ECSA – EUROPEAN CHLORINATED SOLVENT ASSOCIATION

Trichloroethylene
Legislation, Markets and Uses

Mastering Challenges and Increase Sustainability

Fact Sheet

Trichloroethylene

IDENTIFICATION

Names
IUPAC: Trichloroethylene
Other: 1,1,2-Trichloroethene, 1,1-Dichloro-2-Chloroethylene, 1-Chloro-2,2-Dichloroethylene, Acetylene Trichloride,

Abbreviations
TRI, TCE, Trike

Trade names
NEU-TRI, HI-TRI, Triklone, Triclene, Trimar, Trilene

Identifiers
CAS number 79-01-6
EINECS number 201-167-4

PROPERTIES

Boiling Point:	87 °C
Vap. Pressure	5.78 kPa (20 °C)
Density(20 °C):	1.465 g/cm^3
Vapor density:	4.45 g/l
Flash Point:	no (DIN51755)
Evap. Energy:	31.5 kJ/mol
Solubility	
TRI in water:	0.1 wt% (20 °C)
Surface Tension:	26.4x10^{-3} N/m
Biodegradation:	not biodegrad.
Degrad. in Air:	6 - 8 days

General

Trichloroethylene (TRI) is a chlorinated hydrocarbon used a) as feed-stock to produce fluorinated hydrocarbons and fluorinated polymers and b) as an industrial solvent in various applications. It is a clear non-flammable liquid with a low boiling point ,has good chemical stability, is non-miscible with water and has a low evaporation energy (about 9 times lower than water). This makes TRI well-suited for recycling and constant re-use in closed loop systems at high quality levels. TRI provides excellent solubility for oils, greases and resins combined with the non flammability, easy drying and low surface tension which have made TRI a widely used solvent for a large range of substances and applications.

Production

Strong decline & consolidation

TRI is primarily manufactured using oxichlorination or non-catalytic chlorination processes starting from ethylene dichloride (EDC) or other chlorinated C2-hydrocarbons. An alternative process, in use in Europe since 1986, starts from Perchloroethylene uses catalytic hydrogenation.

Due to industry rationalization and consolidation over the last few decades,he number of European TRI producers declined from > 10 in 1984 to 2 in 2009. The majority of produced TRI goes into intermediate applications today (ca. 80%)

The use of TRI as solvent dropped by 85% from 1984 until 2006, with a further estimated decline of 60% from 2006 until 2010.

184000 mt of TRI were used as solvent in 1984. The consumption dropped to 25000 mt in 2006. This continous decline is related to: stricter regulation, the reclassification of TRI in 2002, the use in closed systems and further industry risk reduction measures such as voluntary industry commitment and closed loop systems (see below).

Regulations

Well established frame to drive closed systems

Classification & Labeling: Since the 28th Adaptation to Technical Progress (EC/2001/59) the TRI classification reads as:

Toxic
Carc. Cat. 2; R45,
Muta. Cat. 3;
R68, R67,
Xi; R36/38, R52/53

Workplace Regulations/ OELs: The EU Scientific Committee for Occupational Exposure Limits (SCOEL) recently proposed a new Occupational Exposure Limit (OEL) (8-hour TWA) for TRI of 10 ppm with a Short-Term Exposure Limit (15 min) of 30 ppm. SCOEL recognised in it new evaluation of the toxicological database that a threshold exists for the carcinogenicity of trichloroethyelene. Closed surface cleaning equipment is able to meet these values *(Grote,2003)*. A major TRI producer in Europe[1] has introduced an internal exposure limit of 5 ppm which is communicated to end users via the Safety Data Sheets.

Emission Regulations: Since 1986, Germany is regulating the emissions of halogenated solvents in industrial surface cleaning uses (2.BImSchV). This has led to the development of modern sealed surface cleaning equipment with internal solvent recycling reducing the solvent

[1] Dow Europe GmbH and its affiliated companies

consumption by up to 90% (1). Such sealed machines are today Industry Standard in Germany. Since 2007 all installations consuming >1t/yr have to comply EU wide with the European Solvent Emission Directive (SED, 1999/13/EC). This directive is setting emission limits, which for fulfillment request users to apply closed equipment.

Restrictions: Consumer uses are prohibited EUwide, due to TRI classification as a carcinogen. A national ban of the use of TRI as a solvent is active in Sweden restricting its use to those users having been granted a time limited authorization. Contrary to the German approach to force users to apply closed systems but not ban TRI, the Swedish approach failed to reduce consumption and exposure of workers in the same extend as in Germany *(Birkenfeld et al, 2005)*

TRI Charter

closing regulatory gap and re-enforcing closed systems

The Charter has been developed in consultation with the European Commission and European Member States aiming to adequately control the risks related to the use of Trichloroethylene in metal cleaning as identified in the EU Risk Assessment.

Contrary to the German halogenated solvents emission regulation (2.BImSchV), the European Solvent Emission Directive (SED) includes a consumption cut- off limt of 1 t/yr for its validity. This leaves surface cleaning applications with <1 t/yr consumption exempted from the need to convert to closed systems. To close the 1t/yr regulatory gap and as an additional risk management measure, producers of TRI have signed the TRI Charter to implement the **Industry Self Comittment** to only deliver TRI for surface cleaning after December 31, 2010 into closed equipment[2]. TRI producers are strongly comitted to this TRI Charter as an essential contribution to increase the safe use of TRI and its sustainability: **After December 31, 2010 customers using open cleaning machines for metal cleaning will no longer be supplied with trichloroethylene by the European manufacturers of Trichloroethylene.**

Risk Mgmt

voluntary measures

The EU paper on "Communication from the Commission on the results of the risk evaluation and the risk reduction strategies for the substances: trichloroethylene, (2008/C 157/01)" generally states "The legislation for workers' protection currently in force at Community level is generally considered to give an adequate framework to limit the risks of the substance to the extent needed."

Nevertheless Industry has implemented additional voluntary risk management measures:

- Delivery, transport, handling and storage of TRI via a closed loop system by the use of closed loop safety containers (e.g. SAFE-TAINER™) with vapour return line. A major producer has ceased supply of TRI in drums as of April 2009 in Western Europe. This approach is being evaluated for all of Europe.
- Solvent Services including monitoring and re-stabilization to enhance the lifetime of the solvent and reduce solvent consumption. These services meet the demand of modern vapour degreasing machines which include internal solvent recycling through distillation.
- Waste-take back in closed loop safety containers.
- Industry provided training and consultancy

If TRI is handled correctly using available tools, there should be little risk of over-exposure. Standard Personal protection Equipment (PPE) for handling chemicals is recommended, such as safety glasses or goggles, depending on the task at hand, and appropriate chemical resistant gloves. If there is a potential to exceed existing exposure limits, respiratory protective equipment is recommended; Depending on the operation, this may include positive-pressure supplied-air.

Market Trends

Increasing intermediate & declining solvent demand

There are two major market segments for TRI :

A) the use as an INTERMEDIATE, mainly as feedstock for the production of fluorinated hydrocarbons and fluorinated polymers.

B) the use as a SOLVENT in various industrial applications.

Consumer uses of TRI are prohibited in the EU by the Market and Use Directive, 76/769/EC.

Consumption of TRI as an INTERMEDIATE is mainly driven by the market needs for various fluorocarbons and linked to the Montreal Protocol requesting substitution of the chlorofluorocarbons (CFC). TRI is the feedstock to produce CFC substitutes which are primarily used in refrigeration and air conditioning. Approximately 75% of the total TRI production goes into intermediate applications. Contrary to the use as an intermediate the use as a

[2] [ECSA Charter Document: http://www.eurochlor.org/upload/documents/document282.pdf]

SOLVENT shows a strong decline. This is due to on-going substitution of TRI by alternative products and technologies,

- conversion to closed systems in surface cleaning minimizing solvent emissions and reducing solvent consumption.
- maximizing the lifetime in closed systems through service concepts offering solvent maintenance including solvent monitoring and stabilization adjustments.
- use of Closed loop Safety containers with vapour return connections avoiding emissions during filling[3]. A major producer (Dow Europe GmbH and its affiliated companies/SAFECHEM Europe GmbH) has ceased as of April 2009 the supply of TRI in drums in Western Europe and this approach is being evaluated for all of Europe.

The Solvents Emissions Directive (SED) and anticipation of REACH as well as the of voluntary industry commitments and specific programs of producers e.g. CHEMAWARE™ (www.CHEMAWARE.org) for knowledge sharing and awareness raising and the active conversion program to closed loop safety containers reinforced the trend to conversion to closed systems or substitution.
REACH will reinforce the use of closed systems e.g. as the only registered use for surface cleaning. By year end 2010 with the REACH implementation and the TRI Charter full in vigour (see below) the implementation of closed systems should be completed, Due to the use of closed systems resp. substitution to other solvents the TRI consumption into solvent applications is expected to **drop an additional 60% compared to 2006 consumption**.

In 2007 the TRI solvent use accounted for about 25% of TRI production in the EU and intermediates 75%. This is an inversion of the TRI use pattern in the 1980s when TRI was used up to 75% as solvent and intermediate use was only 25% of the EU TRI production.

Solvent Uses

Consolidation of use pattern
Closed systems progressing

The major use segment of TRI as a solvent is INDUSTRIAL SURFACE CLEANING. Other minor uses include the use of TRI for:
SPECIAL ADHESIVE production and its use in mines and in rubber coating, ASPHALT TESTING, WOOL SCOURING, high-tech CERAMIC GOODS PRODUCTION, PROCESS SOLVENT, HEAT TRANSFER FLUID.
The use of the special adhesives in mines and in rubber coating, are the only uses were closes systems are not suitable, all other uses are in closed systems or closed system use is well progressing. Other open applications, like solvent in paints, solvent in stone treatment are not of relevance anymore today.

Surface Cleaning

Major use for TRI as solvent
Well controlled in closed systems

Closed systems, including closed supply and take-back systems in safety containers (like SAFE-TAINER™ system) are today Industry Standard and commonly used in Germany, Austria and Switzerland due to stringent national legislation enforced prior to SED (e.g. German 2BImSchV). In remaining Europe compliance with SED requires companies using TRI in volumes >1mt to utilize closed systems in order to meet stringent emission requirements. Together with the voluntary industry commitment (TRI Charter), which pertains to all end-users independent of volume, all companies using TRI for surface cleaning will be required to use closed systems not later than year end 2010. REACH will reinforce the use in closed systems as the only registered use for surface cleaning. Implementation of SED, requiring conversion to closed systems, substitution of TRI or ceasing cleaning is progressing but not yet fully finalized in all regions of the EU.

The benefit of conversions to closed systems and impact on worker exposure has been analysed by a thesis done at the poly-technical University (ETH) of Zürich (Grote, 2005). Subject of the thesis was the development of exposure levels and the number of peoples exposed as function of legislative as well as equipment technology developments related to the Greman market. The thesis concluded that as a result of automated closed systems and solvent substitution[4], the estimated exposure of worker in the near range of closed systems dropped to below 10 ppm, with more sophisticated closed machines below 5 and with best available technology closed machines below 2 ppm. The TRI concentration in the far range of the cleaning equipment dropped to near or below the detection limit of the monitoring method (1ppm). As a result the estimated number of potentially exposed workers dropped significantly to 500 - 1000 . For Germany, this represents more than a 95% reduction in workers potentially exposed to TRI.

The German 2.BImSchV has required closed machines for surface cleaning ~10 years prior to the European solvents Emission Directive (SED). Since the SED together with the voluntary industry commitment leads to the

---

[3] SAFE-TAINER™ trademark system is an example of such a closed supply, use and take-back system offer by SAFECHEM Europe GmbH

[4] The German 2.BImSchV forced either substitution or the use of closed systems for any volume of halogenated solvent used

same requirements on the use of closed machines as the 2.BImSchV, the German experience on the use of TRI in surface cleaning can be taken as a model. It is expected that by beginning of 2011, once SED and the voluntary industry commitment are fully implemented, all of the EU will be converted to the same equipment technology that is already used successfully in Germany to minimize worker and environmental exposure.

ECSA fully anticipate that conversion to closed system in applications such as surface cleaning will succeed based on the experience in Germany as previously discussed. With a closed system, the end user may expect to see up to an 80% reduction in solvent consumption by running a single solvent load for up to 2 years. Also producers are committed to closed systems. Switching to closed systems is generating new business opportunities for the solvent manufacturer by offering solvent services. New business models (Chemical Product services / Chemical Leasing) have emerged from this changed market situation and have already been implemented.

MINOR USES

Minor Uses for TRI as solvent are:

a) Production of Special TRI containing Adhesives: Approximately 1% of TRI production is used in this application. The formulation of the adhesives occurs under industrial conditions in a closed batch process. These adhesives are exported (~50% of the produced adhesive) and are in the EU used for:

i) the repair of conveyor belts in mines (~0.25% of TRI production). In underground mining, non-flammable solvents are essential.

ii) The adhesion of rubber coatings onto vessel walls (~0.2% of TRI production). Exposure control is realized through controlled venting of the vessels and additional protective respiratory equipment if needed.

b) High-tech Ceramic production: TRI is used as a solvent to dissolve very specific binders used to keep the green ceramic mass in shape and control shrinking during burning. The TRI is evaporated during the drying process of the applied green ceramic mass. Closed equipment and TRI recovery re-use as a solvent from exhaust air is employed.

c) Wool scouring: The wool scouring process is similar to dry-cleaning. New installations for washing with chlorinated solvents avoid groundwater contamination and are fitted with closed-loop systems to minimize air-stream exhaust to the outside environment. Under these conditions (minimize losses), prevent potential contamination of groundwater from diffuse pollution and accidents), the IPPC document of Best Available Techniques (BAT) for the textile industry determines wool scouring with a chlorinated solvent (PER and TRI) as BAT. The solvent process has significant advantages over the water-based scouring techniques which employs 10-15 litres of water per kilogramme of greasy wool processed and comparatively larger energy demands and heavily loaded waste water generation. The solvent process also enables pesticide-free clean wool as pesticides partition strongly to the solvent and are removed with the grease.

d)Asphalt testing: TRI is the solvent listed in national analytical standard procedures. It serves to remove the bitumen fraction of asphalt probes liberating the gravel fraction for particle distribution analysis. Closed analytical equipment has been developed and is used in the testing laboratories as typical risk management measure to minimise exposure during the analytical process.

e) Heat transfer fluid: TRI is used as a heat transfer medium in the closed secondary heat transfer in industrial climate controlled installations such as wind tunnels in the automotive and aeronautic industry.

f) Process solvent: TRI is used as a process solvent in the production of some pharmaceutical products. These are fully-closed processes with recovery of TRI as solvent for re-use.

Substitution

Essential uses remain

Alternatives are: other chlorinated solvents like perchloroethylene (PER) and methylene chloride (DCM), oxygenated solvents, hydrocarbon solvents or aqueous systems.

PER has similar solvent properties as TRI but will not be able to match the performance requirements of a cleaning solvent in all cases because of its higher boiling point and the lower solvency power.

Oxygenated and hydrocarbon solvents used in cleaning applications have much higher boiling points. These are flammable solvents which can pose a safety risk and need to be handled appropriately. Recycling within the cleaning equipment is less efficient due to lower recycling performance because separation of oils from the solvent becomes much less effective. This leads to reduced overall cleaning performance and potentially increased waste and costs.

Aqueous systems have the disadvantage of much higher energy demand, if dry parts are required, and non-universal material compatibility (combined cleaning of different materials is restricted) *(Ecobilan, 1997)*.

The experience in Germany shows that TRI can be substituted in a number of non-critical cleaning applications with low surface complexity and reduced quality requirements. In addiiton, the experience in Germany also shows that despite 10 years of substitution efforts, many critical applications will remain, where the use of TRI is essential and critical for the process and/or the quality of goods produced, such as cleaning of very complex surfaces with

narrow tolerances, cleaning of surfaces for safety related goods like brakes and aerospace parts, or innovative high tech products like ceramic coatings.

For these cases it has been demonstrated that TRI can continue to be safely used in closed systems.

Literature References:

(Grote, 2003)
Julia von Grote, Occupational Exposure Assessment in Metal Degreasing and Dry Cleaning – Influences of Technology Innovation and Legislation, Dissertation No. 15067, ETH Zurich 2003

(Birkenfeld et al,2005)
Birkenfeld et al, Product ban versus risk management by setting emission and technology requirements, Diskussionsbeitrag Nr. V-37-05, Passau 2005, Volkswirtschaftliche Reihe ISSN 1435-3520

(Ecobilan, 1997)
Ecobilan, Life Cycle Assessment: Comparison of trichloroethylene and aqueous solutions for metallic parts degreasing, commissioned by ECSA, Brussels 1997, http://www.eurochlor.org/news/detail/index.asp?id=38&npage=23&archive=1