# VINYL CHLORIDE

E. U. classification: F<sup>+</sup>: Highly flammable





T: Toxic

UN N°: 1086 MARPOL: Not relevant SEBC classification: G (Gas)



### CHEMICAL RESPONSE GUIDE

# VINYL CHLORIDE

PRACTICAL GUIDE INFORMATION DECISION-MAKING RESPONSE

This document was drafted by the Centre de Documentation, de Recherche et d'Expérimentations sur les Pollutions Accidentelles des Eaux (*Cedre*) with financial support from ATOFINA, TOTAL and the Technical Committee of ATOFINA.

The information contained in this guide is the result of research and experimentation conducted by the *CEDRE* which cannot be held liable for the consequences resulting from the implementation of the information contained herein.

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### Purpose of this guide

As part of the research funded by the French Navy, TOTAL and ATOFINA, *Cedre* has published a series of response guides intended to mitigate chemical hazards. They can be used to assist in an emergency response, an accident or an incident involving a vessel or a barge carrying hazardous substances likely to pollute the water and the water column.

These guides are an update of the 61 "mini response guides" published by *Cedre* at the beginning of the 90s and are intended to afford rapid access to vital information, in addition to providing relevant bibliographical sources to retrieve extra information.

They also contain the results of scenarios relating to accidents having occurred in the Channel, the Mediterranean and in rivers.

These scenarios are only intended to provide response authorities the emergency information they need. Each accident has to be viewed on it's own merits and the response authorities will not be able to forego on in-situ measures (air, water, sediment and marine fauna) in order to determine exclusion areas.

The guides are intended primarily for specialists who know which techniques to use in the event of an emergency in addition to the relevant operational response measures. Even though our main concern is to mitigate the consequences of an oil spill, we cannot afford to overlook responder safety and human toxicology.

To contact the duty engineer at *Cedre* (7/24) Please call: 33 (0) 2 98 33 10 10

### National toxicology surveillance system in the event of a major toxicological threat

A hotline is manned 7/24 by Division 7of the General Department of Health (SD7/DGS).

During opening hours please call: Tel. 01 40 56 47 95 Fax 01 40 56 50 56

And outside normal working hours please call the Prefecture or other relevant authority

#### Poison control Centres in France

Angers (Centre Hospitalier d'Angers) Tel.: 02 41 48 21 21 Bordeaux (Hôpital Pellegrin-Tripode) Tel.: 05 56 96 40 80 Grenoble (Hôpital Albert Michallon) Tel.: 04 76 76 56 46 Lille (Centre Hospitalier Régional Universitaire) Tel.: 08 25 81 28 22 Lyon (Hôpital Edouard Herriot) Tel.: 04 72 11 69 11 Marseille (Hôpital Salvator) Tel.: 04 91 75 25 25 Nancy (Hôpital Central) Tel.: 03 83 32 36 36 Paris (Hôpital Fernand Widal) Tel.: 01 40 05 48 48 Reims (Hôpital Maison Blanche) Tel.: 03 26 78 48 21 Rennes (Hôpital de Pontchaillou) Tel.: 02 99 59 22 22 Rouen (Hôpital Charles Nicolle) Tel.: 03 88 37 37 37 Toulouse (Hôpital de Purpan) Tel.: 05 61 77 74 47

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# What you need to know about vinyl chloride

#### Definition

With a boiling point of -13.9°C, vinyl chloride is carried as a liquefied gas. It is extremely flammable and explodes when in contact with air.

#### Uses

Vinyl chloride is mainly used to produce PVC for vehicles, furniture, packing materials and PVC copolymers, such as films and resins.

#### Risks

- Polymerisation at high temperatures, or when in contact with oxidizers. Vinyl chloride can polymerise violently (and even cause the storage tank to explode).
- Toxicity: Vinyl chloride is carcinogenic for humans which is why it is classified T: Toxic.

If vinyl chloride vapours are inhaled, they can cause bronchial irritation, drowsiness, CNS impairment, unconsciousness and even death if the explosion persists.

Contact with liquefied vinyl chloride can cause burns to the skin and frostbite

around the eyes.

• Fire: always approach the scene of a vinyl chloride spill upwind and wear PPE, a respirator and carry gas meters.

#### Behaviour in the environment

When spilled in water, 10 to 20% of liquefied vinyl chloride evaporates instantaneously. The rest of it floats (specific gravity = 0.91), and forms a slick that will spread and evaporate. vinyl chloride vapours are heavier than air and tend to hug the water surface.

Some of it will solubilise and accumulate slightly in aquatic organisms.

# First line emergency data



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### First aid information (ICSC, 1994 ; FDS ATOFINA, 2004)

#### Immediately remove all soiled or spotted clothes

#### Poisoning by inhaling

- Take victim outside in the open air;
- Apply O<sub>2</sub> therapy or artificial respiration if necessary;
- Entrust the victim to a healthcare professional (MD);
- Admit to hospital;
- Have the patient monitored for neurological and liver symptoms.

#### Skin contact

**B1** 

- Rinse with a lot of water (warm if possible) the skin area that has been exposed to vinyl chloride;
- Treat frostbite as thermal burns.

#### Eye contact

- Rinse with a lot of water for several minutes;
- Remove contact lenses if possible;
- Consult an eye specialist if irritation persists.

Do not administer catecholamines as the heart has been sensitised by the vinyl chloride.

### ID card<sup>1</sup>

# VINYL CHLORIDE

**Gross formula**: C<sub>2</sub>H<sub>3</sub>Cl **Semi-developed formula**: CH<sub>2</sub>=CH<mark>Cl</mark>

#### Synonyms

Vinyl chloride monomer, Monochlorethylene, Chlorethylene, Chlorethene, Monochlorethene, Ethyl monochloride, vinyl chlorideM (vinyl chloride monomer)

#### **E.U.** Classification

T: Toxic

#### F<sup>+</sup>: Highly flammable

R12 - Highly flammable

R45 - Can cause cancer

S45 - In the event of an accident, see a doctor immediately

S53 - Avoid exposure, get special instructions before use.

CAS N°:	75-01-4
CE N° (EINECS):	200-831-0
Index N°:	602-023-00-7
(	Classification for transport
UN N°:	1086
Class:	2 (RID/ADR/ADN/ADNR)
Class:	2.1 (IMDG/IATA)

1 For extra data and sources refer to annex 1

**B2** 

### **Physical data**

Conversion factor (a	air 25°C)
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1 ppm = 2.6 mg/m<sup>3</sup> 1 mg/m<sup>3</sup> = 0.385 ppm

Melting point	- 153.7°C
Boiling point	- 13.9°C
Critical temperature	158.4°C
Relative density (water = 1)	0.9121 at 20°C
Relative vapour density (air = 1)	2.15 at 20°C
Soluble in freshwater	1,100 mg/L at 25°C
Pressure/Vapour tension	340 kPa at 20°C
Olfactory threshold in air	260 - 3,000 ppm
Diffusion coefficient in water	1.2.10 <sup>-6</sup> cm <sup>2</sup> /s at 25°C
Diffusion coefficient in air	0.106 cm <sup>2</sup> /s at 25°C
Henry's law constant	2.73.10 <sup>3</sup> Pa.m <sup>3</sup> /mol at 25°C

Definitions in the glossary Sources in annex 1

### Flammability data

• Explosiveness limits by volume (% in air) Lower limit: 2.5 or 25,000 ppm Upper limit: 33 or 330,000 ppm	FDS ATOFINA, 2004
• Vinyl chloride can form an explosive mixture with air	INRS, 2000
• Regression speed : 4.3 mm/min	CHRIS, 1999
• Flash point (in a closed capsule): - 78°C	INRS, 2000
• Self ignition point: 472°C	INRS, 2000
• Specificity of vinyl chloride vapours at high temperature In the atmosphere vinyl chloride molecules react to UV radiation and produce free radicals that in turn react with vinyl chloride molecules. At very high temperatures (a fire outbreak) these reactions generate toxic white smoke on account of the presence of Cl <sup>+</sup> cations.	Lewis, 2000

FDS : Data safety file

Definitions in the glossary

### **Toxicological data**

#### Acute toxicity for humans

- Skin contact: irritation and frostbite.
- Eye contact: corneal impairment is reversible, frostbite.
- Inhalation (main route): moderate irritation of the bronchial tract.

Drowsiness, central nervous system depression, dizziness, disorientation sleepiness, loss of consciousness, death if exposure persists.

Inhaling high concentration vapours will induce anaesthesia from 10,000 ppm upwards and can cause heart or lung failure at high concentrations.

#### Toxicological thresholds

#### Occupational exposure

VME: 1 ppm (2.6 mg/m<sup>3</sup>) (France) TLV-TWA ACGIH: 1 ppm (2.6 mg/m<sup>3</sup>) (USA)

#### Risk management figures for the population at large

IDLH: no data

- TEEL 0: 1 ppm (2.6 mg/m<sup>3</sup>) (USA)
- TEEL 1: 5 ppm (13 mg/m<sup>3</sup>) (USA)
- TEEL 2: 5 ppm (13 mg/m<sup>3</sup>) (USA)
- TEEL 3: 75 ppm (195 mg/m<sup>3</sup>) (USA)

MRL, by inhalation: 0.5 ppm (1.3 mg/m<sup>3</sup>) (USA)

#### Chronic toxicity for humans

- Skin and bone trophic impairment characterised by bone loss in fingers (other bones can be affected), Raynaud's disease and a kind of skin sclerosis (in the event of high exposure).
- GI effects: abdominal discomfort, nausea, anorexia, hepatomegaly, associated often with splenomegaly. Liver impairment comprises initial cytolysis followed by fibrosis and cirrhosis.
- Other effects: impairment of blood cell lines. Difficulty breathing. Peripheral neuropathy.

#### Specific effects

Carcinogenic effects: objectivated, C1 group Effects on fertility: not demonstrated Teratogenic effects: unconfirmed Genotoxic effects: globally genotoxic Mutagenic effects: yes

Inresholds for toxic effects (Fra	nce):					
Concentration (ppm)	1 (min)	10 (min)	20 (min)	30 (min)	60 (min)	
Lethal effect threshold	603,000	235,000	176,000	149,000	112,000	INERI3, 2003

Lethal thresholds are in the upper flammability range for vinyl chloride between 2.5 % & 33 % (v/v), namely 25,000 and 330,000 ppm.

### **Ecotoxicological data**

#### Acute ecotoxicity

Bacteria (anaerobic)	CI <sub>50</sub> (3.5days)	= 40 mg/L
Bacteria (Pseudomonas putida)	CE <sub>5</sub> (16h) ≥	135 mg/L
Seaweed (Scenesdesmus quadricauda)	CL <sub>3</sub> (8 days) =	710 mg/L
Micro-crustaceans (Daphnia magna)	CE <sub>50</sub> (48h) = (estimated according	103 mg/L to TGD)
Fish ( <i>Brachydanio rerio</i> )	CL <sub>50</sub> (96h) =	210 mg/L

**PNEC** (Predicted No-Effect Concentration): according to the Technical Guidance Document pursuant to (CE) regulation 1488/94 concerning risk assessment for existing substances, the PNEC for water will be 103  $\mu$ g/l (applying a safety factor of 1000 to the lowest figure of three trophic levels).

Chronic ecotoxicity: no data.

### Persistence in the environment

#### Abiotic degradation

Vinyl chloride decomposes quickly in air as it reacts with hydroxyl radicals. Degradation products are: hydrogen chloride and formaldehyde chloride (INERIS, 2001).

#### **Biodegradation**

In soil, aerobic and anaerobic degradation are usually slow (INERIS, 2001).

In water, vinyl chloride does not hydrolyse and is not easily biodegradable in aerobic conditions (16% after 28 days).

In anaerobic conditions, biodegradation reaches 80% after 28 days (FDS ATOFINA, 2004).

#### Volatility process

Vinyl chloride evaporates quickly on water surfaces ( $t_{1/2}$  life = 4.7 h in a river and 43.8 h in a pond) and on the ground (main route) (INERIS, 2001 ; DFDS ATOFINA, 2004).

#### Bioaccumulation

According to the Kow and the BCF, vinyl chloride is hardly bio-accumulable in aquatic organisms.

<b>Partition coefficient for organic carbon and water</b> Koc = 8 at 98 l/kg	Hempfling (1997), Howard (1989), Koch (1988), Streit (1992), US-EPA (1996) in INERIS (2001).
Partition coefficient for octanol and water log Kow = 1.58 measured	OECD ,2001
<b>Bio concentration factor, BCF</b> (aquatic organisms) BCF = 4.06 (log BCF = 0.609)	INERIS, 2001

Definitions in the glossary Sources in annex 1

### Classification

#### IGC classification (IMO, 1993)

- Type of vessel: 2G gas tanker for products such as acetaldehyde, anhydrous ammonia, vinyl chloride, ethylene..., which require serious measures to prevent spillages /2PG (gas tanker with an OAL of 150 metres or less) to be used for shipping products such as acetaldehyde, anhydrous ammonia, vinyl chloride, which require serious measures to prevent spillages and that use segregated type C cargo tanks with a MARVS of at least 7 bars and a calculated temperature for the cargo storage system of at least -55°C or more. It is worth noting that vessels complying with this description but that are more than 150 metres long must be considered as type 2G tankers.

- Separate type C tank: -

- Cargo tank atmosphere control: -
- GSMU table number: 340
- Vapour detection: F + T (detection of toxic and flammable vapours)

- Cargo measurement: C types of authorised equipment

*indirect type:* that measures cargo quantity by mass or by flow metre etc.

*closed type:* that does not enter the cargo tank devices using radio-isotopes or ultrasound *closed type:* that does enter the tank but is part of a sealed off system that prevents cargo spillage (float device, electronic sensor, magnetic sensor and precision level indicator, for instance). Devices of these kinds not located on the tank wall itself must have a cut-off valve located as close to the tank as possible.

#### Standard European Behaviour Classification: G (Gas)

MARPOL classification: irrelevant

E.U. classification

		R12 R45 S45 S53	Highly flammable. Can cause cancer. In case of accident or dis- comfort, see a doctor imme- diately (and if possible show him the label). Avoid exposure, get special
F⁺: Highly flammable	T: Toxic	200-831-0	instructions prior to use. EC labelling

### **Special risks**

#### Polymerisation (INRS, 2000)

Vinyl chloride polymerises easily in sunlight, heat or catalysers (peroxides, ozone. persulfates).

To avoid this during transportation and storage, a small amount of inhibitor can be added to the cargo, which will usually be a phenol derivative. The cargo can be stabilised with an inhibitor such as phenol: 40-100 ppm.

(CHRIS, 1999).

#### Danger (CEFIC, 2003)

- Exposure to heat or light, shock or contact with other chemicals may cause a spontaneous increase in pressure or self-ignition capability.
- Heating the tank will increase pressure and risk of explosion (BLEVE or UVCE).
- Contact with vinyl chloride can cause frostbite and serious eye conditions.
- When vinyl chloride heats up or burns, toxic and irritating vapours can be produced.
- Vinyl chloride gas is invisible and vinyl chloride vapours can enter the sewers, underground areas and confined spaces.
- Heat can destroy the inhibitor. Please contact the manufacturer.

### Stability and reactivity (FDS ATOFINA, 2004 and INRS, 2000)

- Conditions to be avoided: in the presence of water and high temperatures (> 100°C), it can corrode iron and steel. Keep it well away from heat or ignition sources.
- Avoid the following: oxidizers (can otherwise cause exothermal polymerisation).
- Explodes when in contact with air.
- Dangerous decomposition products: at 450°C, it forms acetylene and after burning produces hydrogen chloride, carbon monoxide, carbon dioxide and traces of carbonyl dichloride, phosgene and highly toxic smoke (Lewis, 2000).

Other reactions: it reacts with heated concentrates and produces hydrogen chloride and reacts strongly to oxidizers and metals (copper, aluminium).

### Transportation, handling and storage

#### Transportation (FDS ATOFINA, 2004)

UN N°: 1086

Land transportation: RID (rail) /ADR (road)

Danger ID number: 239

Class: 2 Packing group: -Classification code: 2F Labels: 2.1

#### Inland waterway transportation:

ADN/ADNR Class: 2 Classification code: 2F Labels: 2.1

Shipped by sea: IMDG (Amendment 31, 2002) Class: 2.1 Packing group: -Marine pollutant (MP): NO Labels: 2.1

Air freight: IATA Class: 2.1 Packaging group: -Labels: 2.1+C (Cargo only) Forbidden on passenger airliners

Handling (FDS ATOFINA, 2004)

- Ventilate and evacuate appropriately.
- Provide showers and eye washers.
- Provide a breathing set nearby.

- Forbid all sources of sparks and ignition.
- Do not smoke.
- Handle far from flames.
- Only use it in a closed system.
- Avoid build up of electrostatic charges.
- Only use explosion-proof equipment.

Storage (FDS ATOFINA, 2004 and INRS, 2000)

- Vinyl chloride is stored and shipped in liquid form. It can be stored in a pressure vessel (usually at 3 bars) at ambient temperature and more often between -10°C and -14°C at low pressure (1,050 hPa).
- Always keep it far from all sources of ignition.
- Keep it away from heat.
- Provide a dike area.
- Use electrical appliances and equipment fit for explosive atmospheres and ensure they are grounded.

Incompatible with: Oxidizers

Recommended packing material: Steel

С

## **Results of accident scenarios**



### **Reminder of chemical properties**

#### Transportation

Vinyl chloride is carried in tanks and is liquefied.

#### Density and vapour tension

- Density of liquid vinyl chloride: 0.9121 at 20°C
- Vapour density: 2.15 at 20°C
- Vapour tension: 340 kPa at 20°C

#### Solubility

Vinyl chloride solubility in freshwater is 1,100 mg/l at 25°C. Solubility and vapour tension (340 hPa at 20°C) rank it as a gas (G).

### Behaviour of vinyl chloride when spilled in water

When spilled in water, 10 to 20% of liquefied vinyl chloride will vaporise immediately. The rest floats (density = 0.91), and forms a slick that will spread and vaporise in the space of a few minutes or twenty to thirty minutes depending on how much has been spilled, water temperature, air temperature, wind speed and atmospheric turbulence. A small fraction will solubilise (solubility =1,100 mg/l).



### Accident scenarios

When a chemical parcel tanker is rammed sideways, the wing tanks are holed and they may contain vinyl chloride.

In a case such as this, there are three vinyl chloride spill scenarios involving four different quantities of cargo:

10 kg/h 1,000 kg/h

100 t/h

500 t (instantaneous spill)

#### The scenarios

#### "Channel"

- location 50° N ;1° W
  (60 km north of Cherbourg)
- air and water temperature: 10° C
- two wind speeds: 3 and 10 m/s
- wave height: 1 m
- current : 0,5 noeud

#### "Mediterranean"

- location 43° 10′ N ; 5° 20′ E
- (30 km from Marseille)
- air and water temperature: 20°C
- two wind speeds : 3 and 10 m/s
- wave height : 1 m
- current : 0.5 knot

#### "River"

- current 0.5 m/s
- temperature of air and water : 10°C
- wind speed: 3 m/s
- flow rate: 250 m<sup>3</sup>/s

#### A wreck

A wreck is lying on the seabed 100 metres below the surface not far from an inhabited coastline and is leaking slightly.

The decision to be taken will include a number of elements:

- Effective solubility of vinyl chloride in accident conditions;
- Leakage rate and droplet diameter;
- Currents;
- Access to tanks;
- Lifetime of the polymerisation inhibitor.

As far as we know, there are no indications enabling us to predict the quantity of product that will be dissolved during up welling and what the leakage rate will have to be for the vinyl chloride to reach the surface in noticeable quantities and evaporate.

If the wreck leaks:

- Take measurements in air and water;

- Plug the holes.

- If the wreck is not leaking (or no longer leaking)
- Commence recovery procedures and consider burning the vinyl chloride on the water surface.

<sup>\* 1</sup> knot = 1.852 km/h or 0.5148 m/s

#### Modelling

ALOHA (Area Locations of Hazardous Atmospheres) has been used to model hypothetical spillages of vinyl chloride in water ands is a Gaussian type atmospheric dispersion model developed by NOAA and the EPA (National Oceanic and Atmospheric Administration, Environmental Protection Agency) in the USA. ALOHA calculates gas cloud envelopes. It has to be pointed out that results are valid only for calm sea conditions as it does not use current speed data.

#### Results of the ALOHA model

- Weather conditions must be the following:
- stable conditions (wind speed = 3 m/s under a cloudy sky);
- unstable conditions (wind speed = 10 m/s under a sunny sky);
- average air humidity.
- Surface roughness in this case is 0.06 cm.
- Spillage location is 3 metres above sea surface.

- The gas cloud is delineated as follows:
- TLV-TWA: 1 ppm (weighted average eight hours a day and forty hours a week);
- TEEL 2: 5 ppm (maximum concentration of a substance in air below which people can be exposed for an hour without experiencing or developing symptoms or serious or irreversible effects or reducing their capacity to protect themselves);
- TEEL 3: 75 ppm (maximum concentration of a substance in air below which most people could be exposed for an hour without experiencing or developing deadly effects);
- LEL (Lower explosive limit): 2.5% = 25,000 ppm, LET (Lethal effects threshold): 30 min 149,000 ppm.



#### Results of the "Channel" scenario

Quantity spilled	Wind	Concentration (ppm)	Maximum distance Length by width	Protection
		1 (TLV-TWA)	400 m by 200 m	В
		5 (TEEL 2)	180 m by 100 m	В
	3 m/s	75 (teel 3)	44 m	С
		25,000 (LEL)	11 m	D
40 / //		149,000 (LET)	*	D
10 kg/h		1 (TLV-TWA)	41 m	В
	10	5 (TEEL 2)	19 m	В
	10	75 (teel 3)	*	С
	m/s	25,000 (LEL)	*	D
		149,000 (LET)	*	D
		1 (TLV-TWA)	4.6 km by 2 km	В
		5 (TEEL 2)	2 km by 1 km	В
	3 m/s	75 (TEEL 3)	500 m by 300 m	С
		25,000 (LEL)	22 m	D
1.000 loss //b		330,000 (LET)	*	D
1,000 kg/n		1 (TLV-TWA)	1.5 km by 1 km	В
		5 (TEEL 2)	665 m by 400 m	В
	10 m/s	75 (TEEL 3)	160 m by 100 m	С
		25,000 (LEL)	11 m	D
		149,000 (LET)	*	D
		1 (TLV-TWA)	> 10 km by 8 km	В
		5 (TEEL 2)	> 10 km by 6 km	В
	3 m/s	75 (TEEL 3)	5.6 km by 4 km	С
		25,000 (LEL)	240 m by 200 m	D
$100 \pm /b$		149,000 (LET)	42 m	D
100 t/1		1 (TLV-TWA)	> 10 km by 8 km	В
		5 (TEEL 2)	7.4 km by 5 km	В
	10 m/s	75 (teel 3)	1.8 km by 1.5 m	С
		25,000 (LEL)	90 m	D
		149,000 (LET)	20 m	D
		1 (TLV-TWA)	> 10 km by 14 km	В
		5 (TEEL 2)	> 10 km by 13 km	В
	3 m/s	75 (TEEL 3)	> 10 km by 10 km	С
500 t		25,000 (LEL)	1.4 km by 1.2 km	D
instantaneous		149,000 (LET)	290 m	D
spill		1 (TLV-TWA)	> 10 km by 12 km	В
(10 minutes)		5 (TEEL 2)	> 10 km by 10 km	В
(	10 m/s	75 (TEEL 3)	> 10 km by 7 km	С
		25,000 (LEL)	630 m by 400 m	D
		149,000 (LET)	100 m by 120 m	D

Upper explosion limit (330,000) is never reached regardless of the spill scenario.

А	No danger.	С	Use PPEs. Use a breathing apparatus.
В	Use PPEs. Use a gas mask.	D	Area where vinyl chloride concentrations reach upper explosive limits. Use a breathing apparatus and explosion proof equipment.

\*: distance is too small to be calculated by the model

Quantity spilled	Wind	Concentration (ppm)	Maximum distance Length by width	Protection
		1 (TLV-TWA)	400 m by 200 m	В
		5 (TEEL 2)	200 m by 100 m	В
	3 m/s	75 (TEEL 3)	46 m	С
		25,000 (LEL)	11 m	D
10 km/h		149,000 (LET)	*	D
то ку/п		1 (TLV-TWA)	42 m	В
		5 (TEEL 2)	19 m	В
	10 m/s	75 (teel 3)	*	С
		25,000 (LEL)	*	D
		149,000 (LET)	*	D
		1 (TLV-TWA)	4.6 km by 2 km	В
		5 (TEEL 2)	2 km by 1 km	В
	3 m/s	75 (TEEL 3)	510 m by 300 m	C
		25,000 (LEL)	23 m	D
1.000 loss /la		149,000 (LET)	*	D
1,000 kg/h		1 (TLV-TWA)	1.6 km by 1 km	В
		5 (TEEL 2)	700 m by 400 m	В
	10 m/s	75 (TEEL 3)	170 m by 100 m	С
		25,000 (LEL)	11 m	D
		149,000 (LET)	*	D
		1 (TLV-TWA)	> 10 km by 8 km	В
	3 m/s	5 (TEEL 2)	> 10 km by 6 km	В
		75 (teel 3)	5.7 km by 4 km	С
		25,000 (LEL)	260 m by 250 m	D
$100 \pm h$		149,000 (LET)	43 m	D
100 (/11		1 (TLV-TWA)	> 10 km by 8 km	В
		5 (TEEL 2)	7.5 km by 5 km	В
	10 m/s	75 (TEEL 3)	2 km by 1.5 km	С
		25,000 (LEL)	86 m	D
		149,000 (LET)	19 m	D
		1 (TLV-TWA)	> 10 km by 14 km	В
		5 (TEEL 2)	> 10 km by 13 km	В
	3 m/s	75 (TEEL 3)	> 10 km by 10 km	С
500 t		25,000 (LEL)	1.3 km by 1.2 km	D
instantaneous		149,000 (LET)	300 m	D
spill		1 (TLV-TWA)	> 10 km by 13 km	В
(10 minutes)		5 (TEEL 2)	> 10 km by 12 km	В
(	10 m/s	75 (TEEL 3)	> 10 km by 8 km	С
		25,000 (LEL) 650 m by 400 m		D
		149,000 (LET)	100 m by 120 m	D

#### Results of the "Mediterranean" scenario

Upper explosion limit (330,000) is never reached regardless of the spill scenario.

А	No danger.	С	Use PPEs. Use a breathing apparatus.
В	Use PPEs. Use a gas mask.	D	Area where vinyl chloride concentrations reach upper explosive limits. Use a breathing apparatus and explosion proof equipment.

\*: distance is too small to be calculated by the model

#### Results of the "River" scenario



Spillage of vinyl chloride in a river. Cloud dispersion will mainly be affected by the wind.

Quantity spilled	antity spilled Wind Concentration (ppm)		Maximum distance Length by width	Protection
		1 (TLV-TWA)	400 m by 200 m	В
	3 m/s	5 (TEEL 2)	180 m by 100 m	В
10 kg/h		75 (teel 3)	44 m	С
0,		25,000 (LEL)	11 m	D
		149,000 (LET)	*	D
		1 (TLV-TWA)	4.6 km by 2 km	В
		5 (TEEL 2)	2 km by 1 km	В
1,000 kg/h	3 m/s	75 (TEEL 3)	500 m by 300 m	С
		25,000 (LEL)	22 m	D
		149,000 (LET)	*	D
		1 (TLV-TWA)	> 10 km by 8 km	В
	3 m/s	5 (TEEL 2)	> 10 km by 6 km	В
100 t/h		75 (TEEL 3)	5.6 km by 4 km	С
		25,000 (LEL)	240 m by 200 m	D
		149,000 (LET)	42 m	D
		1 (TLV-TWA)	> 10 km by 14 km	В
500 t		5 (TEEL 2)	> 10 km by 13 km	В
Instantaneous	3 m/s	75 (TEEL 3)	> 10 km by 10 km	C
spill (10 minutes)		25,000 (LEL)	1.4 km by 1.2 km	D
(10 minutes)		149,000 (LET)	290 m	D

Upper explosion limit (330,000) is never reached regardless of the spill scenario.

А	No danger.	С	Use PPEs. Use a breathing apparatus.
В	Use PPEs. Use a gas mask.	D	Area where vinyl chloride concentrations reach upper explosive limits. Use a breathing apparatus and explosion proof equipment.

\*: distance is too small to be calculated by the model

**C3** 

### **Consumption scenarios**

Since vinyl chloride is a gas, slightly soluble and only slightly prone to bio accumulated in the trophic chain, it is unlikely for it to be present in sufficient and significant quantities to have an impact on people who eat exposed seafood.

# Spill response

Feedback : the Brigitta Montanari	D1
Response recommendations —	D2
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Measurement devices and waste processing	D5

### Feedback: the Brigitta Montanari

(THE SINKING AND FATE OF THE CHEMICAL TANKER *BRIGITTA MONTANARI*, M.AHEL. Centre of Marine Research Zagreb, Rudjer Boskovic Institute, Zagreb YOUGOSLAVIA)

An Italian chemical parcel tanker, the *Brigitta Montanari* carrying more than **1,300 tonnes of vinyl chloride monomer (VCM)** sank in the Adriatic Sea on 16 November 1984, at a depth of 82 m near Sibenik (Yugoslavia).

The response option chosen on this occasion was **to refloat her and pump off** the cargo. This option was selected for ecological, technical reliability, safety and economic viability reasons.

Salvage operations started in August 1987

on the assumption that the cargo tanks containing vinyl chloride were not damaged. But a leakage of 1 kg per day was detected at the outset and was thought to be located portside between the hull and the deck (the wreck was lying on her starboard hull). In such a situation, the first thing to do is to place the wreck on an even keel and is usually the first stage in the refloating procedure, but could have been dangerous due to a sudden and very large release of vinyl chloride. A 5mm hole was drilled in the deck to free the vinyl chloride but a major leakage of VCM occurred immediately (estimated at 3 tonnes a day). The concentration of vinyl chloride in the water column 300 metres from the wreck was more than 5  $\mu$ g/l.

After leaking for several days, divers were able to connect PVC pipes to the holes in the deck. The vinyl chloride was then piped to the surface and either left to disperse in the atmosphere or was burned. The salvage operation was stopped during the winter time of 1987 and resumed the following spring. The wreck was then raised to 55 metres and towed to a sheltered bay near the island of Kaprije and was grounded. She was subsequently raised to 30 metres ensuring that hydrostatic pressure was greater outside the tanks. This precaution was taken to avoid further spillage as the cargo tanks were thought to be corroded by now. Whilst maintaining this depth, 700 tonnes of cargo were lightered to another vessel.

Biological monitoring had been initiated in 1987 on several benthic communities and consisted of pathohistological and biochemical tests. Organisms were harvested from the wreck, around the wreck and from an unpolluted benchmark/reference location. Results showed that the vinyl chloride leakage had not produced acute toxicity for the organisms studied. The wreck was covered with marine organisms despite the fact that VCM concentrations were often seen to be relatively high (in excess of 10 mg/l). In the light of these results, (pathohistological and biochemical) it seems that sub lethal effects may have occurred on sedentary benthic fish populations but these results were not subsequently confirmed.

### **Response recommendations**

### Responders must be suitably trained, if such is not the case let the chemical evaporate.

#### Is response tenable?

- Major fires involving vinyl chloride are virtually impossible to extinguish. Response in a case such as this is impossible as no-one can come closer than 500 metres owing to the risk of explosion.
- Responders approach a wreck such as this from upwind, wearing breathing apparatuses and PPEs that are chemical proof and air tight, they will use gas metres and toxic vapour detectors: HNU photo-ionisation detectors fitted with 10.2 eV lamps and Draëger tubes (n°67 28061; 67 28031, CH 19 601).

In case of fire, use detectors that can identify substances such as phosgene, hydrogen chloride and carbon oxide.

• Equipment must be explosion proof.

D2

• On board responders will have to wear protective coveralls and positive pressure breathing apparatuses.

### Emergency measures in the event of a leakage or a spill.

- Forbid entry to the area until vapours have dispersed. Ban bathing and beaches and advise local populations to stay indoors in unventilated premises.
- Eliminate likely causes of ignition and prevent vapour from entering the area. They could ignite and produce flashback.
- Plug the leak and spot spilled substances if conditions are harmless. Otherwise spray water and protect responders (stay well back from the water cloud).
- Avoid all contact with the liquid and do not breathe in vapours.
- **Contain** the spilled liquid if possible and try to spray the area with fluorinated foam.

### Emergency measures in the event of a fire

- Vinyl chloride fire
- If the leak cannot be plugged, evacuate the area and let the fire burn as this will prevent the accumulation of explosive mixtures.
- To extinguish a small fire, spray foam, dry powder, CO<sub>2</sub> or water.
- If the fire gets out of control or if the tank is directly exposed to flames, retreat 500 metres.

(French National Fire Brigade Federation, 2002)

#### If the fire does not involve any vinyl chloride at all

In the event of an outbreak of fire on board a ship (excluding cargo tanks), the use of thermal cameras will enable hotspot identification. Responders will assess VCM exposure levels and decide if they can respond safely whilst reducing risks.

 If response is envisageable and in a bid to control the fire: try to move the vinyl chloride tanks if possible and if no danger is involved. If not, hose the tanks down if they are exposed to fire, (they could explode). Stay at a safe distance and spray water, keep well away from the ends of the tanks and retreat immediately if the safety valves start whistling or if the tank colour changes.

### **Response techniques**

#### Transhipment

- Unloading a pressurised tank containing liquefied vinyl chloride will require great care and many precautions. Accumulated electrostatic charges can cause the aerosol to ignite.
- Lightering can be done by pumping the cargo or using an inert gas to force the cargo out of the tank (nitrogen or flue gas). Pressure exerted on the tank must never exceed service pressure at which the safety valve will blow.
- Inject a polymerisation inhibitor (phenol derivative) if necessary.
- Recommended equipment is the following:
- Carbon steel NC centrifugal pump with explosion-proof motor, without an admission seal;
- Pipes and connectors made of non-welded carbon steel or stainless steel designed for a minimum service pressure of 690 to 1,035 kPa;
- Pipe seals will be flanged or welded;
- Stainless steel sleeve valves;
- Viton seals (at normal temperature);
- Non recommended equipment: rubber (natural or synthetic), copper, aluminium, brass, and PVDC (polyvinylidene chloride).

#### Responding to spills

#### At sea

Most often, response will be untenable and the only course of action will be to assess the extent of the flammable and toxic plume with forecast models and in-situ control of the plume with gas metres.

#### In a harbour area

When a spill occurs it can be recovered in closed and opaque recipients. The job will have to be done by trained responders and appropriate equipment. Otherwise, the only other alternative is to let it evaporate.

On water areas, booms can be used to contain the slick provided that responders stay clear of toxic and explosive areas. The evaporation process can be curbed by the use of chemical foam.

Containment will be conducted from facilities such as mooring buoys sinkers, banks, etc. and will not require the use of motorised equipment.

Some treatment products can be used such as:

- sorbents: polyurethane

- gelling agents, flocculants, neutralisers Dispersants will be inoperative.

#### Inland waters

Water can be contained by booms providing response is organised quickly. As with spills at sea, recovery will have to be conducted very carefully otherwise it will be best to let it evaporate.

#### On the ground

In case of a spill:

- Make booms to contain the product.
- If temperatures are low and the vinyl chloride is evaporating slowly, it can be recovered by pumping. This will require trained personnel and suitable equipment, other-

wise it will be best to let it evaporate.

- In the event of small spills, natural or synthetic sorbents can be used and recovered by spade later on.
- If a curtain of water is sprayed for protection purposes, run-off water will have to be contained to prevent it from reaching the sewage system or a river as long as the majority of the vinyl chloride has not entirely evaporated.

### **Choosing PPEs**

### Important: Provide maximum protection if toxic concentrations are high.

Choosing breathing apparatuses (Fingas, M., 2000)

Depending on maximum concentrations (CME)<sup>2</sup>:

- Gas masks can be used in concentrations of up to 25 ppm.
- Sealed positive pressure suits: no limit.

#### Choosing protective clothing (CEFIC, 2003)

- Protective clothing for chemicals.
- Protective underclothes and thick fabric or rubber gloves.
- Full face gas masks.
- Protect responders from heat by a water curtain or similar heat protection system.

#### What to use during a spill (Fingas, M., 2000)

- Open circuit on demand positive pressure suits are the best way of protecting responders as they afford a protection factor of about 10,000 (if the VLE is 20 ppm, responders will be protected up to 200,000 ppm in open air).
- Use an open circuit positive pressure suit when confronted with the unknown, entering premises for which toxic concentrations are unavailable or known to be high or if the premises are likely to be lacking in oxygen (confined area).
- Warning: some facial characteristics such as scars, narrow face or facial hair can prevent a good fit and impair protection for responders.

• Problems related to temperature:

In warm weather: profuse sweating will prevent air tightness between the mask and the skin.

In cold weather: ice may form on the expansion valve and the face piece may mist over.

If air breathing systems are to be used, place the oxygen cylinders in heated vehicles prior to use: humidity may freeze the apparatus.

• Problems with lenses:

Warning: ordinary lenses cannot be worn under a mask (get a special pair of lenses). Contact lenses can however be worn with new models that afford air exchange (they do not dry and do not stick to the eye ball).

New mask users are advised to try them on for fit and other users can conduct regular trials.

<sup>2:</sup> CME values can vary from one manufacturer or model to another, please contact the manufacturer for special data.

#### **Chemical resistance**

Permeation times for different fabrics (Forsberg et Keith (1995) In Environnement Canada, 2000)

Nitrile: 300 minutes

Viton: 260 minutes

### Measures required after using PPEs during a spill

- Decontaminate boots after a spill. Use a foot bath and a light detergent. Don't forget to treat the water.
- Decontaminate gloves separately in a bucket with a light detergent.

Materials	Degradation	Permeability	
Neoprene			No data
Polyvinyl alcohol (PVA)			No data
Polyvinyl chloride (PVC)			No data
Natural rubber			No data
Linear Low Density Polyethylene (LLDPE)	No degradation test	soaking time > 480 min permeability > 0.9 µg/cm²/min 0 to 1/2 drop/hour traverses LLDPE	Very suitable

# Measurement and devices and waste treatment

Devices (Environnement Canada, 2001)

Instruments	Manufacturers
Snapshot	Photovac
PID Mini RAE 2000	Manametrics
Photo-ioniser	HNU

#### Waste treatment

- Incineration
- Dilute the pollutant to obtain a 1% solution.

- Pour onto vermiculite, bicarbonate of soda or on a mixture of sand and ashes at a ratio of 90/10.

- Burn in a high temperature incinerator liquid injection incineration (at 650 to 1,600°C) or fluidised bed (450 to 980°C).

Flue gases must be directly purified of all hydrogen chloride.

- Biological treatment is 100% efficient.
- Adsorption on active charcoal granules is about 50% efficient.

#### Addresses where Special Industrial Waste can be treated in France (SIW)

Companies likely to treat SIW can be found at the following address on the web:

http://www.observatoire-dechets-bretagne.org/

#### Vinyl chloride manufacturers (CHIMEDIT, 2004)

ATOFINA, Union Carbide Corp., HydroPolymers Ltd.

# **Supplementary information**

Bibliography	E1
Glossary —	E2
Acronyms	E3
Useful web adresses	E4

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### Glossary

#### Admissible daily dose (ADD)

For humans this dose is the quantity of a substance that can be ingested by an organism in the space of a day for the rest of its life without presenting a health hazard for the organism in question.

#### Adsorption

Elevation of the concentration of a substance dissolved at the interface of a condensed phase and a liquid phase under the influence of surface forces. Adsorption can also occur at the interface of a condensed phase and a gas phase.

#### AEGLs (Acute Exposure Guideline Levels )

Defined by the National Research Council's Committee on Toxicology (USA), AEGLs are three levels above which the general population may experience certain effects. These three AEGLs are given for five exposure times: 10, 30 min, 1, 4 and 8 hours.

<u>AEGL 1:</u> is the airborne concentration (expressed as ppm (parts per million) or mg/m<sup>3</sup> (milligrams per cubic meter) of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic non sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

<u>AEGL 2:</u> is the airborne concentration (expressed as ppm or  $mg/m^3$ )

of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

<u>AEGL 3:</u> is the airborne concentration (expressed as ppm or  $mg/m^3$ ) of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

#### **Bio accumulation**

Continued retention of a substance in the tissue of an organism throughout the course of its existence (the bioaccumulation factor increases all the time).

#### **Bio amplification**

Retention of a substance in the tissue at increasingly higher concentrations the higher one goes in the food chain.

#### Bio concentration

Retention of a substance in the tissue of an organism to the extent that the content of the substance in the tissue exceeds that found in nature at one point in time of the lifetime of the organism.

#### Bio concentration factor (BCF)

According to EPA guidelines, "the BCF is defined as the ratio of chemical concentration in the organism to that in surrounding water. Bio concentration occurs through uptake and retention of a substance from water only, through gill membranes or other external body surfaces. In the context of setting exposure criteria it is generally understood that the terms "BCF" and "steady-state BCF" are synonymous. A steady-state condition occurs when the organism is exposed for a sufficient length of time that the ratio does not change substantially."

#### **Bio transformation**

Biological transformation of substances in a living organism via enzymatic processes.

**BLEVE** (Boiling Liquid Expanding Vapour Explosion) A violent vapour explosion of a liquid that is significantly above its usual boiling point at atmospheric pressure after a tank has failed.

#### Boiling point (cf diagram on page 39)

(measured at a pressure of 1 atmosphere) Temperature at which a liquid begins to boil. More specifically: when the temperature at which saturating vapour pressure of a liquid is equal to standard atmospheric pressure (1 013,25 hPa). The boiling point thus measured depends on atmospheric pressure.

#### Critical pressure

Maximum pressure for which the distinction can be made between a gas and a liquid.

#### Critical temperature (cf figure on page 39)

Temperature at which, when boiling, there is no longer any clear cut transition between the liquid and the gas state.

#### Daily exposure dose

Dose (internal or external) of a substance in an organism compared to the weight of the individual

and the number of days of exposure (in the case of a non carcinogenic substance) and the number of days lived by the organism (for a carcinogenic substance).

#### Decomposition products

Products stemming from chemical or thermal disaggregation of a substance.

#### Efficient concentration 50 ( $EC_{50}$ )

Concentration causing a given effect (mortality, growth inhibition...) for 50% of the population under consideration during a given period of time.

#### Emergency Response Planning Guidelines (ERPG)

The American International Health Alliance, AIHA set three maximum concentrations in 1988 below which a category of effects is not expected for an exposure duration of one hour intended to protect the population at large.

<u>ERPG1</u> is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing other than mild transient adverse health effects or perceiving a clearly defined objectionable odour.

ERPG2 is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to take protective action.

<u>ERPG3</u> is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects.

#### Exposure limit value (ELV)

Ceiling exposure value measured for a maximum duration of 15 minutes.

#### Flash point

The lowest temperature at which a substance generates vapours that ignite or burn immediately when approached by a flame.

#### Foam

Product that forms an abundant amount of foam. The foam layer absorbs most of the vapours, physically eliminates vapours, isolates the chemical from sunlight and ambient air which reduces the amount of heat and subsequent vaporisation.

#### Henry's law constant

Property of a substance to divide itself into two distinct phases of a binary air/water system.

**Immediately Dangerous to Life or Health** (IDLH) Level below which a worker can, without availing himself of a respirator and without impairing his ability to escape to safety in thirty minutes in the event of sudden exposure to a dangerous atmosphere.

#### Irreversible effect threshold (IET)

Concentration, for a stated exposure duration, above which irreversible effects can occur in the exposed population.

#### Lethal effect threshold (LET)

Concentration, for a stated exposure duration, above which mortality can be observed in the exposed population.

#### Lower Explosive Limit (LEL)

Minimum airborne concentration above which vapours ignite.

#### Marine pollutant

Substance, object or matter likely to cause serious damage to the marine environment when spilled.

**MARVS** (Max Admissible Relief Valve System) Indicates the maximum admissible calibration of pressure relief valves of a cargo tank.

#### Mean exposure value (MEV)

Value that has been measured or estimated for a work station lasting 8 hours and is intended to protect workers from long term effects. MEV can be exceeded for very short periods providing the ELV value (should there be one) is not exceeded.

#### Median lethal concentration (LC<sub>50</sub>)

Concentration of a substance deduced statistically that should, during exposure and for a given period of time or subsequently, cause the death of 50% of the animals exposed during a given period of time.

#### Melting point (cf page 39)

Temperature at which solid and liquid state coexist. The melting point is a constant for a pure substance and is usually calculated at standard atmospheric pressure (one atmosphere).

#### Minimum Risk Level (MRL)

This level is an estimate of daily human exposure to a chemical which probably has no appreciable risk of non-carcinogenic harmful effect on health for a specific exposure duration. **Miscible** Matter that mixes easily with water.

#### No Observed Effect Level (NOEL)

The highest dose of a substance that causes no distinct changes as compared with those observed in control animals.

#### N-octanol/water distribution coefficient (Kow)

Ratio of the equilibrium concentrations of a substance dissolved in a two phase system made up of two solvents that virtually do not mix.

#### Olfactory threshold

Minimum air or waterborne concentration to which the human nose is sensitive.

### Organic carbon/water distribution coefficient $\left(\text{Koc}\right)$

(for organic substances) Ratio of the amount of compound absorbed per unit mass of organic carbon in the soil or in a sediment and the concentration of the same compound in a water solution in a state of equilibrium.

#### Photo-oxidation

Oxidation of a chemical compound caused by exposure to light energy.

#### Polymerisation

This term describes the chemical reaction generally associated with the production of plastics. Fundamentally, the individual molecules of a chemical (liquid or gas) react together to form a long chain. These chains can be used for many applications.

#### Protective equipment

This means the respiratory or physical protection of a human being. Protection levels have been defined, including both protective clothing and breathing apparatus as accepted by response authorities such as the USCG, NIOSH and the EPA (US).

Level A : an SCBA (Self contained breathing apparatus/ respirator) and fully air and chemical-tight over suits (that resist permeation).

Level B : an SCBA and an over suit that protects against liquid spray (splash proof).

Level C : a full face mask or goggles and a suit that protects responders against chemicals (splash proof).

Level D : overalls without a respirator.

#### Rate of evaporation or volatility (ether = 1)

The rate of evaporation expresses the number of times that a product takes to evaporate as

compared with a benchmark substance (ether for instance) This rate varies with the nature of the product and temperature.

#### Regression speed

Speed at which a burning liquid slick reduces in thinness. For a given liquid, this speed is constant regardless of the slick surface (slick diameter bigger than 2 metres). Regression speed allows to estimate the total duration of a fire if no-one tries to extinguish it. For instance for a 1,000 mm thick slick, the regression speed may be 10 mm/minute the fire lasts for 1,000/10= 100 minutes

#### **Relative density**

Ratio of the mass of a substance to that of water for a liquid or to that of air for a gas.

#### Relative vapour density

Weight of a volume of vapour or pure gas (without air)

compared to that of an equal volume of dry air at the same temperature and pressure. A vapour density lower than 1 indicates that the vapour is lighter than air and will have a tendency to rise. When vapour density is higher than 1the vapour is heavier than air and will tend to stay near ground level and spread.

#### Self-ignition temperature

Minimal temperature at which vapours ignite spontaneously.

#### Solubility

Quantity of a substance dissolved in water. It will depend on salinity and temperature.

#### Source of ignition

Examples of sources of ignition: heat, sparks, flame, static electricity and friction. Sources of ignition should always be eliminated when handling flammable products or responding to an emergency in risky areas (use explosion proof pumps and VHF walky-talkies.

#### Surface roughness

Length of a transfer area between the atmospheric layer and a contact surface. This will depend on the mean size of the roughness of the contact area and atmospheric parameters near the water surface. When the sea is calm it is of the order of 0.02 to 0.06 cm.

#### Surface tension

A constant that expresses the force owing to molecular interaction exerted at the surface of a liquid when it comes into contact with another surface (liquid or solid) and that affects surface dispersion.

### **Temporary Emergency Exposure Limits** (TEEL) Exposure times when there is no ERPG.

TEEL 0 is the threshold concentration below which a large part of the population will experience no effect on health.

TEEL 1 is equivalent to ERPG1, TEEL 2 is equivalent to ERPG2 and TEEL 3 is equivalent to ERPG3.

#### Threshold Limit Value (TLV)

Average limit value (weighted as a function of time) that people can be exposed to regularly at work 8 hours a day, 5 days a week without experiencing harmful effects. This value was defined and determined by ACGIH.

#### TLV-STEL

Mean weighted 15 minutes concentration that must never be exceeded at any time during the day.

#### <u>TLV-TWA</u>

Man weighted values for an eight hour period per day and forty hours a week.

TLV-ceiling

Ceiling values never to be exceeded not even for an instant.

#### Unconfined Vapour Cloud Explosion (UVCE)

Explosion of a gas cloud or slick of combustible vapours in an unconfined environment.

#### Upper Explosive Limit (UEL)

Maximum airborne concentration of a compound above which vapours will not ignite for lack of oxygen.

#### Vapour pressure or tension

Partial pressure of gas molecules in a state of equilibrium with the liquid phase for a given temperature.



### Acronyms

ACGIH	American Conference of Governmental Industrial Hygienists			
	Accords De Navigation Accord européen relatif au transport international des marchandises Dangereuses par veie de			
ADINK	Navigation intérieure ("R" sur le Rhin)			
ADR	Accords européens relatifs au transport international des marchandises dangereuses par route			
AEGLs	Acute Exposure Guideline Levels			
AFSSA	Agence Française de Sécurité Sanitaire des Aliments			
AIHA	American International Health Alliance			
ALOHA	Areal Locations of Hazardous Atmospheres			
AFFF	Agent Formant un Film Flottant			
APRA	Appareil de Protection Respiratoire Autonome			
ATSDR	Agency for Toxic Substances and Disease Registry			
BCF	Bio Concentration Factor			
BLEVE	Boiling Liquid Expanding Vapour Explosion			
CAS	Chemical Abstracts Service			
CE	Concentration Efficace			
CEA	Commissariat à l'Energie Atomique			
CEDRE	Centre de Documentation de Recherche et d'Expérimentations sur les pollutions accidentelles			
	des eaux			
CEFIC	Conseil Européen des Fédérations de l'Industrie Chimiques			
CHRIS	Chemical Hazards Response Information System			
CL	Concentration médiane Létale			
CME	Concentrations Maximales d'Emploi			
CSST	Commission de la Santé et de la Sécurité du Travail			
CSTEE	Scientific Committee on Toxicity, Ecotoxicity and the Environment			
CIE	Centre Technologie Environnementale			
DDASS	Direction Départementale des Affaires Sanitaires et Sociales			
DDE	Direction Departementale de l'Equipement			
DJA	Dose Journaliere Admissible			
DJE	Dose Journaliere Efficace			
DRASS	Direction Regionale des Affaires Sanitaires et Sociales			
	Directions Regionales de l'Industrie, de la Recherche et de l'Environnement			
ECB	European Chemicals Bureau			
EINECS	European Inventory of Existing Chemical Substances			
	Environmental Protection Agency			
	Equipement de Flotection individuelle Emorgonou Posponso Planning Guidalinos			
	Einergency Response Flamming Guidelines Fiche de Doppées de Sécurité			
	Hazardous Substances Data Bank			
ΙΔΤΔ	International Air Transport Association			
IBC	International Rulk chemical Code			
	International Chemical Safety Cards			
	Immediately Dangerous to Life or Health concentrations			
IFREMER	Institut Français de Recherche nour l'Exploitation de la Mer			
IGC	International Code for the Construction and Equipement of Shins Carrying Liquefied Gases in Rulk			
IMDG	International Maritime Dangerous Goods			
IMO	International Maritime Organization			
INCHEM	INternational CHEMical industries			
INERIS	Institut National de l'Environnement Industriel et des Risques			

INRS	Institut National de Recherche et de Sécurité pour la prévention des accidents du travail
	et des maladies professionnelles
IPCS	International Programme on Chemical Safety
IPSN	Institut de Protection et de Sécurité Nucléaire
IUCLID	International Uniform Chemical Information Database
LEL	Lower Explosive Limit
LET	Lethal Effect Threshold
LLDPE	Linear Low Density PolyEthylene
MARPOL	MARine POLlution
MARVS	Maximale Admissible Relieve Valve System
MCA	Maritime and Coast Guard Agency
MEDD	Ministère de l'Ecologie et du Développement Durable
MP	Marine Pollutant
MRL	Minimum Risk Level
NIOSH	National Institute for Occupational Safety and Health
NOAA	National Oceanic and Atmospheric Administration
NOEC	No Observed Effect Concentration
OCDE	Organisation de Coopération et de Développement Economique
OMI	Organisation Maritime Internationale
OMS	Organisation Mondiale de la Santé
PEC	Predicted Effect Concentration
PID	Photo-ionisation Detector
PNEC	Predicted No-Effect Concentration
ppm	Partie par million
pTBC	para Tertio Butyl Catéchole
ROV	Remot Operated Vehicle
PVC	Poly(Vinyl Chloride)
PVDC	Polychlorure de vinylidène
PVDF	Polyfluorure de vinylidène
SEBC	Standard European Behaviour Classification System of Chemicals spilled into the sea
SIDS	Screening Information DataSet
SIW	Special Industrial Waste
TEEL	Temporary Exposure Limits
TGD	Technical Guidance Document
TLV-ceiling	Threshold Limit Values - ceiling
TLV-STEL	Threshold Limit Values - Short Term Exposure Limit
TLV-TWA	Threshold Limit Values - Time Weighted Average
TNO	Toegepast - Natuurwetenschappelijk Onderzoek
	In english: the Netherlands Organisation for Applied Scientific Research
UEL	Upper Explosive Limit
UIISC	Unité d'Instruction et d'Intervention de la Sécurité Civile
US EPA	United States Environmental Protection Agency
UVCE	Unconfined Vapor Cloud Explosion
VHF	Very High Frequency
VLE	Valeur Limite d'Exposition
vinyl chlorideM	Vinyl Chloride Monomer
VME	Valeur Movenne d'Exposition
v/v	volume à volume
ZDO	Zone de Défense Ouest

### Useful web adresses

Accord de Bonn, Système européen de classification, [on line], Available at: http://www.bonnagreement.org/fr/html/counter-pollution\_manual/chapitre25.htm AFSSA (Agence Française de Sécurité Sanitaire des Aliments), [on line], Available at: http://www.afssa.fr/ ATOFINA, [on line], Available at: http://www.atofina.com/groupe/gb/f\_elf\_2.cfm ATSDR (Agency for Toxic Substances and Disease Regestry), [on line], Available at: http://www.atsdr.cdc.gov/tfacts53.pdf Cedre (Centre de documentation de recherche et d'expérimentations sur les pollutions accidentelles des eaux), [on line], Available at: http://www.cedre.fr/ CEFIC (European Chemical Industry Council), [on line], Available at: http://www.ericards.net/ Chemfinder : [on line], Available at: http://chemfinder.cambridgesoft.com/ CHRIS (Chemical Hazards Response Information System), [on line], Available at: http://www.chrismanual.com/ CRIOS (Carcinogenic Risk In Occupational Settings), [on line], Available at: http://cdfc.rug.ac.be/HealthRisk/default.htm CSST (Commission de la Santé et de la Sécurité du Travail), [on line], Available at: http://www.reptox.csst.gc.ca/ CSTEE (Comité Scientifique sur la Toxicité, l'Ecotoxicité et l'Environnement), [on line], Available at: http://europa.eu.int/comm/food/fs/sc/sct/out117\_en.pdf CTE (Centre de Technologie Environnementale du Canada) [on line], Available at: http://www.etc-cte.ec.gc.ca/etchome\_f.html Environnement Canada : Mesure de la pollution, [on line], Available at: http://www.etcentre.org/databases/fuelcalc\_f.html European Chemicals Bureau, Risk Assessment, [on line] Available at: http://ecb.jrc.it/existing-chemicals/ Hygiène et sécurité du travail, Listes des Valeurs Limites d'Exposition et des Valeurs Moyennes d'Exposition, [on line], Available at: http://www.inrs.fr/produits/pdf/nd2098.pdf ICSC (International Chemical Safety Cards) Programme International sur la Sécurité des Substances Chimiques (Fiches), [on line], Available at: http://www.cdc.gov/niosh/ipcs/french.html IDLH, Documentation for Immediately Dangerous to Life or Health Concentrations, Liste de 387 produits (originales et révisées) [on line],

Available at: http://www.cdc.gov/niosh/idlh/intridl4.html

**INCHEM** (International Chemical Industries.Inc.), [on line], Available at: http://www.inchem.org/ **INCHEM,** Liste des limites d'exposition par pays, [on line], Available at: http://inchem.org/pages/ilodb.html

**INERIS** (Institut National de l'Environnement Industriel et des Risques), [on line], Available at: http://www.ineris.fr/

**INRS** (Institut National de Recherche et de Sécurité pour la prévention des accidents du travail et des maladies professionnelles), [on line],

Available at: http://www.inrs.fr/index\_fla.html

IPCS (the International Programme on Chemical Safety), [on line],

Available at: http://www.ilo.org/public/english/protection/safework/cis/products/icsc

Lyondell, entreprise chimique, [on line],

Available at: http://www.lyondell.com/html/products/products/sm.shtml

**NIOSH** (National Institute for Occupational Safety and Health), [on line], Available at: http://www.cdc.gov/niosh/homepage.html

**NOAA** (National Oceanic and Atmospheric Administration), historical incident search page, [on line], Available at: http://www.incidentnews.gov/incidents/history.htm

**Sécaline** (Système d'informations et de conseils sur les produits et déchets toxiques), [on line], Available at: http://www.secaline.alison-envir.com/

SHELL, Fiche de sécurité (MSDS), [on line],

Available at: http://www.euapps.shell.com/MSDS/GotoMsds

UIC (Union des Industries Chimiques), [on line],

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**UNEP** (United Nations Environment Programm), OECD Initial Assessment Reports for High Production Volume Chemicals including Screening Information Data Sets (SIDS), [on line] Available at: http://www.chem.unep.ch/irptc/sids/oecdsids/sidspub.html

Université de Nancy-Metz, (fiches de sécurité, traitement des déchets, écotoxicité des produits chimiques) [on line],

Available at: http://www.ac-nancy-metz.fr/enseign/physique/chim/sc\_fds.htm

**US Departement of Energy's,** Chemical Safety Program, liste des ERPG, [on line], Available at: http://tis.eh.doe.gov/web/chem\_safety/teel.html

US EPA (Environmental Protection Agency), [on line],

Available at: http://www.epa.gov/

US EPA, liste des AEGLs, [on line],

Available at: http://www.epa.gov/oppt/aegl/chemlist.htm

### ANNEXES

### Annex 1: Extra physical and toxicological data

Annex 2: Fax format data card

#### ANNEX 1: ADDITIONAL PHYSICAL AND TOXICOLOGICAL DATA

### Classification (ICSC, 2000 et INRS, 2000)

CAS N°: 75-01-4 EC N°(EINECS): 200-831-0 UN N°: 1086 Index N°: 602-023-00-7 Class: 2

#### Physical data

Conversion factor: in air  $1 \text{ ppm} = 2.6 \text{ mg/m}^3$  $1 \text{ mg/m}^3 = 0.385 \text{ ppm}$ 

Molar mass: 62.5 g/mol

Liquid volume mass At 20°C: 910 kg/m<sup>3</sup> At -14°C: 970 kg/m<sup>3</sup>

Volume mass of vapour At 15°C: 8 kg/m<sup>3</sup> (2,900 hPa)

#### Physical state

At normal temperature and pressure conditions Appearance: gas. Colour: colourless. Odour: ethereal, hardly noticeable. Is generally used after pressurised liquefaction.

#### Density

Density of the liquid (water = 1): 0.9121 to 20°C Density of gas (air = 1): 2.15 to 20°C Relative density in seawater: 0.884 (liquid 20°C)

#### Solubility

In freshwater: 1,100 mg/litre at 25°C	INRS, 2000
(Range: 915-2,770 mg/litre at 20-25°C)	INERIS, 2001

In other compounds Very soluble in many organic solvents: diethyl oxide, ethanol, chlorinated solvents and lipids. INERIS, 2001

(1996) In INERIS, 2001 FDS ATOFINA, 2004

HSDB (1999), Verschueren

FDS ATOFINA, 2004

INRS, 2000

INRS, 2000

INRS, 2000

INRS, 2000

Vinyl chloride Chemical response guide

#### Vapour tension



**Temperatures to remember** Boiling point at 1 atm: -13.9°C Melting point: - 153.7°C Flash point (in closed container): - 78°C Self-ignition temperature: 472°C Critical temperature: 158.4°C Latent vaporisation heat: 20.62 kJ/mol (at boiling point)

Polymerisation temperature: 4.45 kJ/mol at -150°C 71.18 kJ/mol at 156.6°C

#### Other properties

Henry's law constant: 2.73.103 Pa.m<sup>3</sup>/mol at 20-25°C (Range: 1.88 to 8.103 Pa.m<sup>3</sup>/mol at 20-25°C)

Diffusion coefficient in air: 0.106 cm<sup>2</sup>/s at 25°C

Diffusion coefficient in water: 1.2.10-6 cm<sup>2</sup>/s at 25°C

Dynamic viscosity: vapour: 1.072.10-5 Pa.s at 20°C

Critical pressure: 5.34 MN/m<sup>2</sup> or 52.7 atmospheres

Surface tension of liquid: 0.016 N/m at 25°C

Interface tension with liquid water: 0.03 N/m at 20°C

Olfactory thresholds:

260 ppm 1,200 ppm 3,000 ppm INRS, 2000

INRS, 2000

Kirk-Othmer (1983) In Environment Canada, 1985

Ullmann (1975) In Environment Canada, 1985

Grathwohl (1995), Hempfing (1997), HSDB (1999), US-EPA (1996) In INERIS, 2001 ; FDS ATOFINA, 2004.

US-EPA (1996) in INERIS, 2001.

US-EPA (1996) in INERIS, 2001.

HSDB (1999) in INERIS, 2001

CHRIS, 1999

CHRIS, 1999

CHRIS, 1999

CHRIS, 1999 CSST, 2002 US-EPA, 2003

### Toxicological data

#### Threshold toxicology values

TLV-TWA: 1 ppm (2.6 mg/m<sup>3</sup>) VME: 1 ppm (2.6 mg/m<sup>3</sup>) TEEL: TEEL 0: 1 ppm (2.6 mg/m<sup>3</sup>) TEEL 1: 5 ppm (13 mg/m<sup>3</sup>) TEEL 2: 5 ppm (13 mg/m<sup>3</sup>) TEEL 3: 75 ppm (195 mg/m<sup>3</sup>) Us-ACGIH (2003) in FDS ATOFINA, 2004 INERIS, 2001 U.S. Departement of Energy's, Chemical Safety Program, 2002.

MRL inhalation (acute exposure): 0.5 ppm (1.3 mg/m<sup>3</sup>) MRL inhalation (sub acute exposure): 0.03 ppm (0.078 mg/m<sup>3</sup>) ATSDR (1997) in INERIS, 2001 ATSDR (1997) in INERIS, 2001

#### General toxicity

#### Acute human toxicity

- via the respiratory tract: (INRS, 2000).

- UA moderate irritation of the bronchial tube may occur. If large quantities have been inhaled, the main effect will be a depression of the CNS (central nervous system) preceded by a feeling of euphoria. Signs that have been reported: dizziness, disorientation, drowsiness, loss of consciousness and death if exposure persists.
- Skin contact: (INRS, 2000 et ICSC, 2000) Irritational lesions of the skin have been reported in addition to frostbite.
- Eye contact: (INRS, 2000).
  Liquefied vinyl chloride coming into contact with the eyes can cause reversible corneal impairment.

#### Chronic human toxicity (INRS, 2000)

- In the event of massive exposure, trophic impairment of skin and bone have been reported and characterised by bone destruction in the fingers (but other bones can also be affected) Raynaud's syndrome and a kind of skin sclerosis.
- Digestive effects have been reported and characterised by queasiness, nausea, anorexia, hepatomegaly and often splenomegaly. Liver impairment often involves initial cytolysis followed by fibrosis and cirrhosis.
- Other symptoms can also be described: impairment of blood cell lines, impaired breathing and peripheral neuropathy.

Specific effects (INERIS, 2001, FDS ATOFINA, 2004 et INRS, 2000)

Carcinogenic effects: Classed in group C1 by CIRC-IARC. (Recognized as carcinogenic for humans) Effects on fertility: Not demonstrated. Teratogenic effects: Unconfirmed. Genotoxic effects: Overall genotoxic / causes adducts to the ADN. Mutagenic effects: Yes.

### Ecotoxicological data

#### Acute ecotoxicity

Anaerobic bacteria

 $CI_{50}$  (3.5 days) = 40 mg/L

FDS ATOFINA, 2004

Bacteria (Pseudomonas putida)	$CE_{5}$ (16h) $\geq$ 135 mg/L	FDS ATOFINA, 2004
Seaweed (Scenedesmus quadricauda)	$CL_{3}$ (8 days) = 710 mg/L	Bringmann et al., 1977
Fish (Brachydanio rerio)	$CL_{50}$ (96h) = 210 mg/L Groenev	eld et al., 1993
Micro crustaceans (Daphnia magna)	$CE_{50}$ (48h) = 103 mg/L	INERIS, 2001
INERIS has estimated this value by Q	SAR, on the assumption that the	e substance acts on aquatic
organisms via a non polar narcotic ef	fect and a Kow log number of 1.	54.

Land organisms: no valid trial results have been found in the literature.

**PNEC** (Predicted No-Effect Concentration): according to the Technical Guidance Document pursuant to (CE) 1488/94 concerning risk assessment for existing substances, the PNEC for water would be 103  $\mu$ g/litre (after applying a safety factor of 1,000 to the lowest figure for the three trophic levels).

#### Chronic ecotoxicity

No valid results have been found in the literature for aquatic or terrestrial organisms.

#### ANNEX 2: Fax format data card

#### VINYL CHLORIDE

Monochloroethylene, chloroethylene, chloroethene, monochloroethene, Ethylene monochloride, vinyl chlorideM

CAS N°. 75-01-4 EC N° (EINECS) : 200-831-0 C<sub>2</sub>H<sub>3</sub>Cl /CH<sub>2</sub>=CHCl Index N°: 602-023-00-7 UN N°: 1086 Class: 2

#### First aid data

Airborne poisoning: Go outdoors, breathe oxygen or have Eye contact: Rinse with a lot of water for a few minutes, artificial respiration if needed, admit to hospital, place under remove contact lenses and see an eye specialist if needed. neurological and liver surveillance.

Skin contact: Rinse with a lot of water (warm if possible). Frostbite must be treated as thermal burns

#### Do not treat with catecholamines

#### Conversion factor

 $1 \text{ ppm} = 2.6 \text{ mg/m}^3$  $1 \text{ mg/m}^3 = 0.385 \text{ ppm}$ 

Relative density (water=1): 0.9121 Relative vapour density (air=1): 2.15 Solubility in freshwater: 1,100 mg/litre at 25°C Vapour pressure/tension: 340 kPa at 20°C Olfactory threshold: airborne: 260 to 3,000 ppm Diffusion coefficient in water: 1.2.10-6 cm<sup>2</sup>/s at 25°C Diffusion coefficient in air: 0.106 cm<sup>2</sup>/s at 25°C Henry's law constant: 2.73.103 Pa.m<sup>3</sup>/mol at 25°C Flash point: - 78°C

Melting point: - 153.7°C Boiling point: - 13.9°C





T: Toxic

F<sup>+</sup>: Hiahly flammable

R45 – Can cause cancer.

R12 – Highly flammable.

S45 – In the event of accident or discomfort see a doctor immediately (show him the label if possible).

S53 - Avoid exposure, get special instructions prior to use. 200-831-0 - EC labelling

#### Toxicological data

#### Threshold toxicological values

TLV-TWA: 1 ppm (2.6 mg/m<sup>3</sup>). TEEL 0: 1 ppm  $(2.6 \text{ mg/m}^3)$ VME: 1 ppm (2.6 mg/m<sup>3</sup>) TEEL 1: 5 ppm (13 mg/m<sup>3</sup>) MRL inh. (acute exposure) 0.5 ppm (1.3 mg/m<sup>3</sup>) TEEL 2: 5 ppm (13 mg/m<sup>3</sup>) MRL inh. (sub acute exposure) 0.03 ppm (0.078 mg/m<sup>3</sup>) TEEL 3: 75 ppm (195 mg/m<sup>3</sup>)

#### Acute human toxicity

Skin contact: irritational lesions and frostbite.

Eye contact: reversible corneal impairment.

Airways (main route): moderate irritation of the bronchial tube.

Narcotic effects, depression of central nervous system, dizziness,

disorientation, drowsiness, loss of consciousness, death if exposure persists.

#### Specific effects

Carcinogenic effects: objectivated, group C1. Genotoxic effects: Globally toxic. Effects on fertility: not demonstrated. Teratogenic effects: unconfirmed. Mutagenic effects: yes.

#### Chronic human toxicity

Trophic impairment of skin and bone involving bone destruction of the fingers (other bones also), Raynaud's syndrome and a kind of skin sclerosis (in the event of massive exposure). Digestive effects: abdominal discomfort, nausea, anorexia, hepatomegaly, and often splenomegaly. Liver impairment comprises initial cytolysis then fibrosis and cirrhosis. Impairment of blood cell lines. Impaired breathing

Peripheral neuropathy.

#### Ecotoxicological data Micro-crustaceans (Daphnia magna) : CE<sub>50</sub>(48h) = 103 mg/L Acute ecotoxicity value estimated by TGD Bacteria (Pseudomonas putida): $CE_{5}$ (16h) $\geq$ 135 mg/L Bacteria (anaerobic): Cl<sub>50</sub> (3.5 days)=40 mg/L · Chronic ecotoxicity no data Seaweed (Scenesdesmus quadricauda): CL<sub>3</sub> (8 days)=710 mg/L PNEC: no data $CL_{50}(96h) = 210 \text{ mg/L}$ Fish (Brachydanio rerio): Persistence in the environment Abiotic degradation: Vinyl chloride breaks down quickly in air as it reacts with hydroxyl radicals. Degradation products are hydrogen chloride and formaldehyde chloride. • Volatilisation: Vinyl chloride evaporates quickly from the water surface (half-life: a few hours) or from the soil (main route) Evaporation: half-life is 0.8hours. Biodegradation Standard European behaviour Organic carbon/water distribution - Soil, aerobic and anaerobic degradation is coefficient, Koc = 8 to 98 litres/kg classification: G (Gas) usually slow. Water: non hydrolysable/ not easily · Octanol/water distribution coefficient: Mobile in soil and can reach the underbiodegradable (16% after 18 days). ground water table by percolation. Kow log = 1.58Anaerobic biodegradability in water : 80% after Bio concentration factor, log BCF 4 weeks. (aquatic organisms): 0.609 Special risks Fire Polymerisation Polymerises easily in sunshine, heat or catalysers: peroxides, ozone, Explosion limit in % by volume in air: LEL: 4/ UEL: 22 persulfates. To offset this trend during storage and transportation Self-ignition temperature: 472°C add a small amount of polymerisation inhibitor, (ex: phenol Flash point: - 78°C (in a closed beaker) Fumes: toxic derivative.) Stability and reactivity Danger Conditions to avoid: - Risk of spontaneous increase in pressure or self-ignition by Combined with water and high temperatures, it can corrode iron exposure: heat, light, shock or contact, other chemicals. and even steel. - If the recipient heats up, pressure will build up and the container Keep away from heat and ignition sources. may fail followed by an immediate release of flammable vapours Materials to be avoided: accompanies by an explosion and a pressure wave (Uvinyl Oxidisers (exothermal polymerisation possible). chlorideE). Explodes when in contact with: air. - Gas is invisible and can enter sewage system, underground areas - Decomposition products are dangerous: or closed premises. At 450° C it generates acetylene. - Heat may destroy the inhibitor. If it burns: HCl, CO, CO<sub>2</sub>, traces of carbonyl dichloride, phosgene. Contact the manufacturer. - Other reactions: Can cause narcotic effects and cause loss of consciousness. It reacts with concentrate bases when warm and releases hydrogen chloride Reacts violently with oxidisers and metals (copper, aluminium). Transport Manipulation Stockage Provide ventilation and appropriate General data: UN Nº- 1086 Vinyl chloride is stored and transported in liquid Class: 2 evacuation on board. form. It can be stored in a pressure vessel (at Labels: 2.1 3 bars usually) at ambient temperature and Provide showers and eye washers. Land transportation: often between -10°C and 14°C at low pressure RID/ADR danger ID N°: 239 (1.050 hPa) Have respirators available nearby.

Prohibit all spark and ignition sources. - Keep well away from ignition sources.

Protect against heat.

Use only electric appliances that can operate

in explosive atmospheres and ensure they are

Provide a dyke.

grounded.

Only use the product in a closed system.

Avoid build-up of electrostatic charges.

- Only use explosion proof equipment.

#### Shipping and air freight : IMDG/IATA packaging group : -Class: 2.1 Labels: 2.1+C Marine pollutant: NO Forbidden in passenger planes

Packaging group: -

ADN/ADNR danger ID number: 239

Classification code: 2F

Substance ID N°: 1086

Identification code: 2F