National CTC Phase-out Plan

Selection and safe use of alternatives to CTC

Foundry

gtz PROKLIMA

On behalf of

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On behalf of

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GTZ Proklima, A-33 Gulmohar Park,
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Disclaimer

Though all care has been taken while researching and compiling the contents provided in this booklet, GTZ Proklima accepts no liability for its correctness.

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 (CO_2), the primary 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 Foundry Applications

In foundries solvents like CTC are being used for the following applications.

- Residual particulate analysis (Millipore test)
- Precision cleaning
- Electrical contact cleaning.
- Sampling of raw material

2.1 Residual Particulate Analysis

In precision machined component manufacturing and foundries cleanliness specifications are often determined by the original equipment manufacturer (OEM) in order to avoid costly rework due to improperly cleaned parts.

Contaminants present on the components/castings may affect the performance of the system in which they are employed, as in the cases of hydraulic systems, aeronautics, food processing equipment etc. Cleanliness verification is performed on random samples from every batch. This monitoring is performed through residual particulate analysis, commonly referred to as the Millipore test.

Picture 1: **Equipment for particulate analysis**

Contaminants are removed from the sample part by rinsing, spraying and/or flushing with a solvent (e.g. CTC). The solvent with sediments are collected and this solution is then filtered through a membrane filter which is then analyzed and compared to specific acceptance criteria.

2.2 Precision Cleaning

Picture 2: **High precision component**

Precision cleaning means removal of particulate and/or other inorganic and organic residues from a surface and verifying its cleanliness through analytical methods. It is used to attain a very high degree of cleanliness. For example in foundries critical components are thoroughly cleaned before taking the final measurements, instruments and gauges are subjected to precision cleaning before calibration and also for cleaning of sample components before metallurgical analysis.

High purity solvents and solutions are used with various types of cleaning processes such as ultrasonic and jet spray to achieve the desired level of cleanliness. It should be noted that these cleanliness levels cannot be obtained without a separate clean-room.

2.3 Electrical Contact Cleaning

Picture 3: **Electrical contacts**

Electrical contacts develop carbon deposits over time due to the high voltage sparking at the point of contact and disconnection. These deposits reduce conductivity and result in loss of power and therefore contact cleaning is an integral part of preventive maintenance in every industry. In foundries it is very critical due to higher operating temperatures, dynamic load conditions and exposure to dust, soot, scales, grease etc.

2.4 Sampling of Raw Material

Scrap metal forms a major source of raw materials to foundries. Scrap collected from different sources will contain a lot of contaminants. To decide the actual weight of the metallic part in the scrap, a sample quantity is rinsed with solvents like CTC and then dried through heating. The difference in weight of the sample before and after rinsing determines the quantum of wastage. Since the material is dried directly on a source of heat it is important to select a solvent that is non flammable.

3 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)
- Non-carcinogenic
- Good cleaning efficacy
- Low toxicity
- Non-flammable or low flammability
- Compatible with substrate material (e.g. non-corrosive, non- abrasive)
- Not leaving any residue
- Equal or lower cost compared to CTC
- Locally available
- Can be disposed off easily

3.2 Viable Alternatives

Based on the selection criteria presented above, GTZ-Proklima identified a range of alternatives for varied applications in foundries. Their suitability has been confirmed through industrial trials. Though Trichloroethylene (TCE) has good cleaning properties and is used by many enterprises, its usage is strongly discouraged because of its inherent cancer risk.

For residual particulate analysis / Millipore test, cleaning efficacy, rate of evaporation and ease of filtration through the filter medium are factors to be considered. When the solvent spraying is used as the method for removal of contamination for testing, a solvent like

Methylene dichloride is not suitable as it has high rate of evaporation and may not be able to collect sufficient quantity of solution for analysis.

In electrical contact cleaning, the main contaminants are carbon dust from arcing, metallic oxides, insects and insect body parts and airborne soot and dust. Carbon deposits can be of many kinds - hard coke type, powdery, or sticky bituminous deposits. Selection must be based on the type of insulation material so that it is not affected by the solvent.

In precision cleaning the contaminants are grease, mineral and cutting oils, etc. The suitable alternative has to be selected based on the type of soil that needs to be removed.

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

- Flash Point
- Boiling Point
- Vapour Pressure
- Dipole Moment
- Hansen Solubility Parameter
- Dielectric Strength

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.

Dielectric Constant

The dielectric constant of a solvent is a relative measure of its polarity. The lower the dielectric constant of a solvent the better it is for use as electrical contact cleaner.

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. It should be noted that solvents with Hansen numbers below 17.5 are more effective in cleaning mineral oils, lubricants and greases.

Table 1:
Sector specific viable alternative solvents

Alternatives to CTC			
Millipore test	Electrical contact cleaning	Precision cleaning	Sampling of raw material
Toluene	Methylene dichloride*	Methylene dichloride	Methylene dichloride
Perchloro ethylene	Perchloro ethylene	Perchloro ethylene	Perchloro ethylene
White Petrol	Acetone	Trans-1, 2-Dichloroethylene (trans)	–
Isopropyl alcohol (IPA)	Isopropyl alcohol	–	–
Hexane	–	–	–

*Only MDC is suggested for online cleaning due to its non-flammability and higher rate of evaporation.

Table 2:
Properties of selected solvents

Parameters	Flash point-°C	Boiling point-°C	Vapour pressure-mmHg	Dielectric Constant	Hansen solubility parameter
Acetone	– 20	56	180	20.56	20.0
Isopropyl alcohol	12	82	33	19.92	23.5
Methylene dichloride	None	40	350	8.93	20.3
Perchloro ethylene	None	121	14	2.28	20.3
Toluene	4-7	111	21	_	18.2
Trans -1, 2 Dichloro ethylene	13	83.9	_	10.6	20.8
White Petrol	-18	50-120	180	_	7.3
CTC*	None	77	91	0	17.8

*For comparison only (CTC will no longer be available from 1 Jan 2010)

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. The hazard of electric shock, when coupled with the effects of solvents could be fatal to the personnel.

At the workplace the intake of chemicals occurs mainly through inhalation and skin contact. Another major risk in the electrical systems is flammability. While these hazards affect directly and immediately 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 colour 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

Group	Risk	Inhalation	Skin	Environment	Flammability
E	high	Severely Toxic	Severely Toxic	Very hazardous	Extremly flammable
D		Very toxic	Very toxic		Highly flammable
C		Toxic	Toxic		Flammable
B		Harmful	Harmful	Hazardous	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:

Substance	Inhalation	Skin	Enviro nment	Flamm ability
Acetone	A	A	-	D
Isopropyl alcohol	A	-	-	D
Methylene Chloride / dichloromethane	D	C	-	-
Perchloro ethylene	D	C	E	-
Toluene	D	C		D
Trans -1, 2 Dichloro ethylene	B		C	D
White petrol	D	C*	E*	D*

* Based on limited current information. To be re-evaluated

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 wastes.

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).

Picture 5: **Effect of solvent on skin**

4.3 Checklist

- When deciding on the use of any solvent the following steps should be followed:
- **Prudent substance selection:** Select the safest possible substance (see table 14 'Hazard Ratings of Specific Solvent Alternatives').
- **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. 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.

- **Ensure good ventilation:** 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. The possible options include:
  - 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.

Picture 6: **Local Exhaust Ventilation**

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.

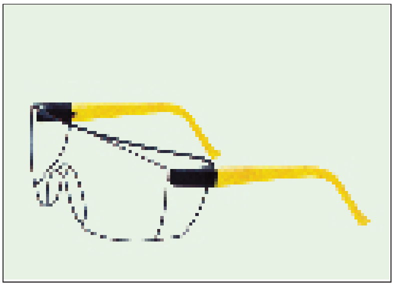
By providing proper ventilation the vapour level can be reduced significantly.

4.4 Personal Protection Equipment

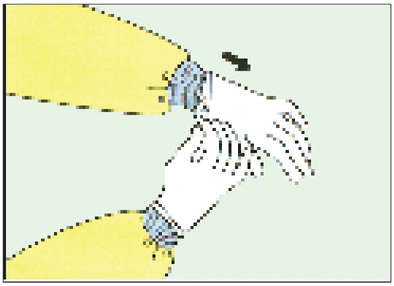
Different types of personal protective equipment exist.

- **Masks:** Masks can help to filter the vapours to a limited extent.
- **Goggles:** Goggles protect the eyes against inadvertent splashes of solvents.
- **Face Shields:** Protect the whole face against inadvertent splashes.
- **Gloves:** Most solvents remove the fat content of the skin. Gloves can protect the skin adequately. The next section provides more details on proper selection of gloves.

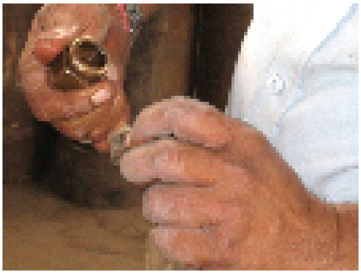
- **Respirators:** In any enclosed or confined space such as the inside of a tank, even a non-toxic solvent may have anesthetic or asphyxiating effects if it is used in large quantities. Breathing apparatus or respirators with a reservoir of oxygen may be required to prevent serious injury or even death.



Picture 7: **Safety goggles**



Picture 8: **Protective gloves**



Picture 9: **Effect of solvent on skin**

4.5 Selection Of Gloves

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. Table 5 guides on the selection of appropriate gloves:

Table 5:
Selection of appropriate gloves

Solvent	Glove Material
Acetone	Butyl, Nitrile, Neoprene, Laminate film
Hexane	Nitrile, Neoprene, Viton
Isopropanol	Nitrile, Neoprene, Butyl, Viton
Methylene dichloride*	Nitrile, for light exposures (splashes), Viton, PVA
Toluene*	Viton, PVA

*will damage all natural and synthetic glove materials

5. Glossary

This glossary defines terms likely to be encountered 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 or 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).

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 with in 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.

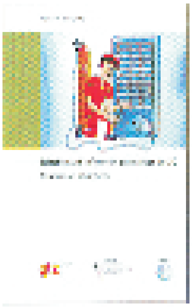
6. Other project publications

Meeting the Challenge provides essential information on the National 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.

Language : 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.

Language: 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.

On behalf of
Federal Ministry
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National CTC Phase-out Plan

Project Office:
A-33 Gulmohar Park,
New Delhi – 110 049, INDIA
Phone : 011–2661 1021
Email : contact@ctc-phaseout.org
Web : www.ctc-phaseout.org

Deutsche Gesellschaft für Technische
Zusammenarbeit (GTZ) GmbH

Dag-Hammarskjöld-Weg 1-5
65760
Eschborn/Deutschland
T +49 61 96 79 - 0
F +49 61 96 79 - 11 15
E info@gtz.de
I www.gtz.de