

# **Montreal Protocol**



## **Process Agents Task Force**

### **Case Study #12**

**Use of CTC in the manufacture of chlorinated paraffin**

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# CS-12 Use of CTC in the manufacture of chlorinated paraffin

## CS-12.1 Introduction

Chlorinated paraffin (CP), with chain lengths between 10 and 26 carbons and chlorine content of 40-70% is produced by chlorination of respective paraffin fractions derived from petroleum refining. These substances are used as high-pressure lubricants, as plasticizer and as flame retardant. The lower members of the family are bioaccumulative and are generally being phased out in developed countries but still used in developing countries such as China.

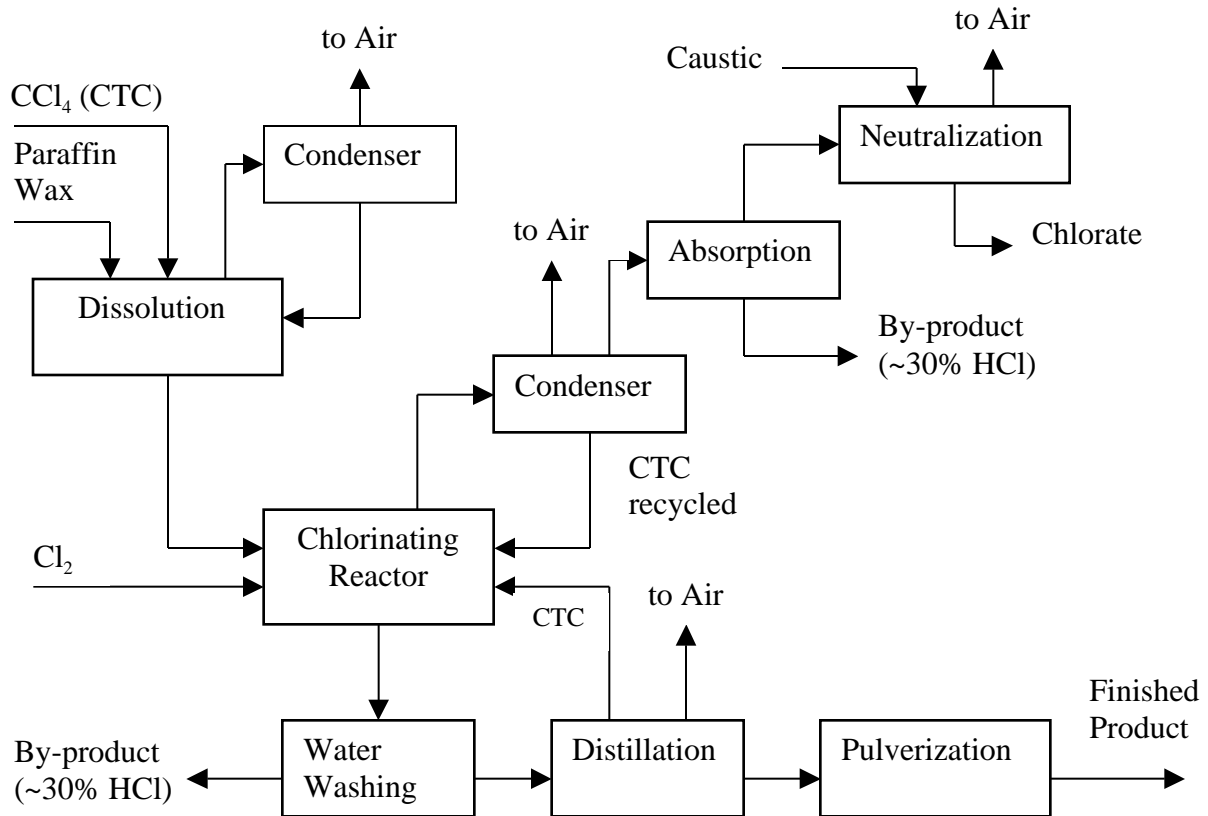
The products with chlorine content of less than 70% such as CP-40, CP-52, CP-60, etc. are usually produced by direct chlorination processes without using any solvents. However, for chlorinated paraffin with chlorine content of 70% (CP-70), carbon tetrachloride (CTC) is used in the manufacturing process as an inert solvent for reducing reactant viscosity, raising product yield and improving product quality.

Chlorinated paraffin 70% content grade is white or light yellow powder. It is indissoluble in water and alcohol but readily soluble in mineral and lubricating oils, benzene derivatives, ethers, etc. The product has an excellent flame-resistant capacity and is extensively used in the manufacture of plastics, rubbers, fabrics, paints and painting inks.

## CS-12.2 CP-70 Manufacturing Process

Paraffin wax is completely dissolved in carbon tetrachloride first, then reacted with chlorine in the presence of CTC as an inert solvent to form chlorinated paraffin with chlorine content 70%. During paraffin dissolution and chlorination, the evaporated CTC is recovered by condensation and recycled upstream for the process. The unreacted chlorine and the gaseous hydrochloric acid generated by side reaction are removed by absorption, neutralization, and water washing operations. The produced CP-70 is then separated by distillation and further pulverized to powder as final product.

### CS-12.3 Flow Chart of the Chinese CP-70 Process



### CS-12.4 Why CTC is used

CTC is used in the CP-70 manufacture process for the following reasons:

- 1 CTC may significantly reduce the viscosity of reactant materials to make more even dispersion of chlorine for paraffin chlorination during the reaction step.
- 2 CTC is fully chlorinated and inert for further chlorination. This is essential for minimizing side reaction with the solvent to prevent unwanted by-products.
- 3 CTC is a non-flammable solvent that allows safe operation and meets the process safety concern for production facilities.
- 4 CTC is immiscible with water and has proper vapor pressure that allows the solvent to be easily recovered by condensation, washed by water and separated by decantation.

- 5 Existing of CTC in reaction step may increase product yield and improve product quality.

### CS-12.5 CTC Consumption and Emission

CTC consumption and emissions in manufacture of CP-70 can be very different from one plant to another due to the specific conditions of the process technology and process operations. The difference also arises from levels of the plant management. In China, there are 10 producers using CTC process agent technology to manufacture CP-70, their CTC consumption and emission data are summarized as below:

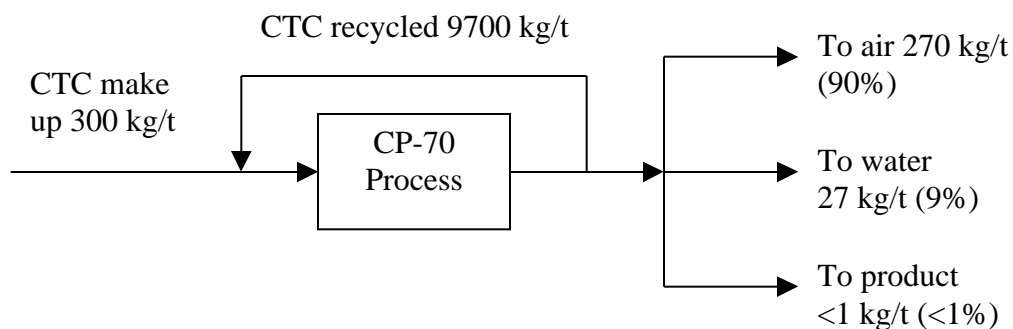
**CTC Consumption and Emissions for CP-70 Production in China (1999)**

Number of Producers	Average Capacity t CP-70 / year	CTC Consumption* kg CTC / t CP-70	Notes
1 Producer	500	6.7	Only run in Winter
3 Producers	500~3000	100	
6 Producers	300~1000	200~300	

\* No CTC destruction technique was adopted in the Chinese CP-70 manufacturing processes and therefore, CTC emission data are exactly equal to the CTC consumption.

### CS-12.6 CTC Balance of the Chinese CP-70 Process

The following figure shows the typical situation of the CTC balance for Chinese CP-70 production:



## CS-12.7

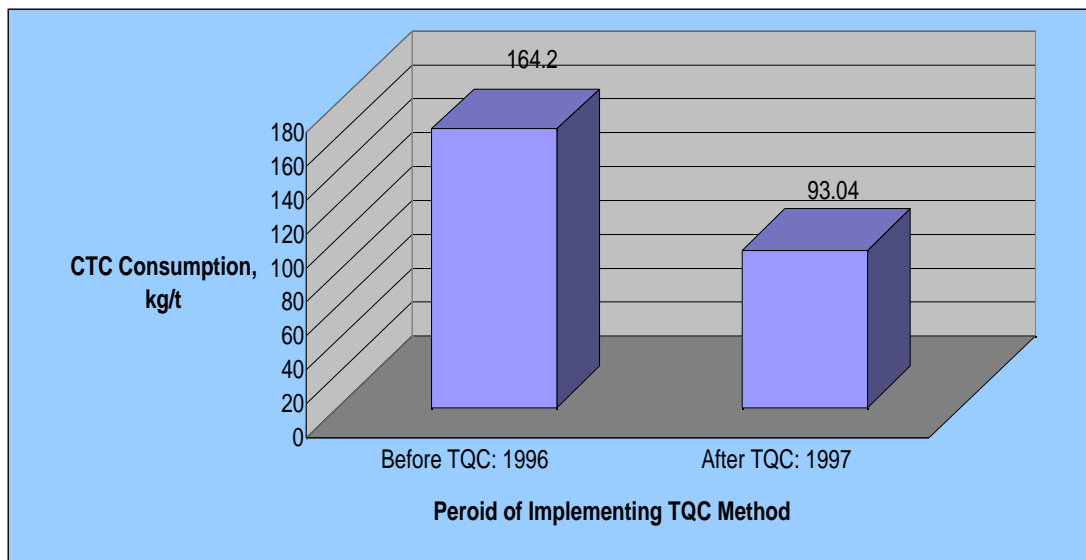
## CTC Emission Control

The following approaches have been practiced to minimize CTC emissions for CP-70 production in China:

- Modifying the Production Facilities
- Enhancing the CTC Recovery System
- Exacting the Operation Conditions
- Implementing Total Quality Control (TQC) method

These approaches had effectively reduced the CTC consumption and emission level. However, since the production scale of CP-70 facilities in China is relative small and runs in simple batch processes, it is difficult to further significantly reduce CTC emissions to an acceptable level without carrying out major modification of facilities and setting up new equipment for monitoring, controlling and destruction technologies.

The following figure shows a comparison of the CTC emission data for one Chinese CP-70 producer in Liaoning Province before and after implementing TQC method.



## CS-12.8 Alternative and Substitute Technologies

Since 1995, lots of efforts have been taken to phase out CTC process agent for CP-70 productions in China. Developments are generally involved in the following three aspects:

- 1 Searching for non-ODS solvents to replace CTC and developing alternative processes for CP-70 production. The R&D work was done in 1999 at the laboratory level. The result showed that the new process without using CTC is practically reasonable, feasible, and more simple. However, detailed information concerned is not provided in the time available.
- 2 Developing aqueous technology to produce CP-70 without using CTC. In China, the aqueous technology was originated in a pilot scale by Anhui Chem. Eng. Research Institute in 1995. The technology has been transferred to about 10 domestic CP-70 producers but most of them ceased using aqueous process to produce CP-70 for technical reasons. However, one producer in Hubei Province has kept running the process till now after some novel innovation and improvement by themselves. The production line using aqueous technology works well with CP-70 production capacity of 1000 t/a. A comparison of the aqueous technology and CTC solvent technology is listed as below:

Item	CTC Solvent Technology	Aqueous Technology for CP-70
Equipment corrosion	Less	Strong
Reactor requirement	Operating at normal pressure	■ Operating at high pressure ■ Anticorrosion
Product quality	Good (high chlorination degree, white color, high purity)	Not so good (limited chlorination degree, light yellow color)
By-product	concentrated 20-30% hydrochloric acid	large amount of 8~12% dilute hydrochloric acid need to treat
Production cost	Not high	higher than CTC technology
ODS emissions	CTC emission to air, water, and residual in product	No ODS emission

- 3 Developing direct chlorinating technology to produce CP-70 without using either CTC or water as reaction medium for chlorination. In this process, key points are temperature and reaction condition control during chlorination. In China, the technology was developed by a manufacturer in Shangdong Province, and had been industrialized in 1998 with annual outputs of 1000 tons of CP-70. A comparison between the direct chlorinating technology and the CTC solvent technology is tabulated as below:

Item	CTC Solvent Technology	Direct Chlorinating Technology for CP-70
Equipment corrosion	Less	No corrosion
Reactor requirement	Operating at normal pressure	<ul style="list-style-type: none"> <li>■ Specially designed serious towers or batch reactors</li> <li>■ Additives required</li> </ul>
Product quality	Good (high chlorination degree, white color, high purity)	Not so good (limited chlorination degree, low soften temperature, light yellow color)
By-product	concentrated 20-30% hydrochloric acid is obtained	concentrated 30% hydrochloric acid is obtained
Production cost	Normal level	Much lower than CTC technology
ODS emission	CTC emission to air, water, and residual in product	No ODS emission