



Selection and safe use of alternatives to CTC

Oxygen Systems

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The reader is advised to confirm specifications and health hazards prior to purchase or use of any substance profiled. No claim is made here in respect of the suitability of any solvent as substitute for CTC in any application. Suitability of a product for a particular application requires to be verified through trials prior to any larger-scale application with due consideration of health and safety aspects.

Information provided here does not constitute an endorsement or recommendation of any brand or product by GTZ Proklima.

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1. The Phase-out of CTC

1.1 About CTC

Carbon tetrachloride (CTC) is a solvent and cleaning agent used widely across many industry segments. Its high solvency power, low cost and the fact that it is non-flammable made it popular in many cleaning applications.

Although CTC is very popular, it is an ozone depleting substance (ODS) like chlorofluorocarbons (CFCs). It destroys the stratospheric ozone layer which protects life on our planet from harmful ultraviolet-B (UV-B) rays. It increases the incidence of skin cancer, eye cataract, suppresses the human immune system, reduces crop yields and affects aquatic life. Another adverse impact of CTC is its contribution to global warming. The global warming potential (GWP) of CTC is about 1,400 times higher than that of carbon dioxide (CO₂), the main greenhouse gas.

At the workplace CTC is an occupational health hazard. CTC is very toxic and is absorbed by the skin and also in the gastrointestinal and respiratory systems. CTC affects the central nervous system (CNS) severely, causing headache, weakness, drowsiness, nausea and vomiting. Inhalation of high levels can permanently damage the liver and kidneys. The severity of the effects depends on the route and frequency of exposure. CTC is proven to cause cancer in animals and is a suspected human carcinogen.

1.2 The Montreal Protocol

To protect the ozone layer, India, along with more than 190 countries has signed the Montreal Protocol to phase out production and consumption of CTC and other ozone depleting substances. Under this agreement India has committed to phase-out the use of CTC as a solvent completely by 31st December 2009.

As the phase-out is progressing, CTC supplies in the market are dwindling rapidly. Beyond 31st December 2009 CTC will not be

available for solvent uses. Given the reduction of supply, the price of CTC has risen substantially making it costlier today than most of its alternatives.

1.3 Role of GTZ-Proklima

For enterprises there is an urgent need to substitute CTC now. But finding suitable alternatives, especially safer ones, is not an easy task. There is no single alternative which can replace CTC in all its applications and in the absence of sufficient information enterprises may substitute CTC with an even more hazardous substance such as Trichloroethylene or Benzene.

Within the framework of the Multilateral Fund of the Montreal Protocol, the Governments of Germany and France have mandated GTZ-Proklima to provide technical assistance to CTC consuming industries in the Indian textiles and metal cleaning sectors. In addition World Bank, UNIDO and UNDP (on behalf of the Government of Japan) are assisting the country in specific industry sectors with large usage of CTC. These activities are coordinated under the National CTC Phase-out Plan by the World Bank as the lead implementing agency and the Ozone Cell of the Ministry of Environment and Forests, Government of India.

GTZ-Proklima offers technical assistance to industries using up to 10 metric tons or 6,250 litres of CTC per year. In close interaction with affected industries, GTZ-Proklima aims to provide competent guidance in identifying CTC substitutes by addressing environmental, health and safety concerns without compromising on quality and cost effectiveness.

GTZ-Proklima maintains strict independence from any branded or proprietary product.

2. CTC in Oxygen Systems

Oxygen is not flammable by itself but supports combustion. Hydrocarbons trapped in an oxygen system create the fuel that can cause an accidental fire or explosion. The higher the oxygen content and/or pressure in a system, the more vigorous the combustion and it can build up to explosive levels.

In many of oxygen manufacturing industries CTC is being used for cleaning of valves commonly known as nozzles, cylinders, compressor casings and heat exchangers.

The most common contaminants encountered by the Oxygen service industries are:

- Machining oils (including residual oil film)
- Hydrocarbon-based grease and lubricants (including compressor oil)
- Some soaps, detergents, solvents and cleaning solutions, especially those that contain organic compounds
- Human skin oil and body fluids
- Insects and insect body parts



Picture 1: Oil and grease contaminants

- Paint, wax, and marking crayons
- Carbon dust from filtration systems
- Airborne soot and dust
- Pipe thread sealants
- Lint from cloths used in cleaning
- Any other material containing organic compounds and hydrocarbon

2.1 Cleaning options in Oxygen Systems

There are several options for cleaning of components, vessels and pipe works used in oxygen systems and services. Solvent cleaning is mostly used by the industry. Detergent cleaning is also equally effective while acid cleaning is used mainly for removal of rust. There are also alternative processes such as ultrasonic cleaning.

Solvent cleaning

Solvent cleaning is preferred when aqueous cleaning is not an option due to the design of the component being cleaned. In some applications it is used out of necessity but in others merely out of convenience. In certain situations where other cleaning methods cannot be applied, solvent cleaning may be considered.

Solvents can be applied in various processes of cleaning. Three such processes are described below:

(i) Wiping

This is the predominant method used for components and equipment cleaning as and when required. It is suitable for most of the external cleaning operations but not for components with intricate shapes. Care should be taken to safely dispose off solvent soaked rags.



Picture 2: Wiping of equipment

(ii) Flushing or spraying

This type of cleaning is accomplished by solvent application with minimal physical action by the worker. Flushing utilizes a



Picture 3: **Spray cleaning**

continuous stream of solvent whereas spraying employs droplets of solvents on the objects. Spraying is restricted to the outer surface only. Both these methods rely on the specific property of solvents to dissolve the soil.

(iii) Immersion cleaning

Immersion cleaning is employed when a large quantity of components needs to be cleaned and where precision cleaning is not critical. It is usually used in conjunction with wiping, flushing or ultrasonic cleaning.



Picture 4: **Immersion cleaning**

Acid cleaning

Acid cleaning is normally carried out with an aqueous solution of acids at ambient temperature for the removal of oxides, rust, light soils, fluxes and certain protective coatings. Phosphoric acid cleaning solution can be used for metals. It involves spraying of cleaning liquid or immersion of components to be cleaned in a tank containing acid. The acid concentrations should be appropriate to the materials/components to be cleaned and the required surface conditions.

After the completion of the acid cleaning operation, all residual cleaning fluid must be completely drained off from the component by flushing with clean oil-free water and purged.

Acid cleaning is not generally used for the removal of oils and grease.

These contaminants, if present, should be removed by a solvent or by an alkaline solution prior to acid pickling.

Detergent cleaning

The degreasing strength of detergents is as good as that of the solvents. This method relates to the cleaning of plant components, vessels, piping systems etc., either externally or internally

The cleaning is carried out in water solutions containing detergents. These detergents should have properties like dirt solvency, dispersion, water softening, corrosion inhibition and wetting. It is normally performed in an alkaline environment; the higher the pH value, the better the degreasing efficiency. It is recommended that the detergent manufacturer be consulted to establish the proper use conditions, including any material compatibility issues. The strength of the detergent can be monitored either by a pH measurement or a simple acid/base titration kit.

Small parts should be cleaned in an ultra sonic cleaner whenever possible for 20-30 minutes using hot water (at approximately 120° to 140° F) and an approved caustic detergent. Parts should then be rinsed with hot water at approximately 120° to 140° F. Final rinse should be done with de-ionized water. Larger parts, piping, tubing and large fittings should be pressure washed using hot water at approximately 120° to 140° F and an approved caustic detergent. Parts may also be dried using heat or filtered Nitrogen as needed.



Picture 5: Cleaning of cylinders with aqueous solution and drying with warm nitrogen

It should be ensured prior to the cleaning activity that detergent chemicals used are compatible with the non-metallic parts. Though aqueous systems have fewer problems with worker safety compared to most other solvents, the waste from water based detergent cleaning needs proper disposal in order to prevent environmental damage.

3. Selecting alternatives to CTC

3.1 Selection criteria

No alternative is ideal in all regards; each one has certain advantages and disadvantages. In order to address environmental, health and safety concerns without compromising on quality and cost effectiveness, any substitute for CTC should meet the following criteria:

- Non-ozone-depleting substance (non-ODS)
- Good cleaning efficacy
- Low toxicity
- High dielectric strength
- Compatible with insulation material (should not damage)
- Not leaving any residue
- Equal or lower cost compared to CTC
- Locally available
- Non-carcinogenic

3.2 Viable alternatives

Based on the selection criteria presented above, GTZ-Proklima identified a range of alternatives for varied applications within the oxygen sector.

The most relevant properties of available generic solvents for selecting appropriate alternatives to CTC are:

Flash point

The flash point (in °C) is the lowest temperature at which a flammable solvent can form an ignitable mixture with air. As a rule of thumb, the higher the flash point temperature the lower is the fire hazard risk. Non-flammable solvents do not have a flash point.

Boiling point

The boiling point (in °C) is the temperature at which the liquid will

start boiling. A lower boiling point means higher losses of solvent into the atmosphere but higher cleaning efficiency.

Vapour pressure

Vapour pressure (in mm Hg) is an indicator for the rate of evaporation under atmospheric conditions. The higher the value the faster the solvent evaporates. If the substance is stored in an open container it can also be considered as a measure of evaporation losses.

Dipole Moment

Dipole moment (in Debye) is a measure of the polarity of a solvent. It determines what type of compounds it can dissolve and with what liquids it is miscible. Typically, polar solvents dissolve polar compounds best and non-polar solvents dissolve non-polar compounds best. Similarly, polar contaminants dissolve best in polar solvents, while non-polar compounds, like oils or waxes, dissolve best in non-polar solvents.

Hansen Solubility Parameter

The Hansen solubility parameter is a numerical value that indicates the relative solvency behaviour of a specific solvent. It is available for every solvent and any liquid or polymer. This number is calculated from the dispersion, polarity and hydrogen bonding properties of the solvent. It is indicative of the forces that hold together the molecules.

Table 1 below presents a comprehensive list of possible alternatives to CTC for varied applications in oxygen service.

Table 1
Properties of selected solvents

Parameters	Flash point °C	Boiling point °C	Vapour pressure mmHg	Hansen solubility parameter
Methylene dichloride	None	40	350	20.3
Perchloro ethylene	None	121	14	20.3
Acetone	- 20	56	180	20.0
Isopropyl alcohol	12	82	33	23.5

Trichloroethylene (TCE) is another cleaning agent offering good efficacy that is used by some industries. Its use however is strongly discouraged because of the inherent cancer risk.

3.3 Selection at a glance

A concise compilation of application specific solvent and safety recommendations is placed below for a quick reference. The reader should however factor in technical specificities involved at their work place/application before making use of this information.

Table 2
Methods of cleaning

Cleaning application	Method of cleaning	Possible cleaning agent	Main hazards	Control measures	Protection
Gas Cylinder	Wiping	PCE, MDC	Very toxic on inhalation; toxic on skin contact	Local exhaust ventilation Use of optimal quantity only	Gloves, Goggles
	Pressure wash	Detergent	Alkaline mist exposure	Waste water disposal	Gloves Face shield Boots
Valves or Nozzles	Immersion & spraying	PCE, MDC	Very toxic on inhalation; toxic on skin contact	Local exhaust ventilation	Gloves Face shield Goggles
	Ultrasonic	Detergent/PCE	Vapour exposure ventilation	Local exhaust	Gloves Goggles
Pipes and tubes	Pressure wash	Detergent	Alkaline mist exposure	Waste water disposal	Gloves Boots Goggles
	Immersion	PCE, MDC	Very toxic on inhalation; toxic on skin contact	Local exhaust ventilation	Gloves Goggles

4. Health and safety


4.1 Hazard potential of alternatives

Any solvent is a potential hazard for health and safety. Most solvents are toxic but the degree of hazard varies from one substance to another. In the context of oxygen system cleaning particularly the risk of flammability needs to be considered.

At the workplace the intake of chemicals occurs mainly through inhalation and skin contact. While these hazards affect directly and immediately at the workplace the environmental hazards like contamination of air and ground water are rather indirect effects not only at the workplace but also on a global scale. Thus this guide rates the hazard of each solvent on these four factors.

Each hazard has been further classified into six grades and each grade is characterized through a corresponding color shade. The least risk is marked in green, followed by shades of yellow and orange. Red represents the most severe risk.

Table 3
Hazard rating

	Risk	Inhalation	Skin	Environment	Flammability	
E	High	Severely toxic	Severely toxic	Very hazardous	Extremely flammable	
D		Very toxic	Very toxic		Highly flammable	
C		Toxic	Toxic	Hazardous	Flammable	
B		Harmful	Harmful		Combustible	
A		Irritant	Irritant		Possibly combustible	
-		Low	None	None	Not classified	Non-flammable

For details on the hazard classification methodology please visit www.ctc-phaseout.org

Table 4 shows the hazard ratings of the alternatives discussed in the previous section.

For comparison the risk levels of Water, CTC and TCE are also shown.

Table 4
Hazard ratings of specific alternatives to CTC

Viable alternatives	Hazard rating			
	Inhalation	Skin	Environment	Flammability
Water				
Isopropyl Alcohol (IPA)	A			D
Acetone	A	A		D
Methylene Dichloride (MDC)	D	C		
Perchloroethylene (PCE)	D	C	E	
Carbon Tetrachloride (CTC)	D	C	E	
Trichloroethylene (TCE)	E	E	C	

Solvents like Perchloroethylene that are rated as ‘Very hazardous’ to the environment are toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment hence care must be taken for safe disposal of used solvents and solvent soaked waste.

The selection of a solvent should be made so as to minimize the hazard. As is apparent from the ratings above, most of the substances are classified as

‘Very toxic’ for ‘Inhalation’ and ‘Toxic’ under ‘Skin’. Safe use can therefore not be ensured by a prudent selection alone. The following section introduces measures to safeguard health and safety while using hazardous solvents.

4.2 Risk control measures

This guide recommends the following general principles of prevention:

- (i) Avoid the need for solvent use;
- (ii) Substitute with less hazardous or non hazardous substances;
- (iii) Reduce risks at source using technically up to date methods;
- (iv) Use measures that give collective protection before considering individual protection;



- (v) Ensure appropriate instruction and training of all staff concerned;
- (vi) Provide adequate personal protective equipment (PPE) if a significant risk still remains;

4.3 Good servicing practices

- **Prudent substance selection:** Select the safest possible substance (see Table 3 'Hazard ratings of specific alternatives to CTC').
- **Consult an MSDS:** Demand a material safety data sheet (MSDS) of the solvent from the retailer. Study specifically the sections on health risks, fire risks and first aid.
- **Limit the quantity:** Often the required quantity for cleaning is overestimated. Therefore assess the required quantity carefully and restrict the use accordingly. It is believed that solvent exposure can be reduced significantly by this measure alone.
- **Purge with inert gases:** Purging with air should be completely avoided as a mix of the solvent with contaminants could prove to be explosive in some cases. Therefore always use only inert gases like Nitrogen.
- All electrical equipment should be properly grounded and de-energised before carrying out cleaning operation. If online operation is inevitable due to equipment design or operational limitations use only insulated hand tools and solvent with low dielectric constant.
- **Ensure good ventilation:** Many solvents are toxic but the hazard risk depends on the actual level of exposure. While performing the cleaning operation the solvent evaporates into the surroundings. If the cleaning personnel experiences drowsiness or nausea, it is an indication that concentration of solvent vapours is above tolerable limits in the surroundings and there is a need for better ventilation of the cleaning area.
 - Shift cleaning operations to an area with high ceilings and cross-ventilation.
 - If there is a perceivable flow of air, clean downwind so that the air first reaches the cleaning personnel and then the part being cleaned.

Good and correct practice



Picture 6: Downwind working position – reduces inhalation exposure levels

Wrong practice

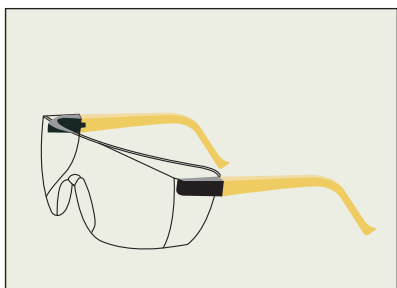


Picture 7: Upwind working position – increases inhalation exposure levels

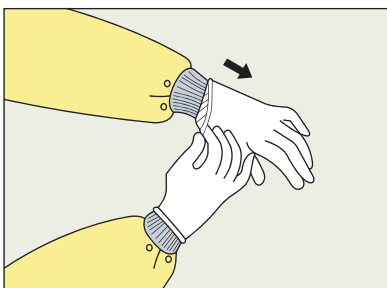
- If none of these prove sufficient, consider the installation of local exhaust ventilation (LEV). LEVs capture contaminants before they disperse into the air of the workplace. Such systems consist of a hood, a duct and an air cleaner. LEVs cannot be bought off the shelf and they have to be sized by experts to meet the specific requirements.



Picture 8: Local exhaust ventilation



Picture 9: **Safety goggles**



Picture 10: **Protective gloves**

- **Wear goggles:** Certain cleaning operations may result in splashing of solvents therefore goggles are required for eye protection.
- **Wear gloves:** Skin contact with the solvent during cleaning occurs regularly. All solvents remove the fat content of the skin. Gloves can protect the skin adequately.

Care should be taken in selecting gloves and other protective clothing as different solvents affect the materials from which they are made in different ways. Some solvents may, for example, pass through some glove materials in a very short time.



Picture 11: **Effect of solvent on skin**

Table 5
Selection of gloves

Chemical handled	Glove Material
Acetone	Butyl, Nitrile, Neoprene, Laminate film
Hexane or White petrol	Nitrile, Neoprene, Viton
Isopropyl alcohol	Nitrile, Neoprene, Butyl, Viton
Methylene dichloride*	Nitrile, for light exposures (splashes), Viton, PVA

*will damage all natural and synthetic glove materials

- **Use respirators:** In any enclosed or confined space such as the inside of a large motor/generator, even a non-toxic solvent may have anaesthetic or asphyxiating effects if it is used in sufficient quantities. Breathing apparatus or respirator may be required to prevent serious injury or even death.
- **Training:** Last but not least, training and instructions are the most important part of personal protection. Ensure that the workers involved in cleaning operations are aware of the hazards associated with the materials used in cleaning and are trained in implementing the preventive measures.

4.4 Fire safety

All organic solvents are prone to catch fire under the right circumstances as indicated by the properties of flash point, etc. (The flash point of a flammable liquid is the lowest temperature at which it can form an ignitable mixture in air). It becomes necessary to prevent conditions that may lead to such incidents.

Any solvent listed with a flash point should only be used in equipment properly designed for low flashpoint or combustible solvents.

Solvents such as IPA and Acetone are good solvents relative to their physical properties and low toxicity. They are easy to dispose off and are inexpensive when compared with other alternatives. However, they are flammable and therefore for using such solvents the surrounding area should also be designed for safety.

The area where the solvents are being used should be well ventilated and if required forced ventilation should be provided. The ventilation could be by exhaust fans or hoods with exhaust facility specifically where the degreasing activity is carried out.

All electrical switches, light fittings and motors should be flame proof and properly earthed. All electrical wire connections should be through gland or tight fittings.

Adequate fire fighting equipments should always be provided.

5. Glossary

This glossary defines terms you are likely to encounter in material safety data sheets (MSDS)

Acute effect: The effect caused by a single short term exposure to a high amount of concentration of a substance.

Aerosols: Liquid droplets or solid particles dispersed in air that are of fine enough particle size (0.01 to 100 microns) to remain dispersed for a period of time.

Alkali: Any of a class of substances that liberates hydroxide ions in and have a pH of more than 7. Strong alkalis in solution are corrosive to the skin and mucous membranes. They are also called bases and may cause severe burns.

Anhydrous: Does not contain water (e.g. anhydrous lime)

Asphyxiation: A condition whereby oxygen in the air is replaced by an inert gas such as nitrogen, carbon dioxide, ethane, hydrogen or helium to a level where it cannot sustain life. Normal air contains 21 percent of oxygen. If this concentration falls below about 17 percent, the human body tissue will be deprived of supply of oxygen, causing dizziness, nausea and loss of coordination. This type of situation may occur in confined work places.

Auto-ignition temperature: The minimum temperature at which a material ignites without application of a flame.

Boiling point: The temperature at which liquid changes to a vapour state at a given pressure (usually 760 mm of Hg or one atmosphere).

Caustic: The ability of an alkali to cause burns.

Chronic (health) effect: An adverse effect on a human body with symptoms developing slowly over a long period of time.

Chronic toxicity: A chronic effect resulting from repeated doses of or exposure to a substance over a relatively prolonged period of time.

Confined space: Any area that has limited openings for entry or exit that would make escape difficult in an emergency, has a lack of ventilation, contains known and potential hazard, and is not normally intended or designed for continuous human occupancy (e.g. a storage tank, manhole of collection conveyances systems in effluent treatment plants).

Dielectric constant: The dielectric constant of a solvent is a relative measure of its polarity.

Explosion proof-equipment: Apparatus or device enclosed in a case capable of withstanding an explosion of specified gas or vapour and preventing the ignition of specified gas or vapour surrounding the enclosure by sparks, flash or explosion and operating at an external temperature so that surrounding flammable atmosphere will not be ignited.

Flammable: A flammable liquid is defined as a liquid with a flash point between 21 and 55 degrees Celsius. It may catch fire on contact with a source of ignition.

Flammable/explosion limits: Flammable/explosion limits produce a minimum and a maximum concentration of gases/vapours/fumes in air that will support combustion. The lowest concentration is known as the lower flammable/explosion limit (LEL), the highest concentration is known as upper flammable/explosion limit (UFL).

Flash point: Minimum temperature at which, under specific conditions, a liquid gives off sufficient flammable gas/vapour to produce a flash on contact with a source of ignition.

General exhaust/ventilation: A system for exhausting or replacing air containing contaminants from a general work area.

Hansen Solubility Parameter: A numerical value that indicates the relative solvency behaviour of a specific solvent. This number is calculated (based on volume percentage) from the properties dispersion, polarity and hydrogen bonding of the solvent. Hansen solubility parameter is available for every solvent, any liquid or polymer.

Hazard: A potential to cause danger to life, health, property or the environment.

IDLH – Immediate danger to life and health: The maximum concentration from which one could escape within 30 minutes without any escape-impairing symptoms or irreversible health effects. Usually used to describe a condition where self contained breathing apparatus (SCBA) must be used

Incompatible: Condition of materials that could cause dangerous reactions from direct contact with one another. Particularly relevant when storing different substances in the same place.

Local exhaust: A system or device for capturing and exhausting contaminants from the air at the point where the contaminants are produced. (e.g. dust in shaving and buffing)

MSDS (Material safety data sheet): Consolidated information on specific identity of hazardous chemical substances, also including information on health effects, first medical aid, chemical and physical properties, emergency measures etc.

OEL, Occupational exposure limit: An exposure level established by a regulatory authority (e.g. OSHA, NIOSH).

Poisoning: Normally the human body is able to cope with a variety of substances within certain limits. Poisoning occurs when these limits are exceeded and the body is unable to deal with a substance (by digestion, absorption or excretion)

Risk: The measured probability of an event to cause danger to life, health, property or the environment.

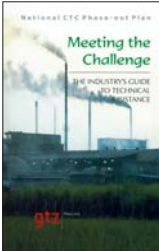
TLV, Threshold limit value: A concentration threshold in the atmosphere which is set specially for each pollutant. It refers to the limit accepted in the atmosphere of working area.

TLV-STEL, TLV short term exposure limit: Concentration threshold in an atmosphere contaminated with a specific type of pollutant for a 15 minute exposure (if not otherwise specified)

TLV-TWA, TLV time weighted average: Concentration threshold in an atmosphere contaminated with a specific type of pollutant, usually for a continuous eight hour exposure

Toxicity: The inherent potential of a chemical substance to cause poisoning.

6. Other project publications



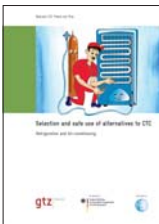
Meeting the Challenge provides essential information on CTC Phase-out Plan and industry sectors most affected by it. The publication elaborates on ‘applications’ across sectors affected by the phase-out of CTC and also GTZ-Proklima’s mandate, approach and technical assistance to affected industries.

Languages: English, Hindi, Gujarati, Kannada and Malayalam



Solvent Alternatives is a compilation of technical information on a variety of CTC alternatives that are in use in industry – across different sectors and applications. The advisory elaborates on the use and potential risks involved therein, with regard to profiled substances

Languages: English



Industry specific guidelines for the substitution of CTC in specific sectors are available. These guidelines inform of alternatives to CTC and their safe use.

Languages: English

All publications are available for free download at our website www.ctc-phaseout.org



Ozone Cell, Ministry of Environment and Forests, Government of India, is the central agency coordinating the phase-out of CTC. The cell has established the regulatory framework and national phase-out plan. It ensures that domestic CTC production and import progressively decrease in compliance with national targets.



The Deutsche Gesellschaft für Technische Zusammenarbeit (GTZ) GmbH is an international cooperation enterprise for sustainable development with worldwide operations. GTZ-Proklima is a sectoral program which implements bilateral and multilateral projects in order to assist partner countries in fulfilling their obligations under the Montreal Protocol. With more than 130 projects, GTZ-Proklima is the largest bilateral partner of the Multilateral Fund of the Montreal Protocol. GTZ-Proklima, on behalf of the Government of Germany and under the overall coordination of Ozone Cell, Ministry of Environment and Forests, provides support to Indian industries for smooth transition to a CTC-free world. In the current project GTZ-Proklima holds an additional mandate on behalf of the Government of France which provides financial support through its French Global Environment Facility (FFEM). GTZ-Proklima does not promote any particular product or brand but provides technical assistance to CTC consuming industries.



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