Annex XV dossier

PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CATEGORY 1A OR 1B CMR, PBT, vPvB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name:1,2,3-trichloropropaneEC Number:202-486-1CAS Number:96-18-4

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PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CATEGORY 1A OR 1B CMR, PBT, VPVB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name: 1,2,3-trichloropropane

EC Number: 202-486-1

CAS number: 96-18-4

- The substance is proposed to be identified as substance meeting the criteria of Article 57 (a) of Regulation (EC) 1907/2006 (REACH) owing to its classification as carcinogen category 1B¹ which corresponds to classification as carcinogen category 2².
- The substance is proposed to be identified as substance meeting the criteria of Article 57 (c) of Regulation (EC) 1907/2006 (REACH) owing to its classification as toxic for reproduction category 1B¹ which corresponds to classification as toxic for reproduction category 2².

Summary of how the substance(s) meet(s) the CMR (1A or 1B) criteria

1,2,3-trichloropropane is listed by Index number 602-062-00-X in Regulation (EC) No 1272/2008 and classified in Annex VI, Part 3, Table 3.1 (list of harmonised classification and labelling of hazardous substances) as carcinogen, Carc. 1B (H350: "May cause cancer.") and toxic for reproduction, Repr. 1B (H360F: "May damage fertility."). The corresponding classification in Annex VI, part 3, Table 3.2 (the list of harmonised classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008 is carcinogen category 2 (R45: "May cause cancer.") and toxic for reproduction category 2 (R60: "May impair fertility.").

Therefore, this classification of 1,2,3-trichloropropane in Regulation (EC) No 1272/2008 shows that the substance meets the criteria for classification as carcinogen and toxic for reproduction in accordance with Article 57 (a) and Article 57 (c) of REACH.

Registration dossiers submitted for the substance? Yes

¹ Classification in accordance with Regulation (EC) No 1272/2008 Annex VI, part 3, Table 3.1 List of harmonised classification and labelling of hazardous substances.

² Classification in accordance with Regulation (EC) No 1272/2008, Annex VI, part 3, Table 3.2 List of harmonised classification and labelling of hazardous substances (from Annex I to Council Directive 67/548/EEC).

PART I

JUSTIFICATION

1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

1.1 Name and other identifiers of the substance

Table 1: Substance identity

EC number:	202-486-1
EC name:	1,2,3-trichloropropane
CAS number (in the EC inventory):	96-18-4
CAS number:	96-18-4
CAS name:	Propane, 1,2,3-trichloro-
IUPAC name:	1,2,3-Trichloropropane
Index number in Annex VI of the CLP Regulation	602-062-00-X
Molecular formula:	C ₃ H ₅ Cl ₃
Molecular weight range:	147.4 gmol ⁻¹
Synonyms:	Allyl trichloride; Glycerol trichlorohydrin; Glyceryl trichlorohydrin; NSC 35403; Trichlorohydrin;

Structural formula:

CI Сí CI

1.2 Composition of the substance

Name: 1,2,3-Trichloropropane

Description: ---

Degree of purity: 83 – 100 % (w/w)

Table 2: Constituents

Constituents	Typical concentration	Concentration range	Remarks	
1,2,3-Trichloropropane	≥ 86 % (w/w)	83 – 100 % (w/w)	Based on the registration	
EC number: 202-486-1			dossiers received so far	

Table 3: Impurities

Confidential (see confidential Annex I)

Table 4: Additives

Confidential (see confidential Annex I)

1.3 Physico-chemical properties

Property	Value	Remarks
Physical state at 20°C and 101.3 kPa	liquid	
Melting/freezing point	-14.7 °C	Lide D.R.; CRC Handbook of Chemistry and Physics. 89th ed.; CRC Press, Taylor & Francis Group, Boca Raton, London, New York, 2008
Boiling point	157 °C at 1013 hPa	Lide D.R.; CRC Handbook of Chemistry and Physics. 89th ed.; CRC Press, Taylor & Francis Group, Boca Raton, London, New York, 2008
Density	1.39 gcm ⁻³ at 20 °C	Lide D.R.; CRC Handbook of Chemistry and Physics. 89th ed.; CRC Press, Taylor & Francis Group, Boca Raton, London, New York, 2008
Vapour pressure (p)	p(37 °C) = 10 hPa p(2 °C) = 1 hPa	Lide D.R.; CRC Handbook of Chemistry and Physics. 89th ed.; CRC Press, Taylor & Francis Group, Boca Raton, London, New York, 2008
Water solubility	1685 mgl ⁻¹ at 25 °C	ECHA, calculation according to EPISUITE performed with the module WSKOWWIN, 2010
Partition coefficient n- octanol/water (log value)	logPow = 2.5	ECHA, calculation according to EPISUITE performed with the module WSKOWWIN, 2010
Surface tension	37.7 mNm ⁻¹ at 20 °C (no information on test concentration)	Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 10.1002/14356007.a06 233.pub2, 2006
Flash point	74.0 °C (no information on pressure)	Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 10.1002/14356007.a06 233.pub2, 2006
Autoignition temperature	304 °C (no information on pressure)	Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 10.1002/14356007.a06 233.pub2, 2006
Oxidizing properties	No oxidizing properties	Due to structural consideration
Explosive properties	No explosive properties	Due to structural consideration

Table 5: Overview of physicochemical properties³

³ The references of the values reported in Table 5 will be available in the technical dossier. In case references need to be included an additional column could be added manually to Table 5.

2 HARMONISED CLASSIFICATION AND LABELLING

Table 6: Classification according to part 3 of Annex VI, Table 3.1 (list of harmonisedclassification and labelling of hazardous substances) of Regulation (EC) No 1272/2008

Index No	International Chemical Identification	Classification		Labelling			Spec.	Notes
		Hazard Class and Category Code(s)	Hazard statement code(s)	Pictogram, Signal Word Code(s)	Hazard statement code(s)	Suppl. Hazard statement code(s)	ent factors	
602-062-00-X	1,2,3- trichloropropane	Carc. 1B Repr. 1B Acute Tox. 4 * Acute Tox. 4 * Acute Tox. 4 *	H350 H360F *** H332 H312 H302	GHS08 GHS07 Dgr	H350 H360F *** H332 H312 H302			D

Table 7: Classification according to part 3 of Annex VI, Table 3.2 (list of harmonized classification and labelling of hazardous substances from Annex I of Council Directive 67/548/EEC) of Regulation (EC) No 1272/2008

Index No	International Chemical Identification	Classification	Labelling	Concentration Limits	Notes
602-062-00-X	1,2,3- trichloropropane	Carc. Cat. 2; R45 Repr. Cat. 2; R60 Xn; R20/21/22	T R: 45-60-20/21/22 S: 53-45		ED

3 ENVIRONMENTAL FATE PROPERTIES

4 HUMAN HEALTH HAZARD ASSESSMENT

5 ENVIRONMENTAL HAZARD ASSESSMENT

6 CONCLUSIONS ON THE SVHC PROPERTIES

6.1 PBT, vPvB assessment

Not relevant.

6.2 CMR assessment

1,2,3-trichloropropane is listed by Index number 602-062-00-X in Regulation (EC) No 1272/2008 and classified in Annex VI, Part 3, Table 3.1 (list of harmonised classification and labelling of hazardous substances) as carcinogen, Carc. 1B (H350: "May cause cancer.") and toxic for reproduction, Repr. 1B (H360F: "May damage fertility."). The corresponding classification in Annex VI, part 3, Table 3.2 (the list of harmonised classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008 is carcinogen category 2 (R45: "May cause cancer.") and toxic for reproduction category 2 (R60: "May impair fertility.").

Therefore, this classification of 1,2,3-trichloropropane in Regulation (EC) No 1272/2008 shows that the substance meets the criteria for classification as carcinogen and toxic for reproduction in accordance with Article 57 (a) and Article 57 (c) of REACH.

6.3 Substances of equivalent level of concern assessment

PART II

The underlying work for development of Part II of this Annex XV report was carried out under contract ECHA/2010/175 SR28 by Entec UK Ltd⁴, IOM Consulting Ltd⁵ and BRE⁶.

INFORMATION ON USE, EXPOSURE, ALTERNATIVES AND RISKS

1 INFORMATION ON MANUFACTURE, IMPORT/EXPORT AND RELEASES FROM MANUFACTURE

1.1 Manufacturing sites

Data searches were carried out to determine manufacturing sites currently producing 1,2,3-TCP. The European chemical Substances Information System (ESIS) at Ex-ECB website lists five producers/importers of 1,2,3-TCP in Europe (Table 8). It is unclear from ESIS which of these are producers and which are importers.

Company	Country
Dow Deutschland Inc., Werk Stade	Germany
Shell Nederland Chemie B.V.	Netherlands
Shell Nederland Chemie B.V.	Netherlands
Solvay Alkali GmbH	Germany
Solvay S.A.	Belgium

It is likely that this information is out of date and so manufacturers were contacted directly. Information obtained on quantities manufactured is included in the confidential Annex II.

Information on the use, production, and emissions of 1,2,3-TCP was requested from Member States Competent Authorities by ECHA. The information provided on manufacture is presented in Table 9.

⁴ 17 Angel Gate, City Road, London, EC1V 2SH, United Kingdom

⁵ Riccarton, Edinburgh, EH14 4AP, United Kingdom

⁶ Bucknalls Lane, Garston, Watford, WD25 9XX, United Kingdom

Member State	Details of production		
Latvia	No production		
UK	No known production		
Netherlands	Two manufacturing sites as listed on ESIS website		
Germany No information beyond the IUCLID (2000) datasheet			
Questionnaire sent to Member States on 12 November 2010			

 Table 9: Member State questionnaire responses on the production of 1,2,3-TCP

1.2 Manufacture, import, export and use quantities

The available literature and consultation with manufacturers suggests that 1,2,3-TCP is manufactured as a by-product of the manufacture of other chlorinated compounds, including epichlorohydrin, dichloropropene, propylene chlorohydrin, dichlorohydrin, and glycerol (ATSDR, 1992; CICAD, 2003; NTP, 2005).

It is estimated that less than 50,000 metric tonnes of 1,2,3-TCP is produced globally each year, as a by-product of epichlorohydrin manufacture (OECD, 2004).

The IUCLID (2000) dataset indicates that between 10,000 and 50,000 tonnes of 1,2,3-TCP were historically produced (before 2000) annually in the EU.

The total volume of 1,2,3-TCP currently manufactured in the EU is estimated in the range of 10,000 and 50,000 t/y.

The available literature suggests that the majority (>80%) of the 1,2,3-TCP produced as a byproduct of epichlorohydrin production is incinerated on-site (CICAD, 2003). However consultation with manufacturers suggests that much less (<5%) is incinerated, at least at some installations.

No information is available on volumes imported to or exported from the EU.

1.3 Trends

Based on the available information, 1,2,3-TCP is only manufactured as an by-product of the production of other chlorinated compounds. Although several routes are known for epichlorohydrin manufacture, most is currently made from propylene and chlorine as primary raw materials in a multi-step process. It is the inefficiencies in the chlorination and hypochlorinated steps that lead to the formation of unwanted chlorinated organics (including 1,2,3-TCP) that are expensive to dispose of.

This amongst other factors (such as the escalating cost of propylene) has accelerated the search for processes that employ less expensive raw materials. One such route is the conversion of glycerine through dichlorohydrin to epichlorohydrin. The reaction effectively stops at a dichlorohydrin stage and there is no exhaustive hydrochlorination to 1,2,3-TCP. Several companies have announced plans to commercialise technology to manufacture epichlorohydrin from gylcerin, including Dow,

Solvay⁷ and Spolchemie⁸ (Bell et al., 2008). This may mean that, in the future, less 1,2,3-TCP will be produced.

1.4 Releases from manufacture

1.4.1 Operational conditions of use and existing risk management structures

Consultation with industry suggests that manufacturing of 1,2,3-TCP takes places under Strictly Controlled Conditions according to Article 18(4) of the REACH Regulation. Further information, including a summary of risk management measures typically implemented during manufacture of 1,2,3-TCP, is included in the confidential Annex II.

1.4.2 Occupational releases and exposure from manufacture

In the following text, exposures are ranked according to the following scheme (based on an assumed inhalation volume of 10 m^3 over a typical 8 hour shift and a bodyweight of 70 kg).

Ranking	Inhalation conc (15 min) (mg/m ³)	Inhalation concentration 8 hours (mg/m ³)	Intake equivalent to the inhalation concentration over an 8 hour shift	Dermal exposure mg/kg/day
Very high	>900	>300	>3000 mg	>428
High	180-900	60-300	600 -3000 mg	85.7-428
Moderate	1.8-180	0.6-60	6-600 mg	8.6-85.7
Low	0.9-1.8	0.3-0.6	3-6 mg	4.3-8.6
Very low	<0.9	<0.3	<3 mg	<4.3

 Table 10: Ranking of exposure levels

Exposure to 1,2,3-TCP may arise during sampling, analysis of the samples, loading of storage or transportation containers and inspection and repair of the manufacturing equipment.

Measured full shift concentrations associated with sampling and analysis are very low and measured concentrations associated with loading are low. Modelled short term peak inhalation exposures for each of these activities are low for analysis and very low for sampling and loading. Modelled dermal exposures are low. Further details are provided in confidential Annex II.

Measured shift mean exposure concentrations (2002-2009) range from low to very low. These measured concentrations do not take account of the use of PPE which would have reduced actual exposures by a factor of 20.

There are virtually no published exposure data for exposure to 1,2,3-TCP during manufacturing. The Concise International Chemical Assessment Document (CICAD, 2003) indicated that a

⁷ See Solvay website: http://www.solvaychlorinatedorganics.com/info/0,0,1000574-_EN,00.html.

⁸ See Spolchemie website: http://www.spolchemie.cz/dwn/factsheet12.pdf.

maximum short-term exposure concentration of 17 mg/m³ was reported in 1985 for maintenance personnel at a chemical plant in the USA. The 1985 study reported that exposure concentrations of 1,2,3-TCP in other workplaces did not usually exceed 0.61 mg/m³. There has been a substantial reduction in exposure to most chemical substances over the last 25 years (Creely et al, 2007) and the data from 1985 reviewed in the CICAD are therefore highly unlikely to reflect current conditions. There are no published measurement data from other sources for the manufacture of 1,2,3-TCP.

Overall, given the high level of containment of the manufacturing process, both dermal and inhalation exposures are anticipated to be low.

1.4.3 Environmental emissions from manufacture

Emissions to air from manufacture have been estimated at substantially less than one tonne per year. Releases to waste water have also been estimated at less than one tonne per year. Total releases to air and waste water combined are estimated to be less than one tonne per year. Details of calculations of environmental emissions are provided in confidential Annex II.

2 USES OF THE SUBSTANCE

2.1 Overview of uses

2.1.1 Historical use

Older reports identified 1,2,3-TCP as a solvent for hydrophobic compounds and resins, as a paint and varnish remover, and as a degreasing agent (Johnson, 1968; Ellerstein and Bertozzi, 1982; Lewis, 1992; BUA, 1993; IARC, 1995). According to NTP (2005), 1,2,3-TCP has been used: for the production of food and beverages; to dissolve oil, fat and wax; as a degreasing agent; for the production of paint/varnish remover; as well as in the production of hexafluoropropylene, thiokol polysulfide, dichloropropene and in chlorinated rubbers and resins.

1,2,3-TCP has reportedly been formulated with dichloropropenes in the manufacture of soil fumigants including 1,2-dibromo-3-chloropropane (DBCP), ethylene dibromide (EDB), D-D (a mixture of dichloropropane and dichloropropene) (IARC, 1995). It is understood that 1,2,3-TCP was not the active ingredient in these pesticides, but may have been present at low concentrations (up to 0.17%) as a by-product of manufacturing (CICAD, 2003). According to the Farm Chemicals Handbook (Sine, 1991), this soil fumigant is no longer available in the United States. No current information is available to indicate that it continues to be used for these purposes in the EU and these uses are not included in the registrations received by ECHA.

In addition, Health Canada (2000) reported that 1,2,3-TCP may be present in formulations employed as a well drilling aid and, as such, lead to contamination of drinking water. However, there is no indication that 1,2,3-TCP is used for this purpose in the EU and this has not been followed up further.

2.1.2 Current use

Available information suggests that 1,2,3-TCP is no longer marketed for use in consumer applications (OECD, 2004; Dow, 2008). There is no evidence from consultation that 1,2,3-TCP is still used directly as a solvent and this use was not included in available registration dossiers.

Today, 1,2,3-TCP is used primarily as a building block for the synthesis of other products, such as:

- Pesticides
- Chlorinated solvents
- Polysulfide elastomers (cross-linking agent)
- Hexafluoropropylene (cross-linking agent)

A breakdown of the uses of 1,2,3-TCP is provided in Table 11. The table indicates that, of the yearly total volume, approximately 90% is used as an intermediate for conversion into other substances. Based on communication with industry, it is understood that conversion takes place under strictly controlled conditions (as defined in article 18(4) of the REACH Regulation).

According to the Allylics REACH Consortium⁹, 1,2,3-TCP has no use as a substance in articles or in preparations.

Application	% of total (approximate)*	Low estimate (assuming production of 10,000t)	High estimate (assuming production of 50,000t)
Intermediate use for chlorinated solvents	55	5,500	27,500
Intermediate use for agricultural products	35	3,500	17,500
Monomer use	5	500	2,500
* Note that of the total amount produced a small proportion is incinerated on site and this is not included in mass			

 Table 11: Uses according to TCP manufacturers

* Note that, of the total amount produced, a small proportion is incinerated on-site and this is not included in mass balance presented here.

2.2 Use #1 – Non-isolated intermediate use in production of chlorinated solvents

2.2.1 Functions of the substance

According to data provided in the questionnaires from industry, 1,2,3-TCP is used as an intermediate in a closed process to manufacture chlorinated solvents in an industrial environment. Details of specific chlorinated solvents are given in confidential Annex II.

In accordance with Article 3(15) of the REACH Regulation, an intermediate is "a substance that is manufactured for and consumed in or used for chemical processing in order to be transformed into another substance (hereinafter referred to as synthesis)". The status of a substance as an intermediate is in fact not specific to its chemical nature but to how it is used following manufacturing. According to ECHA (2010), a substance is an intermediate if the following conditions are met:

- a. The substance is manufactured to be itself converted into another substance on an industrial site.
- b. The outcome of the chemical processing is another manufactured substance on its own but not another substance in an article.

According to industry, this usage of 1,2,3-TCP satisfies ECHA's definition of an intermediate.

⁹ Allylics REACH Consortium website (accessed 22nd November 2010) available online here: <u>http://www.reachcentrum.eu/en/consortium-management/consortia-under-reach/allylics-reach-consortium/allylics-use-descriptors.aspx</u>.

2.2.2 Applications

2.2.2.1 Sectors of use

Chlorinated solvents in general are a large family of chemical compounds that contain chlorine, such as carbon tetrachloride, trichloroethylene, or methylene chloride. They are used for a wide variety of commercial and industrial purposes including degreasers, cleaning solutions, paint thinners, pesticides, resins, glues, and a host of other mixing and thinning solutions. Due to their non-flammability, these compounds have been widely used for cleaning metals in the electronics industry and for dry cleaning of clothes (Eurochlor, 2010).

According to industry 1,2,3-TCP seemed to be used as an intermediate in the production of these chlorinated solvents and is thus chemically transformed in the manufacturing process. No information is available on any residual 1,2,3-TCP present in the resultant chlorinated solvents.

Details of the specific chlorinated solvents in which 1,2,3-TCP is used are considered to be confidential by the manufacturers (see confidential Annex II).

2.2.2.2 Use in preparations/mixtures

1,2,3-TCP seemed to be used as an intermediate in the synthesis of other chemical substances. The lifecycle of 1,2,3-TCP ends in this synthesis. Therefore, it is assumed that no 1,2,3-TCP is used in preparations or mixtures.

2.2.2.3 Processes involved

Details of the production processes involved in the manufacture of specific chlorinated solvents are provided in confidential Annex II.

2.2.2.4 Use in articles

1,2,3-TCP seemed to be used as an intermediate in the synthesis of other chemical substances. The lifecycle of 1,2,3-TCP ends in this synthesis. Therefore, it is assumed that no 1,2,3-TCP is used in articles.

2.2.3 Quantities involved

It is estimated that approximately 55 % (5,500-27,500 t/y) of the total volume of 1,2,3-TCP is used as non-isolated intermediate in the manufacture of chlorinated solvents.

2.2.4 Description of supply chain

Consultation suggests that about 55 % of the total volume is used as non-isolated intermediate directly on-site for the synthesis of chlorinated solvents. It is understood that no 1,2,3-TCP is sold to consumers for this use.

Therefore, the supply chain related to the substance itself is limited to the manufacturer of the substance.

According to Eurochlor (2010), the principal uses of chlorinated solvents are: pharmaceuticals, chemical processing, metal cleaning, dry cleaning and speciality adhesives. The specific chlorinated solvents that are produced using 1,2,3-TCP are used in these types of applications.

2.3 Use #2 – Isolated intermediate use for agricultural products

2.3.1 Functions of the substance

According to information provided by industry, 1,2,3-TCP is used as substance/ intermediate in a closed process to manufacture intermediates for agricultural products in an industrial environment.

In accordance with Article 3(15) of the REACH Regulation, an intermediate is "a substance that is manufactured for and consumed in or used for chemical processing in order to be transformed into another substance (hereinafter referred to as synthesis)". The status of a substance as an intermediate is in fact not specific to its chemical nature but to how it is used following manufacturing. According to ECHA (2010), a substance is an intermediate if the following conditions are met:

- The substance is manufactured to be itself converted into another substance on an industrial site.
- The outcome of the chemical processing is another manufactured substance on its own but not another substance in an article.

Information received from industry suggest that this usage of 1,2,3-TCP satisfies ECHA's definition of an intermediate.

2.3.2 Applications

2.3.2.1 Sectors of use

1,2,3-TCP seemed to be used as an intermediate to manufacture products used in the agricultural sector. It is understood to be completely converted in an industrial process into another intermediate: dichloropropene. In the absence of more detailed information, it has been necessary to rely on information from available literature regarding dichloropropene. According to the Pesticides Properties Database (PPBD, accessed 5th January 2011) this chemical has a range of agricultural applications including use as soil fumigant to control nematodes and as an insecticide for stored grain.

Further details are provided in the confidential Annex II.

2.3.2.2 Use in preparations/mixtures

1,2,3-TCP seemed to be used as an intermediate in the chemical synthesis of other substances. The lifecycle of 1,2,3-TCP ends in this synthesis. Therefore, it is assumed that no 1,2,3-TCP is formulated into preparations or mixtures.

2.3.2.3 Processes involved

1,2,3-TCP is used in the first step of an industrial multistep synthesis.

1,2,3-TCP, water and a phase transfer catalyst are mixed with sodium hydroxide. The aqueous phase is separated and fresh water as well as sodium rhodanide are added and the reaction mixture heated for conversion. This is followed by an aqueous washing before the products are separated by distillation.

2.3.2.4 Use in articles

1,2,3-TCP seemed to be used as an intermediate in the synthesis of other chemical substances. The lifecycle of 1,2,3-TCP ends in this synthesis. Therefore, no 1,2,3-TCP is incorporated in articles.

2.3.3 Quantities involved

Based on information from industry consultation, it is estimated that around 35 % (3,500 - 17,500 t/y) per year of 1,2,3-TCP are used as isolated intermediate for agricultural purposes.

2.3.4 Description of supply chain

As the lifecycle of 1,2,3-TCP ends in this synthesis, there are no further steps in the supply chain.

2.4 Use #3 – Monomer use

2.4.1 Functions of the substance

According to information provided by industry, 1,2,3-TCP is used as a cross-linking agent in a closed process to manufacture polymers such as polysulfides and hexafluoropropylene (CAS: 116-15-4) in an industrial environment.

2.4.2 Applications

2.4.2.1 Sectors of use

The use of 1,2,3-TCP in this instance relates to the preparation of polysulfide polymers.

Cured polysulfide polymers are resistant to ageing and weathering, are highly elastic from -40 to +120°C, and offer good chemical resistance, especially against oil and fuel. Because of their properties, these materials find use as base polymer for sealants applied to fill the joints in pavement, insulation glass units and aircraft structures.

2.4.2.2 Use in preparations/mixtures

1,2,3-TCP seemed to be used as an intermediate in the chemical synthesis of other substances. The lifecycle of 1,2,3-TCP ends in this synthesis. Therefore, it is assumed that no 1,2,3-TCP is formulated into preparations or mixtures.

2.4.2.3 Processes involved

1,2,3-TCP seemed to be used in closed batch processes as a monomer in the manufacturing of polymers.

The synthesis of polysulfide polymers is based on the reaction of a dihalide and sodium polysulfide. 1,2,3-TCP is used as a tri-functional branching agent to introduce cross-linking in the polysulfide polymers. The included part of 1,2,3-TCP is -CH₂-CH-CH₂-. These crosslinks interconnect neighbouring polymer chains, thereby conferring rigidity. According to industry, the lifecycle of 1,2,3-TCP ends in the polymer and it is understood that no chlorine is included in the polymer chains (it is converted into sodium chloride).

Hexafluoropropylene is produced in a six-step reaction beginning with the fluorination of 1,2,3-trichloropropane.

2.4.2.4 Use in articles

1,2,3-TCP seemed to be used as a monomer in the manufacturing of polymers. The lifecycle of 1,2,3-TCP ends in this synthesis. Therefore, no 1,2,3-TCP is used in articles.

2.4.3 Quantities involved

About 5 % (500 - 1,500 t/y) of the total volume of 1,2,3-TCP are estimated to be used in the production of polymers.

2.4.4 Description of supply chain

1,2,3-TCP for the use as a monomer is manufactured at only one European site. Around 150 companies are thought to use these polymers (synthetic rubbers) in the manufacture of sealing compounds.

Available literature suggests that liquid polysulfides are used in the production of synthetic rubber goods¹⁰. Hexafluoropropylene is used mainly as a co-monomer in the production of high quality fluoroplastics and also as a chemical intermediate.

 $^{^{10}\,}$ For example, Industrial Rubber Goods website available online here: www.industrialrubbergoods.com/polysulfide-rubber.html.

3 RELEASES FROM USES

3.1 Occupational exposure

3.1.1 Introduction

The categorisation of exposure levels as set out in Table 10 has been used within this section as a basis for classifying exposure levels. Further information is provided in confidential Annex II.

3.1.2 Use #1 – Non-isolated intermediate use

3.1.2.1 Operational conditions of use and existing risk management measures

According to industry, the use of 1,2,3-TCP as a non-isolated intermediate takes place under Strictly Controlled Conditions according to Article 18 (4) of the REACH Regulation.

3.1.2.2 Releases of the substance

According to ECHA (2010) guidelines, a substance is an intermediate if the following conditions are met:

- The substance is manufactured to be itself converted into another substance on an industrial site.
- The outcome of the chemical processing is another manufactured substance on its own but not another substance in an article.

The use of 1,2,3-TCP as a non-isolated intermediate appears to meet both of these criteria and no further assessment of releases of the substance has been made.

3.1.3 Use #2 – Isolated intermediate use

3.1.3.1 Operational conditions of use and existing risk management measures

The use of 1,2,3-TCP as an isolated intermediate reportedly takes place under Strictly Controlled Conditions according to Article 18 (4) of the REACH Regulation.

3.1.3.2 Releases of the substance

Based on consultation with industry, the transfer of 1,2,3-TCP from container to tank is done via pumping and subsequently conversion is conducted in a closed system which makes emissions very unlikely. The substance is handled as a liquid or in solution during reaction.

The use of 1,2,3-TCP as an isolated intermediate appears to meet ECHA's criteria (ECHA, 2010) for substances considered to be an intermediate. Therefore an assessment of releases of the substance has not been further considered.

3.1.3.3 Environmental emissions from isolated intermediate use

Based on consultation with industry, all process air is subjected to exhaust incineration.

Due to the conversion of the substance with an excess of sodium hydroxide, no residual 1,2,3,TCP is left in the reaction mixture or any process stream. Therefore waste water from the process does not contain any 1,2,3-TCP. However, the waste water stream is submitted to an active charcoal treatment due to the presence of other secondary components. The active charcoal unit is ultimately subjected to incineration.

3.1.4 Use #3 - Monomer use

3.1.4.1 Operational conditions of use and existing risk management measures

Based on information from industry, 1,2,3-TCP is handled under Strictly Controlled Conditions through its whole life cycle including during monomer use.

Further details are provided in the confidential Annex II.

3.1.4.2 Releases of the substance

In relation to short-term exposure, there are no published exposure data. Modelled inhalation concentrations and dermal exposures are very low to low according to the definitions in Table 10.

In relation to long-term exposure, there are no measured exposure data. Given the high level of containment of the polymerisation process, exposures are believed to be similar to those associated with the manufacture of 1,2,3-TCP.

3.1.4.3 Environmental emissions from monomer use

Emissions to air have been estimated at less than two tonnes per year11. Waste water from the process is incinerated, so there are not expected to be emissions to waste water.

3.2 Natural or unintentional formation

1,2,3-TCP is exclusively a man-made chemical and reportedly does not occur naturally in the environment (BUA, 1993; Dombeck and Borg, 2005). Therefore, there are not thought to be any natural emissions of 1,2,3-TCP.

¹¹ Details of calculations of environmental emissions are provided in confidential Annex II.

The presence of 1,2,3-TCP in pesticides and nematicides employed in soil fumigation (Telone, for example, reportedly contains up to 0.17 % 1,2,3-TCP by weight; Zebarth et al., 1998) has been identified as a potential source for the release of the substance into the environment (Zebarth et al., 1998; City of Shafter, 2000). 1,2,3-TCP has reportedly been detected in groundwater samples from Europe (CICAD, 2003). These are all examples of unintentional formation/presence in other products.

4 CURRENT KNOWLEDGE ON ALTERNATIVES

4.1 Use #1 – non-isolated intermediate for manufacturing chlorinated solvents

No information is currently available on alternatives and manufacturers consulted did not know of any suitable alternatives.

4.2 Use #2 – isolated intermediate for manufacturing agricultural products

No information is currently available on alternatives and manufacturers consulted did not know of any suitable alternatives.

4.3 Use #3 – monomer use

No information is currently available on alternatives and manufacturers consulted did not know of any suitable alternatives.

4.4 Other issues

As indicated in Section 1.3, there is reportedly an alternative production process for epichlorohydrin than the one that leads to the production of 1,2,3-TCP. This involves conversion of glycerine through dichlorohydrin to epichlorohydrin. If this process is adopted more widely, it is likely that the production of 1,2,3-TCP as a by-product of epichlorohydrin manufacture will reduce in the future.

5 **REFERENCES**

ATSDR (1992) Agency for Toxic Substances and Disease Registry, Toxicological profile for 1,2,3-trichloropropane. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

Bell, B.M et al. (2008) 'Glycerin as a Renewable Feedstock for Epichlorohydrin Production. The GTE Process', *Clean*, 36 (8): 657 – 661.

BUA (1993) 1,2,3-Trichloropropane. German Chemical Society (GDCh) Advisory Committee on Existing Chemicals of Environmental Relevance (BUA). Stuttgart, Hirzel, pp. 1–97 (BUA Report 154).

CICAD (2003) Concise International Chemical Assessment Document 56: 1,2,3-Trichloropropane. World Health Organization, Geneva. Available online here www.inchem.org/documents/cicads/cicad56.htm#11.1.3

City of Shafter (2000) *Consumer confidence report for water quality*. Shafter, CA, City of Shafter, pp. 1–6.

Creely, K.S., Cowie, H., Van Tongeren, M., Kromhout, H., Tickner, J., Cherrie, J.W. (2007) Trends in inhalation exposure--a review of the data in the published scientific literature. *Annals of Occupational Hygiene* 51(8):665-78.

Dombeck, G. and Borg, C (2005) "Multi-contaminant treatment for 1,2,3-Trichlorpropane destruction using the HiPOx reactor". Reprinted from the Proceedings of the 2005 NGWA Conference on MTBE and Perchlorate: Assessment, remediation and public policy with permission of the National Ground Water Association Press.

Dow (2008) The Dow Chemical Company: Product Safety Assessment *1,2,3-Trichloropropane* available at <u>http://www.dow.com/productsafety/pdfs/233-00534.pdf</u>

ECHA (2008) Guidance for intermediates. Helsinki: European Chemical Agency, 2008.

ECHA (2009) Guidance on information requirements and chemical safety assessment. Chapter R.16: Environmental Exposure Estimation. Helsinki: European Chemical Agency.

ECHA (2010) Definition of intermediates as agreed by Commission, Member States and ECHA on 4 May 2010.

ESIS - European chemical Substances Information System (ESIS) at Ex-ECB website http://ecb.jrc.ec.europa.eu/

Ellerstein, S.M. and Bertozzi, E.R. (1982) Polymers containing sulfur. In: *Kirk-Othmer* encyclopaedia of chemical technology, 3rd ed. New York, NY, John Wiley & Sons.

Eurochlor website (2010) Available online here: http://www.eurochlor.org/mainglossary

European Commission (2003). European Commission, (2003). Technical Guidance Document on Risk Assessment in support of Commission Directive 93/67/EEC, Commission Regulation (EC) No 1488/94, Directive 98/8/EC, Part I. Ispra: Joint Research Centre, European Chemicals Bureau.

Health Canada (2000) Review of contaminant occurrences in drinking water treatment chemicals. Ottawa, Ontario, Health Canada, Health Protection Branch, pp. 1–10.

IARC (1995) WHO International Agency for Research on Cancer *Dry Cleaning, Some Chlorinated Solvents and Other Industrial Chemicals.* IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans, Volume 63. Lyon, France.

IUCLID (2000) Dataset: 1,2,3-Trichloropropane at Ex-ECB website http://ecb.jrc.ec.europa.eu/

Johnson, R. (1968) Polymers containing sulfur. Polysulfides. In: *Kirk-Othmer encyclopaedia of chemical technology*, 2nd ed. New York, NY, John Wiley & Sons.

Kirk Othmer (2000): Polymers containing sulfur, polysulfides, Kirk Othmer Encyclopedia of Chemical Technology.

Lewis, R. (1992) 1,2,3-Trichloropropane. In: Lewis R, (ed.) Sax's dangerous properties of industrial materials. New York, NY, Van Nostrand Reinhold.

NTP (2005) National Toxicology Program *1,2,3-Trichloropropane*, Report on Carcinogens, Eleventh Ed.; U.S. Department of Health and Human Services, Public Health Service, January 2005.

OECD (2004) SIDS INITIAL ASSESSMENT REPORT for SIAM 18 - 1,2,3-Trichloropropane. Published OECD SIDS initial assessments of HPV chemicals: http://www.oecd.org/document/63/0,3343,en_2649_34379_1897983_1_1_1_1,00.html

PPBD (Accessed 5th January 2011) The Pesticides Properties Database. Website available online here: <u>http://sitem.herts.ac.uk/aeru/projects/ppdb/index.htm</u>

Sine, C. ed. (1991) Farm Chemicals Book 1991. Willoughby, OH, Meister Publishing Co.

Zebarth BJ, Szeto SY, Hii B, Liebscher H, Grove G (1998) Groundwater contamination by chlorinated hydrocarbon impurities present in soil fumigant formulations. *Water Quality Research Journal of Canada*, 33(1):31–50.

ANNEX I

CONFIDENTIAL INFORMATION TO PART I OF THE ANNEX XV DOSSIER

ANNEX II

CONFIDENTIAL INFORMATION TO PART II OF THE ANNEX XV DOSSIER