CAS.

b) cold liquid process agent from rupture disk discharge lines are collected in a blowdown collection tank. Cold pellet/process agent slurry rupture disk discharge lines first pass a pellet collection tank before the liquid process agent is recovered in the blowdown collection tank.

c) hot process agent and polymer solution rupture disk discharge lines are connected to a flash tank. Flashing of polymer solution in the flash tank produces a fluffy polymer material that requires separation in a cyclone before the process agent vapors can be collected in the containment tank.

Diffuse emissions from valves, gaskets, etc. inside the building, including the pack change sequence which involves the opening of the spincell to exchange a spin position, are reported as H&V exhaust point source emission to the authorities.

C-10.5.3.a Recovery System Design Considerations:

Measures to collect routine losses previously not controlled:

- enclosure of sheet handling section of spinning machine
- tightening of spincell windows, new gaskets and local CAS vapor evacuation capability in case window has to be opened to remove polymer from inside machine spinning packs to maintain continuity
- additional partition wall in secondary enclosure to avoid dilution and provide second counter current air stripping slot
- installation of containment tanks to capture ODS from overpressurization of spincell and blowdown cell
- Venting of spin deck pack change 'bathtub' arrangement and pack cavity to Carbon Adsorption System (CAS)
- CAS air capacity increased to capture more air from different areas
- enclosure and air sweep to CAS around most centrifugal pumps in recovery and ODS supply system
- slurry pump packings vented to CAS
- all rotating penetrations into spincell vented to CAS
- impulse lines reduced to minimum essential length to avoid fittings at elbows which eventually leak due to associated equipment vibrations

- additional headers with connections to CAS to all areas requiring maintenance work and quick containment of small leaks

Carbon Adsorption System Upgrade:

- Titanium Vessels to fight corrosion from HCl gas, a result of ODS destruction
- CAS Steam-out manifold modified to avoid carbon blow-out and steam channeling
- high pressure steam supply for CAS steam-out; HP/LP steam ratio allows higher steam-out pressure to desorb more ODS
- CAS air capacity increased to capture more air from different areas
- added heater into main air duct to control relative air humidity and reduce competitive adsorption water vs ODS on active carbon
- Insulation of CAS feed air piping
- additional heating coil in the drying air heater to reach max. 80° C drying air temperature

1995/1996

- close monitoring of all CAS valves (corrosion of valves has impaired proper functionality)
- exchange of active carbon after 7 years of service (9 tons of active carbon per bed)
- Control of Losses with Steam Condensate Discharge to Sewer:
- CAS steam condensate is decanted before discharge
- Steam condensate leaving the beds during heat-up is collected in separate tank for ODS vapor recovery before discharge
- CAS and Compression & Condensation System (CCS) combined to minimize caustic turn-around and ODS lost with aqueous discharge
- low temperature discharge and manual draining eliminated
- Steam Condensate multi-stage stripper prior to discharge to plant process sewer

- CAS steam condensate/caustic flows redesigned to scale-down discharge to plant process sewer
- water skimming equipment installed in all three ODS storage tanks for removal of decanted water (water being entrained into the tanks from the caustic neutralization process during recovery)

Pressure Relief Containment:

ODS / Slurry System

- process pressure rating designed to shut down slurry pump rather than have polymer/ODS release to atmosphere
- containment and auto shutdown of slurry pump in the event of cold slurry rupture disc failure
- additional protection of all relief valves with rupture discs
- all cold/slurry relief lines connect to a pellet collection tank tied to the blowdown collection tank for evaporation of the cold ODS

ODS Vapor

Concept: Containment Tanks

- all vessels presenting a vapor space with potential vapor pressure build-up are protected with a rupture disc connected to the containment tanks..
- both the spincell and the blowdown tank are connected to the corresponding containment tank. In case of spincell overpressurization due to recovery equipment (compressor) failure, process agent vapors are also collected in this containment tank.
- Recovery of containment tank vapors takes place via CCS and CAS.
- the spincell containment tank has capacity for 10 minutes of major equipment failure prior to procedural shutdown of the process once the tank level alarms at 75 %
- Polymer Solution and Flush System
- all (17) rupture discs located in the high pressure polymer solution or flush system are connected to a flash tank. Flashing of polymer solution in the flash tank produces a fluffy polymer material that requires separation in a cyclone before the process agent vapors are collected in the containment tank.

C-10.53.b Process Control Strategies:Monitoring

C-10.5.3.b.1 Maximize Process Control

Redundant Distributed Control System (DCS)

- > 300 control loops
- 5000 monitored data points
- Flexible multivariable central control functions
- Computer assisted Carbon Adsorption System Troubleshooting
Process Equipment: Spare and Protection
- Spare ODS Compressor; changed start-up from field to DCS
- Spare Carbon Adsorption System Blower
- Design done with Power-dip consideration allowing ride-through in case of minor interruption (< 0.7 sec.) and safely shutdown with contained ODS situation in case of major power loss

Misoperation and Equipment Failure Protection:

- Power dip ride-through ability up to 15 seconds with main drives of process, automatic shutdown of spinning and solutioning systems in the event of a major power dip in order to maximize ODS containment
- On-line spare ODS compressor available, remote S/U from DCS
- On-line spare CAS blower
- Laminar sparging of spincell with ODS installed to prevent recovery upsets due to excess air
- ODS flushed from Solutioning process and solution filters via additional heat exchanger to Blowdown Cell: ODS is superheated to eliminate liquid accumulation in Blowdown Cell
- Blowdown Cell walls heated to prevent condensation during Start-up and ODS accumulation in polymer mass after shutdown

Focus on Human Control Aspect

Provide adequate Control Tools

- 20 point building air monitoring system for quick detection of local losses
- 3 portable IR analyzers for spot measurements
- H&V exhaust analyzer for area loss detection (baseline between 1-2 ppm, pack changes cause a 4 ppm peak, baseline above 3 ppm triggers an area search using the portable analyzers and the monitoring indications from the multipoint analyzer)

C-10.5.3.c The 'HUMAN' Factor

C-10.5.3.c.1 Training and Failure Prevention

- Operator training; emphasis on process understanding and attention to detail
- Operators utilize all available tools (computerized troubleshooting, portable analyzers) to localize and contain area ODS leaks
- Operator Acceptance Test for process control responsibilities
- Total commitment to control losses from all plant personnel
- Leak incident reporting system with corrective actions
- Computer-based equipment to continuously monitor ODS inventories in tanks, piping systems, vessels, automatically providing alarms as well as day-to-day loss rates to operators and managers
- An operator suggestion system rewarding those suggestions implemented in the field
- Equipment lock-out procedure not only aimed at safety but also at environmental control
- During maintenance activities, ODS drained out of piping, vapors evacuated to CAS, and liquid collected in central drum before being pumped into central process "evaporator"
- Preventive Maintenance program to check mechanical integrity of all rotating equipment in contact with ODS
- Failure Mode and Effect Analysis (FMEA) performed for all routine practices, i.e. filter change, with the purpose of determining potential failures causes and work out procedures and or equipment modifications to avoid occurrence

- 'Zero Leak Team' Effort; cross section of organization analyzed all potential small leak sources and worked out solution to increase containment
- Strong analytical understanding of loss sources & material balances
- True technical team work with US plant & Engineering. counterparts
- Building multi-point analyzer for continuous monitoring
- Wide spread attack with priority for large sources first

C-10.5.3.d Public Opinion:

- Open relationship with local government officials via timely technical information meetings about containment status and programs
- Community Awareness and Emergency Response (CAER) as part of the 'Responsible Care' program to inform local communities of plant activities
- Plant visits by customers, government officials and interest groups are conducted to demonstrate efficient production & recovery facilities and discuss containment strategy

C-10.5.4 Specific regulations affecting operations: (EU plant)

- Plant Permit modified from 10 kg/h in 1991 to 6 kg/h (50 to) since 1992
- Emissions to atmosphere from any point source to be < 27 ppm according to the German TA-Luft
- Diffuse emissions from valves, gaskets, etc. inside the building, including the pack change sequence which involves the opening of the spincell to exchange a spin position, are reported as H&V exhaust point source emissions to the authorities on a monthly basis
- CAS emissions are reported on 30 minute average basis to the authorities on a monthly basis
- Total Investment for Recovery Unit Equipment: 25 million \$

C-9.5.4.1 Reporting Requirements

Emission data from the commercial line are transmitted on a monthly basis to the local administration of the Environment. The data show the year-to-date and monthly loss rate and recovery efficiency of CFC-11, in addition the point source emissions of the H&V exhaust and carbon absorption system (CAS) are reported with indication of the 50 % and 98 % percentile.

C-9.5.4.2 Enforcement:

The plant management and employees are committed to strictly operate the facility according to local and/or international legislation.

C-10.6 Substitutes without CFC-11

C-10.6.1 Description

The fiber manufacturing area, including the solutioning, spinning and process agent recovery equipment, is the source of ODS losses.

No simple, safe, drop-in candidate has been identified to replace CFC-11 in the existing spinning facilities, despite a continuing (more than four years) program that has examined over one hundred possible process agents. In contrast, our technical efforts in the past four years working with our central and corporate R&D lab facilities have successfully focused on developing a zero ozone-depleting process agent, but it requires completely new spinning and recovery facilities to use it.

C-10.6.2 Limitations

A pilot plant in the USA was authorized in January 1991, and was completed in May of 1992 to develop these new spinning processes. Significant learning's from the pilot plant have been incorporated in the new facilities being in a product prove-out mode now.

- THE NEW PROCESS AGENT was one of the compounds in the original patents but, in the late 1960's, non-flammability made CFC's a better choice for development.
- THE NEW PROCESS AGENT has since been demonstrated to yield different sheet properties in commercial plant prototype testing
- This new spinning process includes about 70 % new technology, most of it being associated with the spincell, spin pack hardware and for the commercial operation, the pack change technology used (and patented)
- The pilot plant continues to demonstrate new spinning hardware and procedures that are needed to safely manage the new process agent, combine it with the polymer, manage its recovery and recycling after flash spinning, devolatilize the sheet product, and provide the proper seals and ventilation. Pilot plant tests are refining optimum process conditions and developing the basic data for the major process elements.
- Process safety management is the key to maintain a safe operating environment.

C-10.6.3 Recent replacement

Two commercial lines were started up in mid 1995 but have not reached nameplate capacity mainly due to product property shifts that have required extensive technical work to find new operating conditions that will meet key sheet properties needs.

Delays of 15 months in commercialization were caused by unexpected equipment failures, process safety and training issues.

Different sheet properties and visual appearance slowed customer acceptance.

To date, only 20 % of the complete product offering are considered as being commercial. All other products still require substantial technical development work to match the properties of the CFC-11 product offering.

C-11* Use of Trichloroethane in the production of semiconductors

***Note:** This case study was prepared from information supplied by the supplier of the ODS for this application.

C-11.1 Description of how and why the ODS are used as a process agent

C-11.1.1 Introduction of the process

The chemical 1,1,1-TCA (Trichloroethane) is used for oxidation purposes in the semiconductor industry. The products are DRAM, Microprocessors and discrete semiconductors.

C-11.2 Reason for the use

1,1,1-TCA is used as a liquid chlorine source in order to generate ultra high purity HCL in a diffusion furnace. It is used to reduce heavy metals and mobile ions from furnace tube walls and as a source of HCL for thermal oxidation.

TCA has been used to shrink the size of staking faults and as a gettering source during the oxidation to reduce the effect of mobile ions.

C-11.3 Quality of the product and material specifications

1,1,1-TCA is used only in the semiconductor industry for production of very sensitive devices. The oxide thickness could meet a range of 100 Angstrom, therefore the purity of the chemical should be in the ppb level for metallic elements and for the assay in order to avoid contamination of the silicon device.

C-11.4 Safety aspects in the production

TCA is not corrosive and easy to use. The delivery is made in very pure quartz bubbler with hermetic seals for protecting the chemical from environment influences.

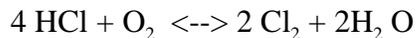
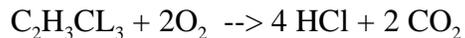
Compared with HCL, the TLV value is very high and is in the range of 200 ppm compared to 5 ppm for HCl. An HCL leak is one of the most destructive occurrences in the operation of a wafer plant. HCL will react with water to form chlorine, a very corrosive chemical which will damage the SS tubing and is dangerous for the humans in the plant.

C-11.5 Consumption

The total consumption for this application in Germany are as follows:

	1996	1992
1,1,1-TCA	100 liters per year	700 l/year
1,2 trans-DCE	600 liters per year	-
Methylene chloride	-	-

In the production, this chemical is used in the high temperature application. The temperature is always in the range of 800 °C to 1150°C. The reaction takes place as follows:



The amount of emitted 1,1,1-TCA is very low, because under normal circumstances a 100% transformation reaction will take place.

C11.6 Opportunities for substitutes for ODS use and limitations

Prior to 1992, 1,1,1-TCA was the preferred source chemical for in-situ generation of HCL. The producer has developed new application for 1,2 -trans DCE and will now substitute the use of 1,1,1-TCA in the semiconductor production. This substitute is now the world wide standard for tube cleaning and oxidation application.

The second alternative is Methylene chloride. This chemical is used partly but the disadvantage is that it could be carcinogenic.

C-11.6.1 Comparison between all three chemicals

Material Identification	Trans-LC	TCA	Methylene Chloride
Flash Point	2 °C	no	no
Auto-ignition temp.	460 °C	540 °C	555 °C
Flammable limits in air	9.7 - 12.9%	7.5 - 14.5 %	12 - 66.4%
Usage compared with TCA	10% more	-	same

C-11.6.2 Cost for retrofit TCA plant to Trans-LC or Methylene Chloride

Trans-LC

Customer must modify the current temperature control system and requalify the process for all kind of semiconductor.

Time required is about 6 months and cost for average plant for equipment modification (30 tubes) is (US) \$30,000. The producer has spent approximately (US) \$5,000,000 for development and change of production.

C-11.7 Pollution abatement

The production plant uses a wet scrubber to reduce the amount of 1,1,1-TCA emitted to the atmosphere.

Under normal conditions, there are no emissions of TCA to the atmosphere. Emissions would only occur as the result of an accident. In Germany where are national regulations for production. The production plant is located in US (Ca) and must comply with applicable national and international regulations.

PATF Comment:

Noting that feedstock is defined as “A controlled substance that undergoes transformation in a process in which it is converted from its original composition except for insignificant trace emissions as allowed by Decision IV/12” it would appear that this is a feedstock application rather than a process agent application.

C-12 Use of CFC 12 in the purification of graphite

C-12.1 Introduction

Graphitization is a method for the thermal treatment of carbon in which the disordered C atom structure is transformed into a parallel-layered grid-like-crystalline system. The transformation of the atomic structure takes place at temperatures of between 2,500 and 3,000 °C.

Thermal treatment takes place in electric furnaces. The material to be graphitized serves as the electric conductor. By supplying electric energy, the material to be graphitized is heated to approximately 2,500 °C, using direct resistance heating.

To obtain high quality special graphite, CFC-12 and nitrogen, serving as reaction gas and purge gas, respectively are fed into the furnace. This takes place during heating and cooling of the furnace at temperatures greater than 1,400 °C.

C-12.2 Why ODS is used

	Purpose
Quality of final product	X
Safety of plant production	
Necessary for the chemical reaction	XX
Yield	
Cost	
Other	

Notes to table: X signifies the main purpose, XX signifies the secondary purpose

Graphite produced using the conventional graphitization technique contains, among others, the elements Al, B, Cu, Fe, Mg, Si, Ti and V as impurities and has a total ash content of more than 1,000 ppm.

Special kinds of graphite with a total ash content of less than 100 ppm are needed for special industrial uses, e.g. X-ray tubes, heating elements and heating systems and for products for the semiconductor industry.

C-12.3 How ODS is used

All of the CFC-12 is decomposed in the process. The halogens from the decomposition of CFC-12 react with the above mentioned impurities to form volatile metal halides.

C-12.4 Pollution abatement

The halogens not transformed in the cleaning process following thermal decomposition of CFC-12 react with water in the air to form hydrochloric acid (HCl) and hydrofluoric acid (HF). The HCl and HF containing waste gas is collected by means of a closed hood situated above

the furnace (encapsulated furnace) and fed to a scrubbing system. In scrubbing, concentrations in the waste gas are reduced to the permissible levels and the waste gas is subsequently vented to the outside.

C-12.5 Substitutes without ODS

Since 1991 the German facility has sought alternatives to the use of CFC-12. The results of tests in which R-134a and R-22 were used at various concentrations have shown that their cleaning effect was insufficient.

A direct change of CFC-12 with another substance does not seem possible at present. The facility is now attempting to modify the process conditions to achieve the same graphite quality using other non-ODS substances.

PATF Comment:

Noting that feedstock is defined as “A controlled substance that undergoes transformation in a process in which it is converted from its original composition except for insignificant trace emissions as allowed by Decision IV/12” it would appear that this is a feedstock application rather than a process agent application.

D

Glossary

ATM	Atmospheric pressure
BAP	Best available technology
BEP	Best environmental practices
CAER	Community awareness and emergency response
CAS	Carbon adsorption system or carbon adsorption stripper
CCS	Compression and condensation system
CFC-11	Trichloromonofluoromethane
CFC-113	Trichlorotrifluoroethane
CR	Chlorinated rubber
CSM	Chlorosulphonated polyolefins
CTC	Carbon tetrachloride
DCS	Distributed control system
DCE	Dichloroethane
DRAM	Digital random access memory
ECO	Ecological
ECTFE	Ethylenechlorotrifluoroethylene
EDC	Ethylenedichloride
eop	End of pipe
ETFE	Ethylenetetrafluoroethylene
EU	European Union
FMEA	Failure mode and effect analysis
H&V	Heating and ventilation
HCFC	Hydrochlorofluorocarbon
HF	Hydrofluoric acid
HFC	Hydrofluorocarbon
HP	High pressure
IR	Infrared
LEL	Lower explosive limit
LP	Low pressure
MACT	Maximum achievable control technology
MT	Metric tonne
NPDES	Non-point discharge elimination system
ODS	Ozone depleting substance
PA	Process agent
PATF	Process Agents Task Force
PAWG	Process Agents Working Group
PFA	Perfluoroalkoxy, fully fluorinated resins
PFC	Perfluorocarbon
ppb	Parts per billion
ppm	Parts per million
PPD	Para-phenylenediamine
PPTA	Polyparaphenyleneterephthalamide
R&D	Research and development
SBR	Styrene butadien rubber
SS	Stainless steel
TEAP	Technology and Economic Assessment Panel
TCA	Trichloroethane
TDC	Terephthaloyldichloride

TFE	Tetrafluoroethylene
TLV	Threshold limit value
UV	Ultraviolet