

Styrene Monomer: Environmental, Health, Safety, Transport and Storage guidelines

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Member Companies

CEFIC is grateful for the valuable contributions and peer review of this document by the following member companies:

- BASF
- Bayer Material Science
- Dow Europe
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- Repsol-YPF
- Sabic Europe
- Shell Chemicals
- Total Petrochemicals

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Latest version

To stay abreast of the latest developments regarding the environmental, health and safety aspects along with distribution guidelines of styrene, the reader is advised to visit the Sector Group section of the CEFIC web site (<http://www.cefic.be>).

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1. Introduction and Purpose

The purpose of this document is to review environmental, health and safety aspects for styrene, i.e. how to handle, store and distribute the material according to current industry standards and guidelines. The Styrene Producers Association (SPA), a Sector Group of the European Chemical Industry Council (CEFIC), encourages customers and potential users of styrene and its precursor ethyl benzene (www.ethylbenzene.org) to review their applications from the standpoint of human health and environmental quality. The **Responsible Care**[®] commitment of the chemical industry represents efforts to assist customers in developing sound product stewardship practices to better safeguard workers and operations, and to protect the environment. A key document in this respect is the [Safety Data Sheet](#). *(note to CWD that this link is to the www.styrenemonomer.org site that will be replaced by this document therefore the link should be updated when published)* It is an invaluable source of health and safety information, and is available in many languages. To help ensure that the product is not used in ways for which it is not intended or tested, producers will assist customers in dealing with ecological and product safety considerations. For information on specific applications of styrene, users are urged to contact the customer service centre of their suppliers.



Responsible Care[®] is a registered mark of CEFIC through the Chemical Industry Association of the UK.

SPA considers the volume and the distribution pattern of styrene as a commodity chemical to warrant specific emphasis on the application of Responsible Care principles in the distribution of styrene. The transfer of styrene by road, rail, sea or inland water is subject to local and international regulations and agreements, which must be observed by all parties involved. National laws may differ from international regulations and may be stricter than the distribution guidelines outlined in this brochure.

The transfer of styrene in bulk road tankers, rail tank cars, seagoing vessel, barges and tank containers is taken into account covering all aspects of the transport activity from loading to delivery point. Reference to existing regulatory controls and measures is made for clarification purposes only. SPA members do not ship styrene in drums, hence specific distribution risk management requirements for drums are not discussed herein. However individual companies will offer guidance to their customers in cases of styrene delivery in drums.

SPA recommends that the Styrene Environmental, Health, Safety and Distribution Guidelines are adopted by all parties involved in the transfer of styrene, including commercial transaction partners for product swaps, toll or trade agreements along with customer collection arrangements. The latter arrangements should adhere to the same distribution safety principles as if conducted by the manufacturing supplier.

2. Product Information and Characteristics

2.1. General Description and Hazardous Properties

Styrene (C₆H₅-CH=CH₂, CAS RN:100-42-5; EC No.: 202-851-5, EEC Annex I Index No.: 601-026-00-0), also known as ethenyl benzene, phenyl ethylene, phenyl ethene, vinyl benzene, cinnamene or styrene monomer, under ambient conditions is a colourless clear liquid with a distinctive sweetish aromatic odour. It is miscible with most organic solvents in any ratio and is a good solvent for synthetic rubber, polystyrene and other high molecular weight polymers. From the environmental impact point of view, it is only slightly soluble in water (approx. 300 ppm at ambient conditions) and consequently the acute hazard of spilled styrene will be very limited for most aquatic species. However styrene may cause tainting (unpleasant taste) in food from aquatic organisms exposed to low environmental concentrations. According to the Standard European Behaviour Classification (Bonn Agreement) styrene is classified as a “floater evaporator”.

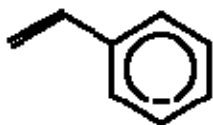


Figure 1: Chemical Structure of Styrene

Styrene is a monocyclic alkenyl aromatic compound with a molecular weight of 104. Being rather volatile and having a flash point of 32 °C, styrene is classified as a flammable substance, which in use may form flammable/explosive vapour-air mixtures. Despite its high boiling point, styrene will eventually end up in the air. For other typical parameters, the reader is referred to Table 1 (§ 2.2): Typical Physical Properties of Styrene.

Short-term exposure to styrene in humans results in respiratory effects, such as throat irritation and lung constriction, irritation to the eyes, and neurological effects such as dizziness (see Section 3 “Health Aspects” for more details). To date styrene is classified in the EU as harmful by inhalation, irritating to the eyes and to the skin (see Section 3 “Health Aspects” for more details).

Very low concentrations of styrene vapour will react with bromine and with chlorine in sunlight to form an extremely potent lachrymatory agent.

The characteristic unpleasant odour and the low odour threshold (0.1 ppm; 0.43 mg/m³) allow styrene to be readily detected in the workplace at levels below the occupational exposure standards.

Styrene will polymerise when contaminated by oxidising agents and most halides. The polymerisation reaction is exothermic and if contained may become violent. If the heat is not removed, the bulk styrene temperature may rise to a level at which polymerisation is self-sustaining and very rapid, evolving the release of large quantities of heat together with volumetric expansion. The most commonly used polymerization inhibitor is tertiary butyl catechol (4-tert-butylcatechol (TBC) or p-tert-butyl catechol; CAS RN 98-29-3; EC No.: 202-653-9). TBC is classified acc. to EC Directive 67/548/EEC, but some suppliers assign a classification as irritant or even corrosive. TBC may cause sensitization by skin contact, is toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment. More details on the inhibition mechanism and polymerisation reaction are highlighted in Section 2.4 and Appendix 2.

Styrene can accumulate static charges; hence special attention should be paid to take precautionary measures against static discharge (spark hazard) (refer to Appendices 3, 4, 5 and 6 for more details).

The carbon:hydrogen ratio of styrene is almost 1:1 resulting in considerable amounts of carbon oxides (CO₂, CO) and free carbon to evolve when burned. Burning styrene can generate large quantities of thick black smoke (refer to Section 7.3.2 for more details).

2.2. Physical Properties

Table 1: Typical Physical Properties.

Property	Common Usage Value & Unit	International System Value & Unit
Physical Form	Colourless, oily liquid	
Colour (acc. ASTM D 1209 / DIN 6271)	10 max. / Pt-Co scale	
Odour	Unpleasant, aromatic	
Odour threshold	0.1 ppm	0.43 mg/m ³
Relative molecular mass	104.14	
Density at 20°C (acc. ASTM D 4052)	0.906 kg/l	906 kg/m ³
Boiling point		145°C
Melting point/Freezing point		-31°C
Kinematic viscosity at 0°C	1.1 cSt	1.1 mm ² /s
at 20°C	0.8 cSt	0.8 mm ² /s
at 40°C	0.6 cSt	0.6 mm ² /s
at 100°C	0.4 cSt	0.4 mm ² /s
Vapour density (air =1)	3.6	
Vapour pressure at 20°C	6 mbar	0.6 kPa
at 50°C	32 mbar	3.2 kPa
at 80°C	121.2 mbar	12.12 kPa
Conductivity, thermal at 20°C	1.6x10 ⁻³ J/(s.cm.K)	0.16 W/m°C
Flash point (ABEL; acc. IP 170)		31-32°C
Autoignition temperature		490°C
Saturation concentration in air at 20°C	5923 ppm (v/v)	25.6 g/cm ³
Explosion limits in air	0.9 - 6.8% vol.	
Miscibility in water	immiscible	
Solubility in water at 20°C	0.029% wt./vol.	0.29 kg/m ³
Solubility of water in substance at 20°C	0.054% wt./vol.	0.54 kg/m ³
Coefficient of Expansion at 20°C		0.979x10 ⁻³ /°C
Specific heat at 20°C		1.73 kJ/kg.°C
Heat of combustion, H _c at 25°C	-1018.83 kcal/mole	-4265.64 kJ/mole
Heat of formation, H _f , gas at 25°C	35.22 kcal/mole	147.46 kJ/mole
Heat of formation, H _f , liquid at 25°C	24.72 kcal/mole	103.50 kJ/mole
Heat of polymerisation, H _p at 25°C	-16.88 kcal/mole	-70.67 kJ/mole
Refractive index	1.546 (n _D at 20°C)	
Rel. evaporation rate (di-ethylether = 1 min.)	12.4	
Source: CEFIC Styrene Distribution Group		

2.3. Manufacturing and Use

The conventional method for producing styrene involves two steps: the alkylation of benzene with ethylene to produce ethyl benzene followed by dehydrogenation of the ethyl benzene to produce styrene (refer to Figure 2). Over the almost fifty years of practicing the conventional two step process refinements have constantly been made to improve conversion and selectivity to ethyl benzene and finally to styrene along with design changes to conserve and utilize the energy in particular from the exothermic alkylation step. The traditional aluminum chloride catalyst used in this alkylation is slowly being replaced by zeolite catalyst technology. Currently the predominant route for the commercial production of styrene is by dehydrogenation of ethyl benzene in the presence of steam over a catalyst (iron oxide) in either fixed bed adiabatic or tubular isothermal reactors. Another route involves co-production of styrene and propylene oxide via hydroperoxidation of ethyl benzene. Limited scale extraction from steam cracker pyrolysis gasoline is also practised.

For more details on production technologies and the latest technology trends, please refer to Reference 1 and 2 of the bibliography.

For more information on ethyl benzene (CAS RN: 100-41-4; EC No.: 202-849-4; Annex I Index No.: 601-023-00-4) please refer to CEFIC's Environmental, Health and Safety Guidelines (www.ethylbenzene.org).

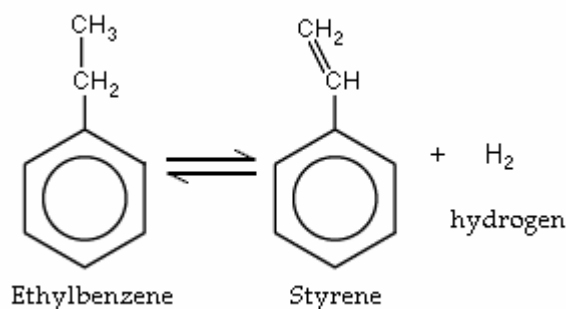


Figure 2: Dehydrogenation of Ethyl benzene to Styrene

The specification and analytical methods for styrene have changed through the years. The majority of the manufacturers have defined their sales specifications according to the standard D2827 "Standard Specification for Styrene Monomer" of the American Society for Testing and Materials (ASTM). Key parameters of a typical sales specification are: a minimum purity of 99.7 wt. % and a maximum colour of 10 on the Platinum-Cobalt (Pt-Co) scale, while the specified impurities and their concentrations depend upon the manufacturing route employed, along with plant performance characteristics. The typical inhibitor content of the standard grade is 10-15 ppm TBC (4-tert-butylcatechol), while a higher dose may be defined in the customer specification depending on the expected storage period and use conditions at the customer site.

Styrene is widely used in the manufacture of resins, plastics, and latices/emulsion polymers by both batch and continuous mass polymerisation; by solution, suspension, and emulsion processes; and by various modifications and combinations of these techniques. Styrene responds to many different initiators, including peroxides and other free radical initiators, redox initiator systems, and ionic initiators. Styrene can be reacted with acrylates, methacrylates, acrylonitrile, butadiene, divinyl benzene and maleic anhydride, to form copolymers.

In 2004 the global styrene demand was reported to be over 24,000 Kt (data calculated from Reference 1). Figure 3 presents the global styrene polymer derivatives demand based on 2004 data. Although declining in proportion polystyrene is by far the largest segment (46%) primarily used in packaging, disposables, electronics and appliances, followed by expandable polystyrene

(16%) and acrylonitrile-butadiene-styrene (ABS) resins (14%). The heat-resistant, tough ABS resins are widely used for appliances and telephone casings, luggage, sporting helmets, pipe fittings and automotive parts. Styrene-Butadiene (SB) latex and SB rubber account for 10% of the global demand. SB latex finds its use as paper coating for glossy magazines, as component of carpet and upholstery backing, for the adhesive production and for latex paints. The majority of SB rubber is consumed in the manufacture of tires, automobile parts and electronic components. Unsaturated polyester resins (UPR) are used over a broad spread of industries, mainly the construction, boat building, automotive and electrical industries (5% of the global styrene polymer derivative demand, see Figure 6). Details on these and other applications can be found in Reference 2 or consult the following website: www.styreneforum.org.

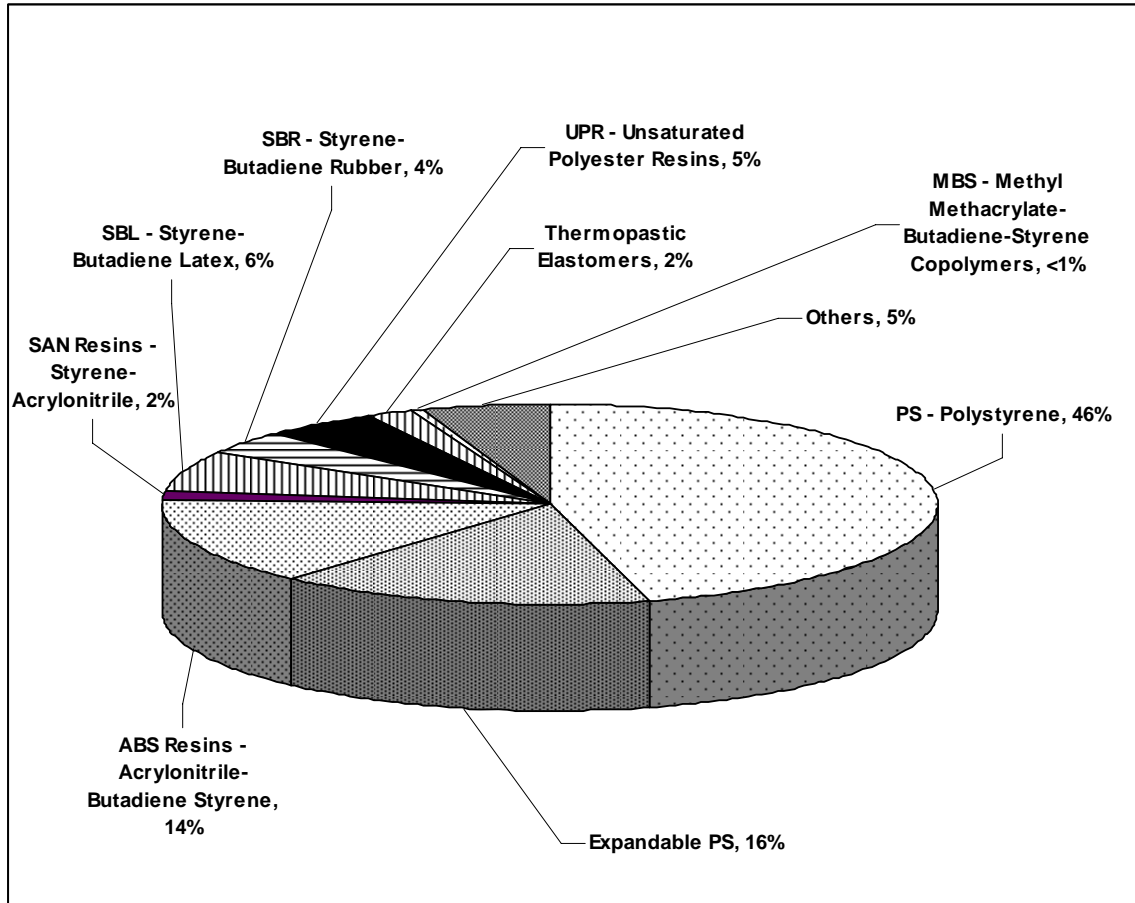


Figure 3: Global Demand for Styrene Polymer Derivatives in 2004

2.4. Inhibition of Styrene (Chemistry, Mechanism and Levels)

2.4.1. Safety and Quality

Styrene is a reactive monomer, undergoing many reactions of an unsaturated compound (such as addition) and of an aromatic compound (such as substitution). Polymerisation generally takes place by free-radical reactions initiated thermally or catalytically. Polymerisation occurs slowly even at ambient temperatures. To maintain the monomer content for quality as well as safety reasons the polymerisation reaction is retarded by phenolic inhibitors. The most commonly used inhibitor is tertiary-butyl catechol (4-tert-butylcatechol (TBC) or p-tert-butyl catechol; CAS RN 98-29-3; EC No.: 202-653-9), but hydroquinone (1,4-dihydroxybenzene; CAS RN: 204-617-8; EC No.: 123-31-9; Annex I Index No.: 604-005-00-4) works also. The polymerisation reaction is exothermic and if contained may become violent. If the heat is not removed, the bulk styrene temperature may rise to a level at which polymerisation is self-sustaining and very rapid, evolving the release of large quantities of heat together with volumetric expansion.

As pictured in Figure 4, oxygen and inhibitor must be maintained at certain minimum levels to prevent oxidative degradation and subsequent (poly)peroxide formation. The presence of oxygen is required for the inhibitor to function properly, therefore styrene needs to be stored under air or inert gas with sufficient oxygen levels (see Table 2 for details on the solubility of gases in styrene).

A recent study on the inhibition chemistry confirmed that free peroxide radicals, such as benzaldehyde and formaldehyde, are formed at the same time. An oxygen level of 5%-vol. in the vapour phase is regarded as being sufficient for inhibition of the liquid phase. This means that limited exposure to air is the best way to keep the content of oxygenates as low as possible.

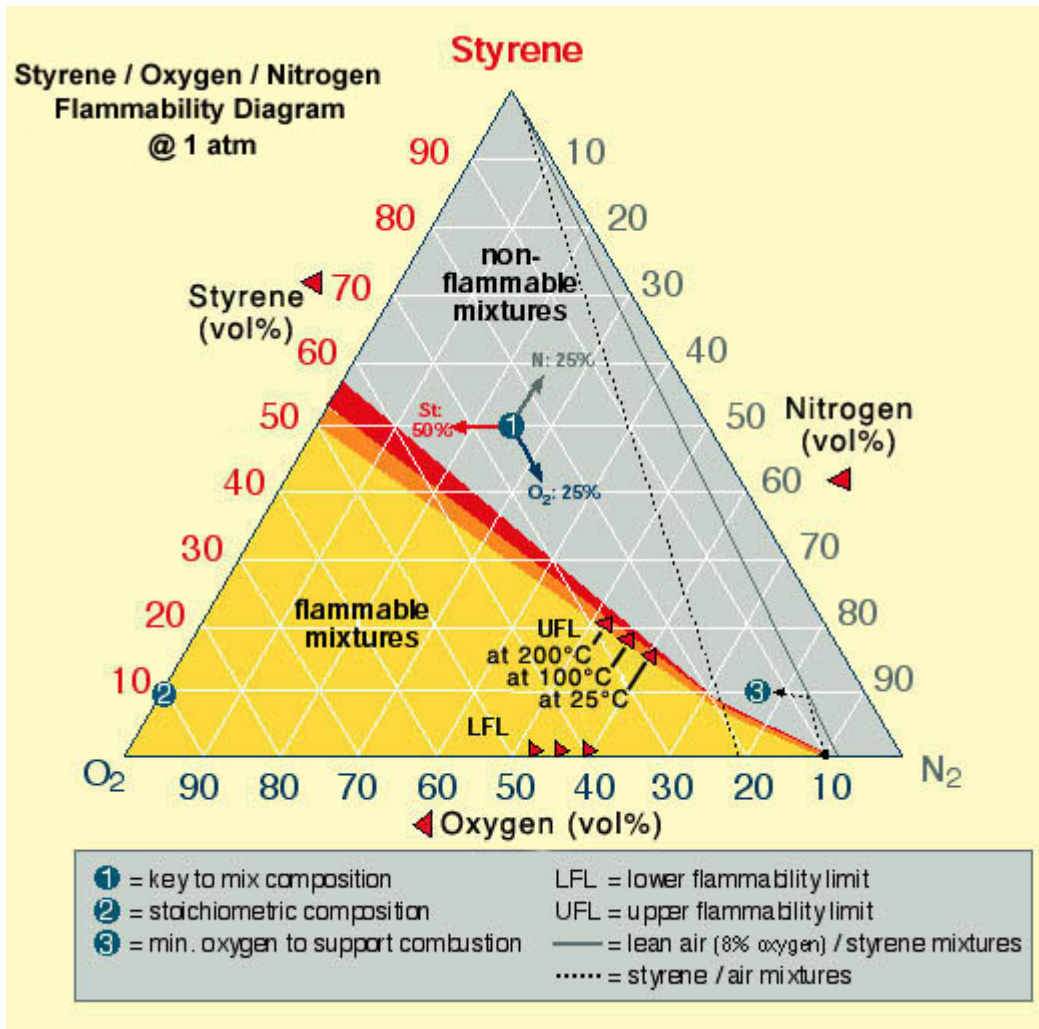


Figure 4: Flammability Diagram for "Styrene/Oxygen/Nitrogen"

It should be noted that in climate zones and in seasons with significant temperature differences between night and day, the styrene vapours evolved in the headspace at higher temperatures will condense on roofs, walls and internal fittings of storage tanks when it cools off. The phenolic inhibitors have high boiling points and stay in the liquid phase, resulting in the condensed styrene vapours containing no inhibitor. Precautions must be taken to prevent polymer build-up on surfaces above the liquid level of tanks and containers, which could result in plugging of pressure-relief valves.

Table 2: Solubility of Gases in Styrene at 25 °C

GAS	CC GAS/CC STYRENE	ppm by wt.
Oxygen	0.4	581
Nitrogen	0.08	102
Air	0.15	198
O ₂ from air*	0.032	50

* amount of oxygen when saturated with air

In warm climates, consideration can be given to applying a coating on the internal surfaces of

tanks, thereby preventing discolouration of the styrene from oxidised iron and minimizing polymer build-up in the headspace. US patent 4,161,554 describes a coating system employing TBC, which upon one single application is expected to last for several years.

It is recommended that the maintenance and inspection schedule for storage of styrene be followed as indicated in Table 3, which includes auxiliaries such as vapour return lines and safety valves.

Table 3: Schedule for Storage Maintenance of Styrene

CHECK POINT	INTERVAL	REMARKS
Inhibitor Analysis	2-3 times weekly	
	Daily	if above 25-30°C
Polymer Analysis	2-3 times weekly	
	Daily	if above 25-30°C
Colour	2-3 times weekly	
Oxygen	Weekly	easier in vapour phase
Monomer Temperature	Daily	
Monomer Vapour Temperature	Daily	
Inspection Points for Polymer		
Air Vent	at least quarterly	
Foam Reservoir	within 5 years	
(Internal) Roof Seal, Sides and Floor	when technically possible	
Vacuum Pressure Relief Valve	at least quarterly	
Flame Arrestor	at least quarterly	
Vapour Return Line	at least quarterly	
Long Product Lines	pending residence time	See Table 3
Product Turnover		
Date of Last Filling	running log	
Volume Before Filling	running log	
Volume After Filling	running log	

2.4.2. Inhibition Chemistry

When styrene monomer (M) is exposed to light and/or heat, it forms radicals (see Figure 5). These styrene radicals (R*) react either with oxygen to form peroxide radicals or with styrene to form polymer chains. In the presence of sufficient oxygen (at least 10-15 ppm), the peroxide formation is significant because this reaction (r1) is much faster (see Reference #3) compared to the polymer formation with styrene (r2). In the subsequent step if the inhibitor (TBC) content is >10 ppm, the peroxide radicals are scavenged via quinone formation (r3), whereas if no or too little inhibitor is present, the peroxide radicals react with styrene to form peroxide chains (r4). Oxygen works as the polymerisation inhibitor while TBC controls its efficient use. In the absence of TBC the peroxy-radicals continue to react with the monomer molecules until the oxygen is completely depleted. The poly(peroxides) are soluble in styrene and will not collect in pockets. Hazardous situations may occur during distillation of styrene contaminated with unstable

poly(peroxides), which may trigger a runaway reaction since with temperature increase a significant number of radicals may be formed.

Note: Considering the minimum oxygen concentration to support combustion (see Figure 4), the IMO related Safety Of Life At Sea (SOLAS) Convention has defined an atmosphere with < 8%-vol. oxygen as inert gas for styrene. As a dissolved oxygen level of 3 ppm is in equilibrium with 1%-vol. oxygen in the vapour phase, the minimum requirement for the proper functioning of TBC is therefore being met with sufficient certainty.

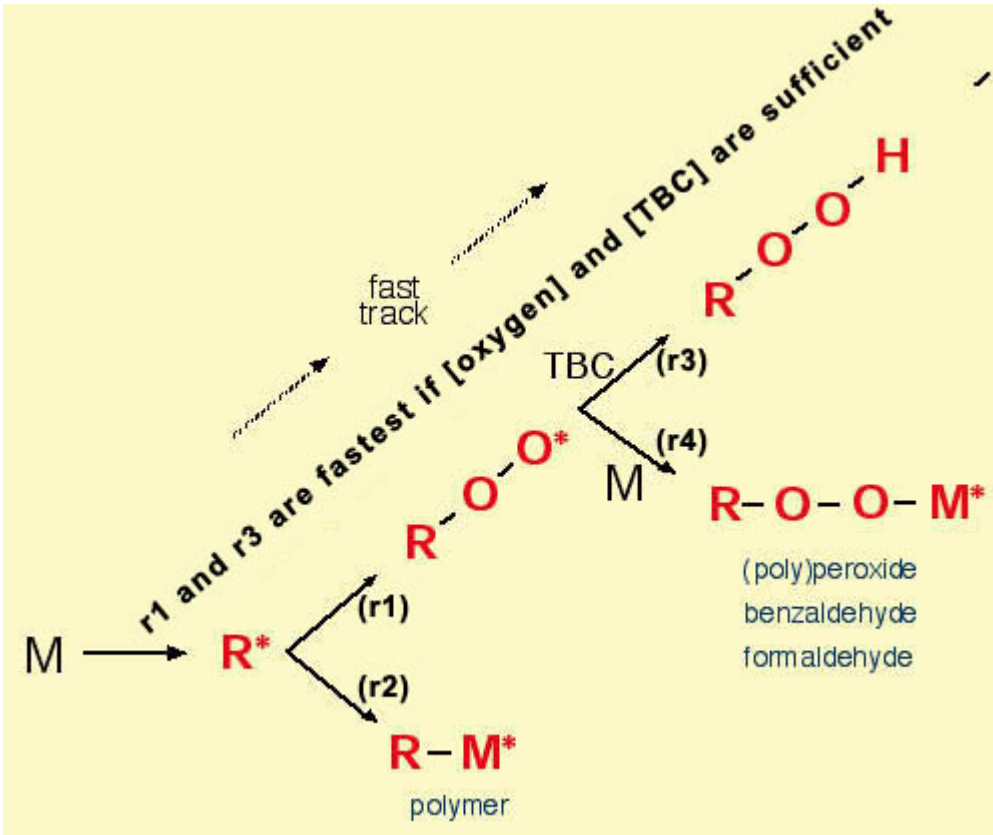


Figure 5: Inhibition Mechanism

2.4.3. Standard Inhibitor Levels

The recommended practice is to maintain the inhibitor (TBC) levels between 10-50 ppm, but higher inhibitor levels may be required depending on the storage conditions, process or specific user requirements. Table 4 below presents typical protection (in days) for styrene when both the inhibitor and oxygen concentrations are above the recommended minimum levels. Styrene users are advised to have a TBC concentrate/solution on-site to restore the TBC level once it falls below 10 ppm. It is stressed, in particular, if styrene is stored under a nitrogen blanket, that users should inject air or oxygen, mix thoroughly, and measure at proper intervals the inhibitor and oxygen levels to ensure homogenous distribution and assurance of the recommended level.

Table 4: TBC Depletion in Styrene (if stored under air)

Temperature	Depletion Days/1 ppm	TBC Content		Shelf Life
°C t		[initial] ppm	[end] ppm	Assured days
25	11	15	10	55
30	7	15	10	35
40	1.5	15	10	7

Note: Oxygen inhibits polymer formation, TBC controls the oxygen depletion rate.

The depletion of oxygen in styrene is not only dependent on the temperature but also on the TBC level added (see Figure 6). At low TBC levels oxygen depletion is rapid and the inhibition system will quickly become ineffective. These tests verified that polymer formation begins once the oxygen content falls below the desired minimum of 10-15 ppm.

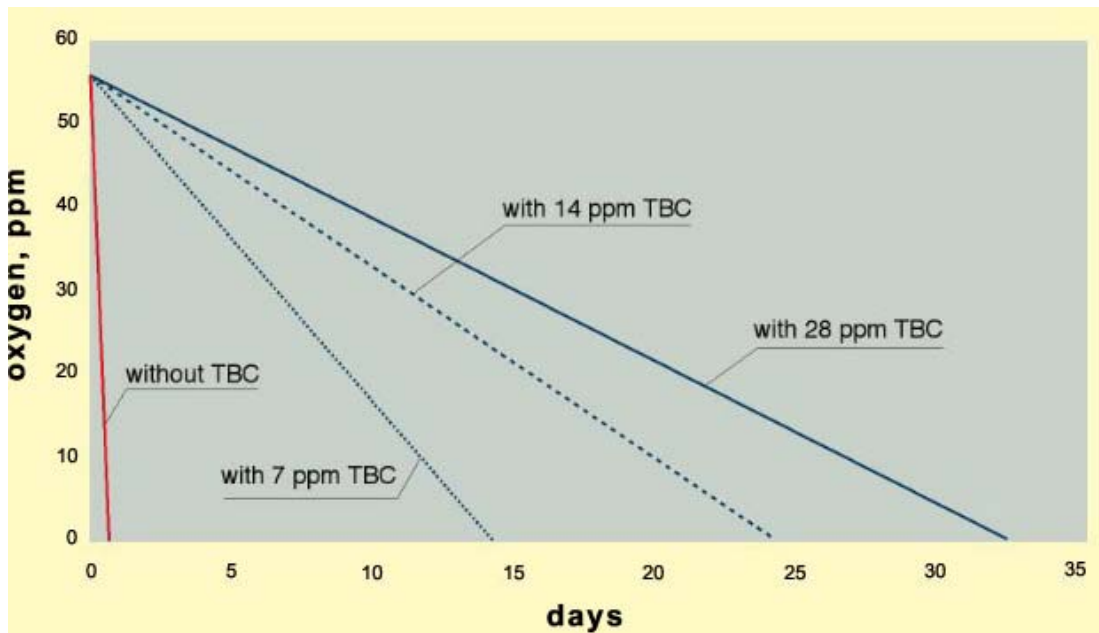


Figure 6: Oxygen Depletion in Styrene at 40°C

2.5. Environmental Effects

The EU authorities have concluded that styrene is not bio-accumulative and meets the "ready biodegradation" criteria of the 29th Adaptation to Technical Progress of the Dangerous Substances Directive. The European Environmental Risk Assessment of styrene has concluded that no classification is needed.

Persistence of Styrene in the environment is very limited because of its volatility from soils and surface waters, its rapid destruction in air and its biodegradation in soils, and surface and ground waters.

Styrene is moderately toxic to aquatic organisms. Due to its high depletion rate from water the exposure rate may be very low.

More details on Styrene environmental effects can be found in Section 4 "Environmental Aspects".

2.6. Transport Classification (Europe)

Rail transport : "Réglement concernant le transport International ferroviaire des marchandises Dangereuses (RID 2005)

ID Type and No: UN 2055

English Name: STYRENE MONOMER, STABILIZED

Class: 3

Classification Code: F1

Label: 3

Packing Group: III

Hazard ID No: 39

Inland waterways : "Accord Européen au transport international des marchandises dangereuses par voie de Navigation du Rhin (ADNR 2005)"

ID Type and No: UN 2055

English Name: STYRENE MONOMER, STABILIZED

Class: 3

Classification Code: F1

Label: 3

Packing Group: III

Barge type: N(ormal).

Bulk marine transport: International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk (IBC Code).

Chapter 17 listed product

Product Name: Styrene Monomer

Marine transport of packaged goods: International Maritime Dangerous Goods Code (IMDG Code, 2004).

ID Type and No: UN 2055

English Name: STYRENE MONOMER, STABILIZED

Class: 3

Packing Group: III

EMS: F-E, S-D

Road transport: The European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR) which can be consulted online at <http://www.unece.org/trans/danger/publi/adr/adr2005/05ContentsE.html>

ADR 2005

ID Type and No: UN 2055

English Name: STYRENE MONOMER, STABILIZED

Class: 3

Classification Code: F1

Label: 3

Packing Group: II

Hazard ID No: 39

Air transport: International Civil Aviation Organisation Technical Instructions (ICAO TI)

UN No: 2055

English Name: STYRENE MONOMER, STABILIZED

Class: 3

Packing Group: III

Label: Flammable liquid

Pass. & Cargo Aircraft Ltd Qty Pkg Inst: Y309

Pass. & Cargo Aircraft Ltd Qty Max Net Qty / Pkg: 10 L

Pass. & Cargo Aircraft Pkg Inst: 309

Pass. & Cargo Aircraft Max Net Qty / Pkg: 60 L

Cargo Aircraft Only Pkg Inst: 310

Cargo Aircraft Only Max Net Qty / Pkg: 220 L

ERG Code: 3L

2.7. European Regulatory Environment

In February 2001 the European Commission issued a White Paper entitled "Strategy for a Future Chemicals Policy" (COM (2001) 88 Final), aiming at complete revision of the existing legislation on chemicals. The overall goals of the new policy are to ensure the protection of human health and environment, maintenance of the competitiveness of the European chemical industry and preventing the fragmentation of the internal market.

Registration, Evaluation and Authorisation of Chemicals (known as REACH) will replace the legislative framework for "new" and "existing" chemicals and extend the requirements for new substances to existing ones. Existing substances available commercially between 1 January 1971 and 18 September 1981 were compiled into the European Inventory of Existing Commercial Substances (EINECS) in application of Article 13 of Directive 67/548/EEC, as amended by Directive 79/831/EEC, and in accordance with the detailed provisions of Commission Decision 81/437. Among the 100,196 EINECS-listed substances is styrene. These substances could be produced and sold without meeting the comprehensive and stringent data requirements demanded for new substances. Under REACH, enterprises that manufacture or import more than one tonne of a chemical substance per year would be required to register it in a central database. Higher tonnage of manufacture will attract an increasing degree of testing. REACH would furthermore give greater responsibility to industry to manage the risks from chemicals and to provide users in the supply chain with safety information on the substances.

The Commission expects entry into force of the Regulation for spring 2007. The operational requirements of REACH are expected to start to be applied from 2008 onwards.

Please review the following websites for more information and to stay on top of developments related to REACH:

<http://ecb.jrc.it/REACH/>

<http://europa.eu.int/comm/enterprise/reach>

<http://europa.eu.int/comm/environment/chemicals/reach.htm>

<http://www.chemicalspolicyreview.org/>

In 1993 the Council of the European Communities adopted Council Regulation (EEC) 793/93 Existing Substances Regulation (ESR), thereby introducing a comprehensive framework for the evaluation and control of "existing" chemical substances. The Regulation was intended to complement the already existing rules governed by Council Directive 67/548/EEC for "new" chemical substances. The evaluation and control of the risks posed by existing chemicals is carried out in four steps: data collection, priority setting, risk assessment and risk reduction.

In the data collection step, styrene was determined to be a "High Production Volume Chemical" (HPVC), i.e. has been imported or produced in quantities exceeding 1000 tonnes per year and produced/imported between 23 March 1990 and 23 March 1994. The data set for styrene in the required electronic format Harmonised Electronic DataSET (HEDSET) was submitted and is now managed by the International Uniform Chemical Information Database (IUCLID). According to Article 8 of 793/93 EEC, four lists totalling 141 priority substances have been published since 1994. Styrene was added to the first priority list (1179/94 EC).

Substances on priority lists must undergo an in-depth risk assessment covering the risks posed by the priority chemical to man (covering workers, consumers, and humans exposed via the environment) and the environment itself (covering the terrestrial, aquatic and atmospheric ecosystems and accumulation through the food chain). Styrene is being assessed by the United Kingdom as the member state rapporteur. The final Risk Assessment Report (RAR) for the environmental part was published on the European Chemicals Bureau (ECB) website (<http://ecb.jrc.it/>) in 2002 (EUR 20541 EN European Risk Assessment Report: Styrene – Part I – Environment, Volume 27). The human health Risk Assessment was presented by the rapporteur for a last visit discussion at the 8th Technical Committee on New and Existing Substances in November 2005 at Arona and the conclusion was that no classification for carcinogenicity and mutagenicity would be required. Denmark, however, announced counterproposal, but failed to submit on time to be discussed during the Classification & Labelling meeting in October 2006. Styrene has therefore on request of Denmark been moved to the waiting list. Further discussion is expected to happen in spring 2007.

The Commission Working Group on the Classification and Labelling of Dangerous Substances: Environmental Effects has agreed not to classify styrene (Annex I Index No.: 601-023-00-4) as dangerous to the environment on the basis of the data in the Risk Assessment Report (Summary Record ECBI/60/99 - Rev. 4; 15-17 September 1999). Ethylbenzene was inserted to Annex I of 67/548/EEC in Commission Directive 93/72/EEC (19th Adaptation to Technical Progress; O.J. N° L258, 16.10.1993, p. 29; O.J. N° L258A, 16.10.1993, p. 1).

Styrene is not listed in the Recommendations of the Technical Committee for Classification and Labelling and Specialised Experts for possible inclusion into the 30th Adaptation to Technical Progress (ATP) or the current 29th ATP (Commission Directive 2004/73/EC).

3. HEALTH ASPECTS

3.1 General Remarks

This section covers the effects of exposure to styrene, i.e. acute toxicity, skin and eye irritation, repeat dose toxicity and carcinogenic potential. The users are recommended to contact their suppliers for the most recent or detailed information regarding chronic hazards, reproductive and developmental toxic effects, hormonal effects and genotoxicity.

According to the EU Dangerous Substances Directive the health effects of styrene are classified as "Harmful by inhalation" and "Irritant to skin and eyes".

3.2 Acute Toxicity

It can be concluded from animal experiments that the acute oral toxicity of styrene is low; the oral LD50 is reported to be well above 2,000 mg/kg body weight. As the oral toxicity is low, any small amounts accidentally ingested are unlikely to cause injury. Ingestion of large amounts of styrene may cause irritation of the mouth, throat and gastro-intestinal tract. Aspiration into the lungs may cause chemical pneumonitis, which can be fatal. Inhalation studies in rats and mice indicate that styrene generally has a moderate acute toxicity (4 hour LC50 >280 -2,800 ppm (2-20 mg/L)), thereby some strains of mice are particularly sensitive i.e. deaths occurred in mice exposed for 6 hours at a concentration of 500 ppm styrene.

Humans exposed at 100 ppm for up to 7 hours have described slight irritation to the eyes and the throat with the effects becoming more severe with increasing dose. Higher styrene exposures (i.e. > 100 ppm), but still well below the lethal dose in the rat, produce immediate eye and nose irritation accompanied by depressant effects on the central nervous system (e.g. narcosis, fatigue, dizziness). As the smell (odour threshold = 0.1 ppm) and the irritant properties of styrene preclude exposures at such high and harmful concentrations, it is virtually impossible under normal working conditions to be exposed to a lethal dose of styrene.

3.3 Skin and Eye Irritation

Repeat dose studies in experimental animals using occlusive applications of styrene have caused moderate to marked irritation. Human experience indicates that liquid styrene can cause defatting of the skin and frequent contact might cause dermatitis. The application of liquid styrene to eyes of experimental animals has been reported to produce moderate irritation, with severe eye irritation being described in rats exposed to a styrene vapour concentration above 11,000 ppm. Human studies indicate that accidental splashing of undiluted styrene can produce slight eye injury while vapour exposures have produced slight eye irritation (100 ppm) with conjunctivitis and more severe eye irritation at 200 ppm. Usually the eye recovers rapidly within 48 hours.

3.4 Sensitization

Extensive human experience indicates that styrene is not a significant skin sensitizer and has no significant asthmogenic potential.

3.5 Carcinogenicity / Genotoxicity

The carcinogenic risk to humans after long-term exposure to styrene concentrations below recommended Occupational Exposure Limits (ranges from 20 to 100 ppm across different countries) is very low. Most international agencies classify styrene as having a very low or no

cancer potency. The International Agency on Cancer Research (IARC) has concluded that there is insufficient evidence for carcinogenicity in humans and limited evidence in experimental animals. Only one study on mice showed an increased incidence in lung tumours after a lifetime inhalation exposure, but recent evidence indicates that mice are not an appropriate model for effects of styrene. Case-control studies with occupationally exposed humans investigating styrene exposure and cancer incidence showed no statistically significant increase in tumour incidence. On this basis it can be concluded that the evidence for carcinogenic activity of styrene in humans is weak.

In vitro mutagenicity tests only yielded positive results for styrene after metabolic activation. In cytogenetic studies with animals or exposed workers positive and negative findings were obtained. Styrene is metabolised to styrene-7,8-oxide, an alkylating epoxide, which was shown to be mutagenic in vitro and carcinogenic in animals only at the site of direct exposure (after oral exposure: stomach). Studies of the bio-kinetic behaviour of styrene and styrene-7,8-oxide in humans, rats and mice have been used to quantify the possible human carcinogenic risk. These data indicate that there is no significant contribution to human cancer risk if the occupational exposure levels are not exceeded.

3.6 Conclusion

The review of the very extensive literature leads to the following conclusions:

- Liquid styrene is irritant to skin and eyes, while higher vapour concentrations may be irritant to the respiratory tract.
- Exposure to styrene above currently recommended workplace limits may cause reversible effects on the nervous system.

The carcinogenic risk to humans is very low if recommended occupational exposure levels will not be exceeded.

4. ENVIRONMENTAL ASPECTS

4.1 General

Persistence of styrene in the environment is very limited because of its volatility from soils and surface waters, its rapid destruction in air and its biodegradation in soils, and surface and ground waters.

4.2 Partitioning to the Air Compartment

The relatively high Henry's Law Constant ($232 \text{ Pa}\cdot\text{m}^3/\text{mol}$) indicates that the primary removal mechanism of styrene from water is volatilisation.

4.3 Partitioning to the Water Compartment

In the event of a spill, styrene will slowly volatilise and little will dissolve. The concentration to which aquatic organisms will be exposed will depend on the air and water temperature and turbulence. The depletion graph shown in Figure 7 gives an illustration of the change of the styrene concentration with time, both in stagnant water and when stirred slowly.

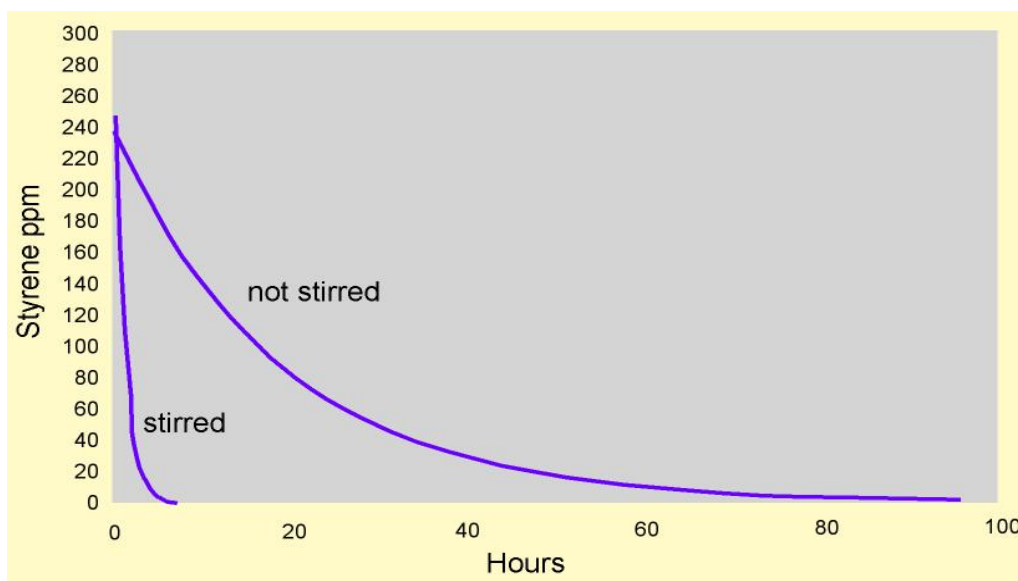


Figure 7: Styrene Depletion from Water at 20-25°C Results from a laboratory simulation clearly show that styrene will disappear from water even when unstirred, but the rate of depletion is much faster in turbulent conditions, i.e. 10 hours vs. 80 hours. In other words, when spilled, the hazard of dissolved styrene will be considerably different from that based on toxicity studies for which the standard protocol is followed.

4.4 Partitioning to the Soil Compartment

Based on its low water solubility and the magnitude of its organic carbon partitioning coefficient (calculated $K_{oc} = 260-550$), the mobility of styrene in soil is considered to be moderate to low.

4.5. Bioaccumulation, Movement and Partitioning

Considering the bioconcentration factor (BCF) for fish and the octanol/water partition coefficient (P_{ow}), the bioconcentration potential for styrene is low. As shown in Figure 7, the primary removal mechanism from water is volatilisation. The exposure of aquatic species will be limited to several hours when exposed to water, which is initially saturated with styrene. As previously indicated the mobility of styrene in soil is considered to be moderate to low. The primary mechanisms for styrene removal from soils are biodegradation, solubilisation by infiltrating water and, in shallow soils, volatilisation.

4.6 Degradation and Persistence

The high biodegradability of styrene is shown by the BOD_{20} and $BOD_{28}/ThOD$ ratio (which is >40) and the OECD test(s) for ready biodegradability, i.e. 60% degradation within 10 days. Although the availability of nutrients, i.e. nitrogen and phosphorous will be the determining factor, styrene is in principle degradable in the (anaerobic) soil environment. Degradation in the atmospheric environment is expected within minutes to hours.

4.7 Aquatic Toxicity

Following the evaluation of several acute toxicity studies with exposure periods of 72-96 hours, it has been concluded that the lowest LC_{50} for fish is 9 mg/l. For waterflea species exposed for 48 hours, the lowest EC_{50} (acute immobilisation) value that has been found is 23 mg/l. Similarly, for 72 hours exposure, the lowest IC_{50} (growth inhibition) for green algae has been determined at 0.72 mg/l. It should be noted that some protocols to assess the aquatic toxicity hazard require that the exposure concentration is maintained during the test and that styrene depletion from water (see Figure 7) is not being considered in determination of the exposure hazard.

4.8 Product Classification (Environmental Effects)

The EU authorities have concluded that styrene is not bio-accumulative and meets the "ready biodegradation" criteria of the 29th Adaptation to Technical Progress of the Dangerous Substances Directive. The European Environmental Risk Assessment of styrene has concluded that no classification is needed.

5. DESIGN AND CONSTRUCTION OF TRANSPORT AND STORAGE EQUIPMENT

5.1. RAILCARS (RAIL TANK WAGONS)

Railcars for the carriage of styrene must meet the design and construction requirements of:

- a) National Regulations or Local Railway Administration Regulations, when used for national transport.
- b) International Regulations, such as the International Regulations concerning the Carriage of Dangerous Goods by Rail (RID), when used for international transport.

In addition it is recommended that railcars are designed and constructed in accordance with the recommendations as described in:

http://www.cefic.org/files/Publications/Rail_FINAL%2004092003.pdf

In addition to the Cefic Guidelines it is recommended that the railcars are coated to prevent polymerization of the styrene. Zinc silicate coating is commonly used.

5.2. TANKTRUCKS (ROAD TANKERS)

Tank trucks used for the carriage of styrene by road must meet the design and construction requirements of:

- a) National Regulations, when used for national transport
- b) International Regulations, such as the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR), when used for international transport.

In addition to the above requirements, it is recommended that tank trucks are designed and constructed in accordance with the recommendations as described in:

http://www.cefic.org/files/Publications/Road_FINAL%2003092003part1.pdf &
http://www.cefic.org/files/Publications/Road_FINAL%2003092003part2.pdf

5.3. TANK CONTAINERS

Tank containers may be used for the carriage of styrene by road, rail, and/or sea. They must meet the design and construction requirements of the appropriate National or International Regulations depending upon the specific transport modes, which are to be utilised.

In addition to the above requirements, it is recommended that tank containers are designed and constructed in accordance with the recommendations in as described in:

http://www.cefic.org/files/Publications/Road_FINAL%2003092003part1.pdf &
http://www.cefic.org/files/Publications/Road_FINAL%2003092003part2.pdf

5.4. VESSELS AND BARGES

Vessels (bulk tank ships) used for the carriage of styrene by sea must meet the design and construction requirements of the relevant International Regulations such as the "International Code for the Construction and Equipment of Ships carrying Dangerous Chemicals in Bulk" as produced by the International Maritime Organisation (IMO).

Barges used for the carriage of styrene by inland waterways must meet the design and construction requirements of the relevant National or International Regulations for the design and construction of barges such as the "Regulations concerning the Transport of Dangerous Substances in Barges on the River Rhine" (ADNR).

In addition to the above requirements, it is recommended that vessels and barges are used that are designed and constructed in accordance with the recommendations contained in Appendix 3.

5.5. STORAGE TANKS

The storage and handling of styrene is subject to legislative controls in many countries. The design and construction of storage tanks for styrene must therefore comply with the relevant national legislative controls.

The general guidelines contained in Appendix 5 exemplifies the best general practice which is followed within the styrene manufacturing industry and should be used provided they do not conflict with any specific legal obligation.

5.6. LOADING AND UNLOADING FACILITIES

As transport and storage equipment have their own specific requirements for design and construction it is essential to ensure the correct design of equipment for loading and unloading facilities.

Loading and unloading facilities should be designed and located to meet appropriate engineering standards having due regard to the hazards associated with the handling of styrene and the transfer rates which are to be achieved. Particular attention should be given to the ergonomics of connecting transportation equipment and to the health and safety protection of operators. Closed loading systems, i.e. vapour return, incineration or vapour adsorbing systems should be considered.

6. TRANSPORT, STORAGE AND HANDLING OPERATIONS

This section describes the operation of transport, storage and handling equipment. All equipment should be properly used and maintained. The transport selected for the carriage of styrene should be on the basis of restricted previous cargoes (see below) The general comments below apply to all forms of transport.

6.1. Training

All companies that are involved in the transport, storage or handling of styrene should have competent personnel that are trained in the proper use of the relevant distribution facilities and for the implementation of the relevant safety regulations as mentioned in this chapter.

6.2. Operating instructions and Regulations

Written operating instructions should be available covering the transport, storage and handling of styrene.

All operations must be conducted in accordance with the relevant national regulations and the requirements of the ADR - RID - ADNR and IMO Regulations as appropriate.

6.3. Inspections

If the customer wishes, the supplier may be prompted to provide him – for information – with technical advisory and safety service. Where appropriate, the customer is recommended to ask for his unloading facility to be inspected by the supplier. If an evaluation is made, the scheme included in Appendix 6 may be used as a checklist. The resulting observations do not in any way render the supplier liable, as the customer remains responsible for the conditions of unloading styrene and the equipment used.

Normally the customer himself should evaluate whether his premises, especially his reception and storage facilities, correspond with the requirements of the scheme included in Appendix 7.

6.4. Loading operations for rail- and road transport

An inspection of the transport equipment should be carried out by the loading terminal staff before, during and after loading. The inspection list detailed in Appendix 5 is recommended for use.

6.5. Unloading operations for rail- and road transport

The unloading operations should be carried out according to the guidelines shown in Appendix 6.

6.6. Vapour control

Because of the flammability hazard (in certain circumstances) and the unpleasant smell, all loading/unloading activities should preferably be carried out, having regard to the prevention of the ignition sources and styrene vapour emissions in the working area.

6.7. Previous cargoes and cleanliness

A tank that carries Styrene Monomer should not have carried the following substances as any of the last two cargoes:

- Caustic soda
- Pyrolysis gasoline
- Fuel oils
- Lube oils

Tanks to be loaded with Styrene Monomer should not be cleaned with materials which are reactive with Styrene Monomer or TBC, or cause increased colour, odour or a chloride problem. Salt water should never be the last wash because of possible chloride contamination.

Because of the effect of the application of heat to styrene, steam cleaning of adjacent tanks to compartments which contain styrene or styrene residues is strictly not allowed.

6.8. Blanketing

Blanketing of tanks for fire protection should be considered if ambient temperatures warrant this ($t > 30^{\circ}\text{C}$). However, exothermic polymer formation is prevented by oxygen, so a minimum level of 15 ppm of dissolved oxygen is recommended. P-TBC should be added at a level depending on the residence time, but minimum at all times to be 5 ppm, to prevent subsequent poly-peroxide formation.

6.9. ROAD Specific Operations

6.9.1. Shipper's responsibility

All CEFIC members use the services of professional road hauliers for distribution of styrene. Road hauliers must meet all relevant national and international transport regulations relating to styrene. Road hauliers should preferably have a Quality system like ISO 9000 in place and have carried out an SQAS assessment (see <http://www.sqas.org>).

It is required that shippers carry out regular checks on compliance of the road transport operations of each of the hauliers.

6.9.2. Haulier's responsibility

The measures taken by the styrene supplier in order to ensure safe transport do not replace or diminish the basic responsibility of the haulier. The haulier is responsible for the safe transport and for compliance with the relevant regulations from the loading point to the discharge (unloading) point. The haulier is also responsible to ensure that the equipment meets the appropriate safety standards and is properly maintained.

6.9.3. Review

It is recommended that all suppliers involved in the transport of styrene should undertake regular reviews of the bulk road haulage operations of each of their hauliers. This will enable each supplier to satisfy himself of the suitability of hauliers employed and ensure that appropriate safety standards are maintained. The SQAS assessment reports can be used for these reviews.

6.9.4. Routing

Safe transport routes should be selected according to the destination; residential areas should be avoided if possible.

6.9.5. Drivers working hours and speed limits

Road hauliers must meet all legal requirements concerning drivers working hours and speed limits.

6.9.6. Safe Parking

Drivers of vehicles conveying styrene must, while on the road, ensure that the vehicle, when not being driven, is either continuously supervised or parked in a safe place. A secure depot or secure factory premises should be used whenever possible. Preferably, parking should be in an isolated position in the open, in an area which is lit at night. It is strongly recommended that receivers of styrene allow secure parking to vehicles which have arrived outside specific access times.

6.9.7. Severe weather conditions

Contracts between shippers and hauliers should provide for the case of severe weather conditions. In such an eventuality, it should be agreed that the driver will contact his employer to advise him of the situation. The vehicle should stop at the next suitable parking place, if possible relatively far away from houses and public areas. (In some European countries, this is mandatory for all hazardous materials).

6.9.8. Delays and transport accidents

All delays during transport, whether caused by severe weather conditions, break down or any other reason must be reported to the supplier as soon as possible. Transport accidents must also be reported to the supplier as soon as possible.

6.9.9. Subcontracting

Contractual arrangements between suppliers and hauliers should explicitly state that the transport must not be sub-contracted without the prior written approval of the supplier.

6.9.10 Transport Emergency Cards or Tremcards

One of the specific requirements of ADR not applicable to other modes of transport for the consignor is to provide "instructions in writing" to truck drivers. These instructions, for which the format and required content have been established, should enable the truck driver to be aware of the dangers of the products transported and to take the necessary actions in case of an accident or emergency. They must be provided in a language that the driver is able to read and understand, as well as in the languages of all the countries of origin, transit and destination. The standard written instructions developed by Cefic are known as Transport Emergency Cards or Tremcards.

Instructions on how to obtain the styrene Tremcard in various languages are found on the Cefic website at: <http://www.cefic.org/Templates/shwStory.asp?NID=27&HID=382&PHID=381>

A specimen of Cefic's Tremcard for styrene is available in Appendix 9.

6.10. Intermodal transport

Intermodal can be used after a review of the whole transport chain. This review should be repeated at regular intervals.

6.11. Ferries selection

The supplier will ensure that he knows which ferry operators are being used.

6.12. RAIL Specific Operations

6.12.1. Transport responsibilities

The appropriate railway authorities are responsible for the safe transport of styrene by rail from the dispatch siding to the final reception siding. The selection of route, intermediate stopping locations and cessation of traffic due to severe weather conditions are matters to be decided by the railway authorities or the railway company owner of the rail network.

6.12.2. Rail Operators

Rail operators should preferably have a Quality system like ISO 9000 in place and participate in SQAS-Rail. (See Appendix 1).

6.13. Barges and Sea Operations / Cargo separation for safety purposes

6.13.1. Reactive Products

Products having known reactivity with styrene should not be loaded in cargo tanks, which have a common bulkhead (also corner-to-corner), pump or transfer piping.

6.13.2. Separate Systems

Tanks containing styrene shall have separate pumping and piping systems which should not pass through other cargo tanks containing incompatible cargoes and have separate vapour return lines.

6.13.3. Temperature

Styrene should not be loaded into cargo tanks adjacent or corner-to-corner to a cargo having a temperature of 30°C (86°F) or higher. Heating styrene to above this temperature will reduce shelf life and increase the risk of polymerisation in the cargo tank.

6.13.4. Heating coils

Heating coils in tanks carrying styrene shall be blinded off.

6.13.5. Edible products

Edible products shall never be loaded with bulkhead to bulkhead contact with styrene and piping systems should be entirely separate.

In addition, review US Coast Guard compatibility charts (Title 46, Code of Federal Regulations, part 150).

6.14 Barge Specific Operations

6.14.1. Barge selection

It is recommended that all suppliers involved in the transport of styrene should undertake inspections of barges or participate in a common inspection scheme. This will enable each supplier to satisfy himself of the suitability of barges employed and ensure that appropriate safety standards are maintained. Double-hull barges are preferred. By participating in the EBIS scheme the inspection reports are readily available.

6.14.2. Loading/unloading procedures

These operations should be carried out according to the latest edition of the ADNR checklist.

6.14.3. Board-to-board trans-shipments

If a board to board ship transfer is required, this should be subject to the authorization of the PORT AUTHORITY. If the PORT AUTHORITY permits ship to ship transfer, it should impose conditions such as special safety check lists and control of the place where the operation may be undertaken, taking into account the particular hazards involved.

6.15. SEA Specific Operations

6.15.1. Parties involved

Because of the nature of the activity, a number of different parties may be involved in the operation of transporting styrene from supplier to customer. These may include the shipping company, port or harbour authorities, terminal owners and hauliers.

6.15.2. Certification

All bulk tankships used for the transport of styrene must carry the relevant IMO certificates.

6.15.3. Vessel loading and unloading procedures

Vessel loading and unloading should be conducted in accordance with the "IMO Recommendations for the safe transport, handling and storage of dangerous substances in port areas", using in particular the ship/shore safety check list.

6.15.4. Vessel selection

Vessels for the carriage of styrene should be selected using the CDI-M protocol. Company templates are to be applied to check compatibility with the company's requirements. Alternatively, a company-vetting system should be used.

6.16. TANK STORAGE OPERATIONS

6.16.1. Certification

All bulk storage CDI-T operations must meet the requirements of the relevant national regulations.

6.16.2. Inhibitor control

During storage the inhibitor content should be tested at regular intervals and as necessary restored to the required levels.

6.16.3. Loading / unloading lines

The use of dedicated loading and unloading lines is recommended.

6.17. CUSTOMER COLLECTION

Customer collection should be minimised. When customer collection cannot be avoided, the same criteria for transportation equipment and haulier selection should be applied as when the supplier arranges transportation.

The equipment should comply with the specifications indicated in the Appendices 5, 6 and 7.

7. EMERGENCY PROCEDURES

7.1. Emergency Planning

All styrene producers involved in transporting styrene in Europe should have an established Emergency Plan for receiving transport incident reports and for providing expert advice by telephone and, as necessary, at the incident scene to the Emergency Services on how to minimise any danger arising from an incident on road, rail or waterway. The CEFIC document "Distribution Emergency Response - Guidelines for Use by the Chemical Industry" provides advice on setting up a Company Emergency Plan. (<http://www.cefic.be/activities/logistics/ice/ice-guide.htm>).

7.1.2. CEFIC ICE

With the objective of ensuring that expert advice is available as promptly as possible at the scene of any styrene transport emergency; all European styrene producers should participate in a national schemes set up under the CEFIC ICE concept.

7.1.3 Response Plan

In the same way, facilities using styrene should have developed and implemented a comprehensive spill prevention and emergency response plan.

This plan should address:

1. Spill detection methods,
2. Emergency notification procedures,
3. Community contacts for notification and advice on evacuation needs,
4. Fire prevention and protection,
5. Provisions for spill containment/clean-up,
6. Environmental protection,
7. Compliance with applicable local regulations or laws.

7.1.4. Fire

In the event of a fire, the emergency response plan should take into account not only the potential impact on the site operations but also the impact on the neighbouring community. The response plan should include notification to local authorities and communications to the public.

7.2. Measures in the event of a release of styrene

7.2.1. Emergency Response Team

Fire fighting crews must take note of hazards unmatched by any other occupation and therefore must take note of the styrene specific hazards, i.e. flammability and explosion potential above 31°C.

A runaway reaction (uncontrolled polymerisation) may lead to violent eruption of vapour from vents and if these are plugged sufficient pressure can be created to rupture the container. For further information about styrene polymerization in storage please refer to Appendix 2.

Vapours are heavier than air and therefore safe distances must be maintained. Smoke may contain styrene in addition to unidentified toxic and irritating compounds and therefore requires the use of a self-contained breathing apparatus. For a comprehensive set of product data aspects and personal protection, see [Safety Data Sheet](#) and also Section 8.

7.2.2. ERICards

Emergency Response Intervention Cards are a set of emergency instructions that provide guidance on initial actions to be taken by fire brigades when they first arrive at the scene of a chemical accident. ERICard for styrene is attached in Appendix 8. (www.ericards.net).

7.2.3. Spills and Leaks

Because styrene is only slightly soluble in water and extremely flammable at ambient temperatures, spills and leaks require prompt response to minimise the risk of fire and/or explosion, as well as to limit fugitive emissions. The first thing to do is to try to plug the leak. Afterwards, a decision may be taken to transfer the styrene to another container.

Styrene is toxic to aquatic organisms and therefore entry into drains, sewers and watercourses must be prevented if at all possible.

Since flammability is the main hazard is, it is important to eliminate all sources of ignition in the area of the spill. Styrene vapour is invisible, heavier than air and spreads along the ground.

To limit the flammability, exposure and environmental hazards, every effort must be made to contain spilled material and the evaporating area restricted as much as possible by erecting a physical barrier around the spill. Therefore, in the engineering phase, a bund and optionally a remote emergency containment system should be provided for the storage tank and unloading station, to achieve a limited evaporation surface, better foam effectiveness and improved run-off control of contaminated fire and sprinkler water. Overflow of hydrocarbons from bunds due to addition of fire, water can be avoided by installing an underflow weir or siphon. Advise the Water Authority if spillage has entered a watercourse or external drainage system.

Spilled monomer can be removed safely by covering it with a suitable absorbing agent such as sand. However, some absorbing agents, such as untreated clays and micas, may cause an exothermic reaction, which could ignite the monomer. Absorbing agents should be tested for their effect on monomer polymerisation before they are used on large spills. If the spill is on a hard surface, the area should be scrubbed with soap and water after the bulk of the monomer has been removed. When spills occur within a bund confined area without an impervious base, water should be pumped into the area immediately. This will prevent the monomer from soaking into the ground and will allow it to be pumped off the water layer for later recovery.

7.2.4. Accidental Release

In the event of a significant spill of styrene, all non-essential personnel should be evacuated and all sources of ignition extinguished immediately. After the appropriate personal protective equipment has been issued, the spill can be covered with fire-fighting foam as quickly as possible to minimise emissions and the potential of fire hazards. The released liquid must then be recovered and transferred to sealable tanks or drums. Any remaining quantities of styrene should be absorbed into suitable materials such as sand and transported in closed drums to a suitable processing installation. The recommended method of disposal is by incineration.

Depending on the volume and location of the spill, it can be recovered by an inert padded vacuum truck or with solid sorbent and placed in appropriate containers for disposal. Spills into surface water may be cleaned up using a skimmer or vacuum system because styrene floats on water and tends to polymerise to form a surface film.

7.2.5 Drums leaks

Any leaking drum must be turned around so that the leak is at the top, thus preventing any further liquid from being released. Where the leak cannot be sealed on the spot, the leaking drum should be put into an oversized, preferably, plastic drum.

7.3. Fire Fighting

7.3.1 Exothermic reaction

If styrene vapour ignites and the temperature of the liquid reaches 52°C, the stabilising effect of the inhibitor will be lost. There is then a serious risk that the liquid will auto-polymerise with the generation of considerable heat. Styrene tanks, which are heated by an external fire or other means pose a severe risk of bursting and explosion. See Appendix 2.

7.3.2 Fire Suppression

Fires involving styrene can be safely extinguished with foam, dry powder, water fog or carbon dioxide. However, water is not an effective extinguishing agent for use on water insoluble monomers such as styrene. Water jets should not be used, as these may simply spread the fire, styrene being both immiscible with water and lighter than water. Burning styrene may produce carbon, carbon monoxide, carbon dioxide and large quantities of thick black smoke. Fire fighters should wear breathing apparatus.

7.3.3 Foam

For extinguishing a fire and limiting evaporation, Aqueous Film Forming Foam or Alcohol Type Concentrate have been proven to be effective, i.e. that the lower flammability limit is not attained above the layer. Because a foam layer can break down, this function must be watched and maintained. As a few inches of foam are sufficient to smother a fire inside a container, the contained amount of water is unlikely to trigger a so-called slop over; larger amounts may do so.

If electrical equipment such as motors, open hot plates, or open electrical switches are involved, foam should be used with caution.

7.3.4. Water Spray

Styrene tanks or containers in the vicinity of a neighbouring fire should be kept cool by spraying with a water spray. Consider removing other flammable liquids in the vicinity.

A water spray has been proven to be the most effective way for product cooling, but its efficiency and effectiveness must be weighed against the risk of spreading styrene across the water surface, the chance of a slop over when water comes inside the tank, and the possibility to keep

the product within a containment system. Because of its flammability and explosion hazard, styrene must be prevented from entering sewers. Also the control of the disposal of deluge and/or spray water is important because the contained styrene is an acute hazard both for public sewers and wastewater treatment plants. In case of such a release, Local Authorities must be informed immediately.

8. PERSONAL PROTECTION, FIRST AID AND MEDICAL TREATMENT

8.1 Introduction

8.1.1. Exposure to styrene

During the manufacture and handling of styrene the substance may be released as a liquid or vapour resulting in pollution of air, soil and/or water.

The potential for exposure to styrene while handling the product exists mainly through skin and eye contact.

8.1.2 Occupational Health Aspects

Occupational Exposure Limits in European countries range from 20 to 100 ppm. To limit occupational exposure, the following principles should be followed and in the following order of priority:

1. Substitution – investigate the use of a less hazardous process
2. Isolation - the possibility of placing a barrier between the hazard and the worker (e.g. full enclosure or a fume hood) should be considered.
3. Ventilation – via engineering control of local and general ventilation

Personal protective devices, such as chemical resistant goggles or an apron, are last-resort types of control, and are to be used only where engineering controls cannot be made adequate.

8.2 Personal protection

8.2.1 Personal Hygiene

Remove contaminated clothing immediately, wash skin area with soap and water, and launder clothing before reuse.

8.2.2 Protective Equipment

8.2.2.1 Respiratory Protection

In order to protect worker health adequate engineering controls need to be in place. For the specific conditions of use and for meeting relevant workplace-related legislation suitable respirator protection should be selected. When used with an air filtering respirator an appropriate filter for protection against inhalation exposure to styrene is Type A for organic gases and vapours with a boiling point > 65 °C and meeting EN141 (to be superseded by prEN14387 in due course). If there is the potential for a mist to be present also, then a combined organic and particulate filter is appropriate. Particulate filters should meet EN143^{*)}. The respiratory protection devices are compressed air line breathing apparatus for use with a full-face mask, half mask or a mouthpiece assembly. The selection of an appropriate mask will be dependant on the use conditions and the likely airborne concentration.

*)Type A filters come in varying levels of capacity, 1,2, or 3 (3 being the greatest capacity). Particulate filters also come in varying efficiency classifications (P1 – low efficiency, P2 – medium efficiency, P3 – high efficiency). An example of such a combined filter is A2P3.

8.2.2.1 Hand Protection

Where contact with styrene may occur gloves approved to EN374 made from Nitrile Rubber, Neoprene Rubber or Viton are suitable. The suitability and durability of a glove is dependant on

frequency and duration of contact, chemical resistance of glove material, glove thickness and dexterity. In any case glove suppliers should be contacted for additional advice. Contaminated gloves should be replaced.

8.2.2.2 Eye Protection

Chemical splash goggles are recommended.

8.2.2.3 Protective Clothing

Under usual working conditions chemical resistant gloves/gauntlets, boots and apron are recommended. If there is a risk of styrene splashing or in a styrene spillage a chemical resistant one-piece overall with integral hood and chemical resistant gloves (see above: hand protection) should be worn.

8. First aid & Medical treatment

Acute intoxication with styrene or pTBC - symptoms and treatment

8.1. Eye

Can irritate the eyes. Immediately flush eyes with large amounts of water for at least 15 minutes while holding eyelids open. Transport to the nearest medical facility for additional treatment.

8.2. Skin

Can irritate the skin after prolonged and/or repeated contact. Remove contaminated clothing. Immediately flush skin with large amounts of water for at least 15 minutes, and follow by washing with soap and water if available. If redness, swelling, pain and/or blisters occur, transport to the nearest medical facility for additional treatment.

8.3. Inhalation

The vapour can irritate the nose, throat and lungs. After inhalation the vapour can be absorbed into the bloodstream and then cause toxic effects such as nausea, vomiting, loss of appetite and general weakness. Remove to fresh air. Do not attempt to rescue the victim unless proper respiratory protection is worn. If the victim has difficulty breathing or tightness of the chest, is dizzy, vomiting, or unresponsive, give 100% oxygen with rescue breathing or CPR as required and transport to the nearest medical facility.

8.4. Ingestion

May be aspirated into the lungs. If swallowed, do not induce vomiting. Transport to nearest medical facility for additional treatment. If vomiting occurs spontaneously, keep head below hips to prevent aspiration. Give nothing by mouth.

The ideal treatment for ingestion of small amounts of styrene is to give activated charcoal followed by a saline purge. Where excessive amounts might have been ingested, gastric lavage may be performed.

However, because of the attendant serious hazard of aspiration into the lungs, the relative dangers of aspiration as opposed to systemic absorption have to be considered. If lavage is not considered advisable, dilution with water and absorption by activated charcoal is necessary, followed by a saline purge. Observe the patient for a few days in case renal or hepatic injury develops (albuminuria, urobilinuria).

8.5. Contact with inhibitor

Eye:

If PTBC has entered the eyes, flush them immediately with water for 15 minutes. Obtain medical attention.

Skin:

Wash off with water immediately and use soap if available. Remove contaminated clothing immediately and wash it before re-use.

8.6. Sign and symptoms of prolonged exposure

Headache, fatigue, drowsiness, insomnia, anorexia and weight loss, pain in limbs, nervousness, impairment of memory. Transitory EEG anomalies, immune system changes and liver damage, may be present after prolonged exposures above the exposure limit.

For further information about the health aspects of styrene please refer to Section 3 "Health Aspects".

9. REACH AND STYRENE

9.1. What is the purpose of this page?

Under the REACH legislative system (**R**egistration, **E**valuation and **A**uthorisation of **C**hemicals) all companies working with chemical substances have specific obligations. This page is an initiative of the Styrene Producer Association (SPA) to assist the styrene industry, including downstream users with respect to the implementation and compliance with the REACH legislative framework. SPA is a sector group of Cefic, the Council of European Chemical Industry Federations.

9.2. How is the SPA organised for REACH?

SPA set up a REACH Task Force to develop and implement a REACH compliance strategy. One of its responsibilities is to prepare the formation of a registration consortium of manufacturers, importers, data owners and downstream users of styrene and ethyl-benzene, open to non-SPA members that will help future registrants to meet their Substance Information Exchange Forum (SIEF) obligations and make joint submissions.

9.3. What are SIEFs and what is their role with consortia?

A SIEF, or a **S**ubstance **I**nformation **E**xchange **F**orum, will be defined for each substance that is pre-registered between June 01st and December 01st 2008. The REACH legislation does not provide details on how SIEFs should operate. SPA identified a need to create consortia that will offer to coordinate the work done in the SIEFs for styrene and to some extent for ethyl-benzene. Participation of a SIEF member in a consortium is voluntary. Conditions for membership of a consortium will be fair and non-discriminatory.

9.4. What does SPA recommend to EU Manufacturers, Importers (M/I) and Downstream Users (DU) of styrene and ethyl-benzene?

SPA recommends that EU Manufacturers, Importers, or M/I, (represented by their "Only Representative"), Downstream Users (DU) of styrene and ethyl-benzene and Data Owners do the following:

- Understand the legislation and its guidance and determine if they need to register the production, importation or use of these two substances (and if applicable pre-register; the pre-registration period will begin on 1 June 2008 and will end on 1 December 2008);
- Determine from the information given on this page, if they are likely to belong to a SIEF together with SPA members;
- Decide whether they will wait for the publication by the European Chemical Agency (EChA) (list of SIEFs) or whether they prefer to contact SPA proactively to declare their interest in joining the styrene or ethyl-benzene REACH Registration Consortium.

Downstream Users are encouraged to contact their suppliers for any additional information. Downstream Users should be aware that REACH created several obligations and rights with respect to the substances they use. One of these obligations is to provide substance use exposure information to be included in the registration dossier, if the use is also to be registered. Cefic recommends to the extent possible that the definition and standardization of exposure scenarios be coordinated by downstream users with their respective trade associations. Should these trade associations identify within their industry exposure scenarios linked to the use of styrene or ethyl-benzene, they should also contact SPA.

9.5. What are the benefits for M/I in informing SPA of their intent to pre-register styrene or ethyl-benzene or for DU in informing SPA of their uses?

There are several important reasons to inform SPA of the intent to pre-register and subsequently, to possibly register styrene or ethyl-benzene, and/or to inform SPA of their uses, including:

- The time allocated by the REACH Regulation for the organisation of the consortia and its relationship with the respective SIEF is very short; by proactively notifying SPA of their interest, non-SPA member companies will benefit from better preparation;
- If M/I, DU or Data Owners have physico-chemical, toxicological or eco-toxicological data on styrene or ethyl-benzene, these data can be more readily incorporated into the existing database of studies lowering the overall cost by allowing an earlier decision not to undertake additional testing, thereby avoiding testing whenever possible and in accordance with guidelines;
- Begin work as soon as possible to establish "sameness" of the substances added to the SIEF (see RIP 3.10 for details).

9.6. What about Confidentiality?

SPA staff is prepared to address questions concerning the confidentiality of information provided by any third party expressing an interest in joining a styrene or ethyl-benzene REACH registration consortium.

9.7. When will SPA set up a Consortium?

It is expected that a consortium will be set up on 1 June 2008.

9.8. What SPA will not do

SPA will not provide "helpdesk" services to non-members to help them understand their obligations under the REACH Regulation. The role of SPA is strictly limited to facilitating the formation of a consortium of future SIEF members with an interest in styrene or ethyl-benzene. Cefic, national chemical industry trade federations, EChA and the national authorities have set up several websites and contacts to help parties concerned understand their respective obligations.

For more information on REACH, visit the following websites:

[Cefic REACH information page](#)
[European Commission information page](#)
[European Chemical Agency](#)

For more information on the formation of styrene or ethyl-benzene consortia contact:

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Cefic

Phone: +32 (2) 676 7227

e-mail: pmb@cefic.be

or

Celine Oostens

Phone: +32 (2) 676 7262

APPENDIX 1: CEFIC AND RESPONSIBLE CARE

1. Responsible Care – A Public Commitment

"Chemical companies shall demonstrate their commitment to continuously improve all aspects of performance which relate to protection of health, safety and the environment."

2. Prevention of Accidents

Within Responsible Care, the CEFIC ICE prevention programme provides a valuable tool for reducing the number of incidents during the distribution of chemicals, from the time they leave the factory gate until their arrival at the customer's premises.

The objective is to minimize the possibility for incidents to happen. Since most distribution activities are subcontracted and since compliance with regulations is a necessary but not a sufficient condition to prevent accidents, there is a need for uniform safety & quality criteria against which distribution companies can be regularly assessed.

Unlike ISO 9002, which concentrates on quality, at a level set by the individual distribution company, SQAS - Safety & Quality Assessment Systems - provide objective performance indicators, which allow the monitoring of continuous improvements.

Based on detailed questionnaires, distribution contractors can be assessed by a qualified third party. Questions relate to management, equipment and operations, split by: statutory requirements, additional chemical industry requirements and desirable items. Scoring results can be presented in different ways but it is up to each individual chemical company to evaluate the results according to its own standards.

The distribution contractors will include:

- Marine transport: Vessels and barges
- Road transport: Road carriers
- Storage operations: Terminals/Warehouses
- Ferry operators
- Rail contractors

3. Emergency Response

The ICE Emergency Response programme aims to minimise the consequences of transport incidents involving chemicals by:

- Providing uniformly competent assistance in each European country.
- Coordinating Emergency Response particularly across national boundaries

The chemical industry commits itself to make its expertise available to authorities - who are normally in charge of the emergency - in three levels of assistance:

Level 1: Remote information and general advice by telephone or fax.

Level 2: Presence of an expert who will provide advice at the scene of an incident.

Level 3: Actual help with equipment and personnel at the scene of an incident.

Detailed information on this subject is contained within "the CEFIC Distribution Emergency Response Guidelines for use by the Chemical Industry",

4. CEFIC Recommendations on Safe Management Practices in Distribution

These recommendations conform to the principles of Responsible Care and include the following topics.

1. Safety, health and environmental policies
2. Auditing
3. Risk reduction
4. Specification of packages, tanks and other equipment
5. Incidents evaluation
6. Codes and regulations
7. Control of operations
8. Training
9. Selection and monitoring of Contractors
10. Data and information
11. Emergency Response
12. Information to the public

Although these Guidelines for the distribution of styrene are product specific, it is essential that policies, systems and procedures as described in the CEFIC Recommendations on Safe Management Practices in Distribution are in place and well maintained.

APPENDIX 2: STYRENE POLYMERISATION IN STORAGE

The following are a series of Questions and Answers on the subject of Styrene Polymerisation. The purpose of these Q & As is to facilitate the decision making process in the event of a Styrene polymerisation situation.

What parameters should be measured if polymer content is rising?

- Polymer content (< 10 ppm, depending on product spec.)
- Temperature (<< 2-3°C/day). If the temperature rises 1°C/day, it is advised to be alert and keep monitoring the temperature actively. Re-circulation could stop the temperature rise. A 2-3°C/day temperature increase is a typical indication of the onset of a runaway polymerization. The temperature needs to be monitored continuously.
- p-TBC levels (target >10 ppm wt). At temperatures below 20°C in the tank/container weekly sampling should be sufficient; above 27°C daily sampling is recommended. Normal p-TBC levels are between 10 and 15 ppm (for some applications higher concentrations are required). Below 10 ppm p-TBC polymer levels can slowly increase; below 4 ppm the p-TBC is not effective and accelerated polymerisation will occur.
- Oxygen levels (~ 10 ppm in solution).

What do we exactly define as polymer content – polystyrene or dimers, trimers, oligomers?

The ASTM D2827-04 standard specification of styrene monomer, prescribes that the polymer content is analyzed by means of ASTM test method D2121 A. This test method utilizes the fact that polystyrene is insoluble in methanol and will not detect dimers and trimers. Any oligomer containing four or more monomer molecules is therefore defined as polymer.

How often should the styrene be analyzed for polymer levels?

Under normal storage conditions: typically 2-3 times/week for product quality.
If product temperature is above 27°C: daily.

How can we ensure thorough mixing of the inhibitor if there is insufficient circulation?

When selecting a tank for SM storage, circulation should be a minimum requirement to make sure that

- temperature readings are indicative for the bulk
- inhibitor and oxygen are mixed well with the tank contents

If tank contents are not homogeneously mixed and, in the undesired situation that the tank is not equipped with facilities to circulate, the following measures can be considered. In order of preference and availability:

- Use circulation pump
- Try circulation with existing equipment like transfer pumps, minimum flow lines, sample loops
- Connect temporary pump (e.g. compressed air driven)
- Bubbling air (has also got the advantage that oxygen is present to enable pTBC to be effective) through a utility connection on the tank.
- Bubbling nitrogen through a utility connection on the tank. Beware of asphyxiation. If dissolved oxygen concentrations become too low, this might affect the effectiveness of the inhibitor.
- Add solid CO₂ into the tank. The generated vapour bubbles will mix tank contents. This also cools the tank contents somewhat. Make sure that tank venting capacity (emergency relief valve) is large enough to cope with the vapour. This would be a last resort and is not “proven technology” in styrene storage. In oil tanks at refineries this is sometimes used. Beware of

asphyxiation, the large volume of CO₂ could displace (part of) the oxygen that is required for the p-TBC to be effective.

When adding air, nitrogen or carbon dioxide it is strongly recommended to contact technical support to make sure that the situation is not made worse by e.g. over-pressuring the tank.

What measures can be taken to reduce the rate of polymerisation?

- Reduction of tank temperature (if not yet too high):
 - Use refrigeration facilities if available (circulation through cooler). Make sure that the heat exchangers are designed for the temperature of the styrene product.
 - Use external water spray. This has a limited effect and unmanned hoses should be used. When the tank is insulated, insulation needs to be removed first, otherwise this has no effect at all.
 - Remove insulation
 - Use ice. Place into the styrene product in sealed metal (free of rust) containers, not directly into the product. Make sure that the tank temperature is not higher than 100°C to avoid flashing of the water inside the containers, causing severe damage.
- Increase inhibitor levels by dosing p-TBC (up to 100 ppm is acceptable for some customers), aerate the tank contents, and:
- Mixing of bulk contents to make sure that the inhibitor and oxygen are effectively mixed.
- At higher polymerization rates (i.e. possible HSE risk), mitigate by adding a large enough volume (4:1) of cold inert material (Ethyl benzene (EB), xylenes, toluene) to dilute and cool the styrene. The resulting product cannot be sold and needs to be re-worked or burned as fuel.

When adding EB at 20°C to polymerising SM at 50°C, a (conservative) EB-dosing rate of 7 kg/hr/ton storage is required to absorb the generated heat of reaction, provided that the tank is well mixed.

This can ONLY be done if the temperature of the tank is well below the boiling point of the diluent (136°C for EB), otherwise it may vaporize or flash off violently, causing damage to the tank or container. Also, the reaction rate at such high temperatures is so high that unfeasibly high EB pump rates are required to absorb the generated heat.

At high temperatures (>52°C) pTBC is not an active inhibitor (reaction rates and therefore pTBC consumption are high). A retarder like DNBP can then be considered.

Does a high polymer level always mean the bulk of the product is polymerising?

No.

- Bulk polymerisation can be recognized by a gradual increase of the polymer levels, a gradual depletion of p-TBC levels and a slight increase in temperature.
- Condensing styrene vapour against tank roof or internals does not contain inhibitor and can form polymer stalactites. These can break off and dissolve in the bulk. This can be recognised as a sudden increase in polymer levels and constant p-TBC levels.

Sections of piping where there is no flow of material (deadleg) can polymerise over time. Examples of such sections are: low points of pipework, pumps (e.g. spare pumps), sampling systems, etc. When circulating the bulk contents this polymer can dissolve. This leads to a sudden (or gradual, but not following the polymerisation kinetics) increase in polymer content (note: p-TBC levels and temperature will remain constant).

Can there be a runaway reaction if there is inhibitor present in the styrene?

Not under normal storage conditions, but it is possible under uncommon, favourable conditions:

- Contaminants (e.g. insufficient/incorrect cleaning of storage/transportation medium) that initiate polymerization and overwhelm the inhibition effects of p-TBC. Known contaminants that initiate polymerization are: acids, peroxides, iron chlorides.
- Rust (particles) inside the tank can form fertile seeds to initiate polymerisation.

- High enough (local) temperature ($\sim > 40-50^{\circ}\text{C}$) (e.g. exposure to heat from adjacent tank fire). p-TBC is not active long enough at high temperatures, since the reaction rate and therefore the depletion rate becomes too high.
- Non-homogeneous distribution of the p-TBC and oxygen in the tank contents: If the p-TBC concentration is low at certain zones in the tank, this could lead to runaway zones in the bulk contents.

As polymer levels increase, will there be a concomitant rise in temperature?

That depends:

- No, when the increase in polymer levels is caused by polymer dissolving from tank internals or piping there will be no temperature increase.
- Yes, when the bulk contents are polymerizing a $2-3^{\circ}\text{C}$ temperature increase is observed per 1% SM polymerisation.

But please note: temperature indicators in styrene tanks may only measure local temperatures and are misreading when the content is not well mixed!

What polymer and temperature levels are indicative of a runaway reaction?

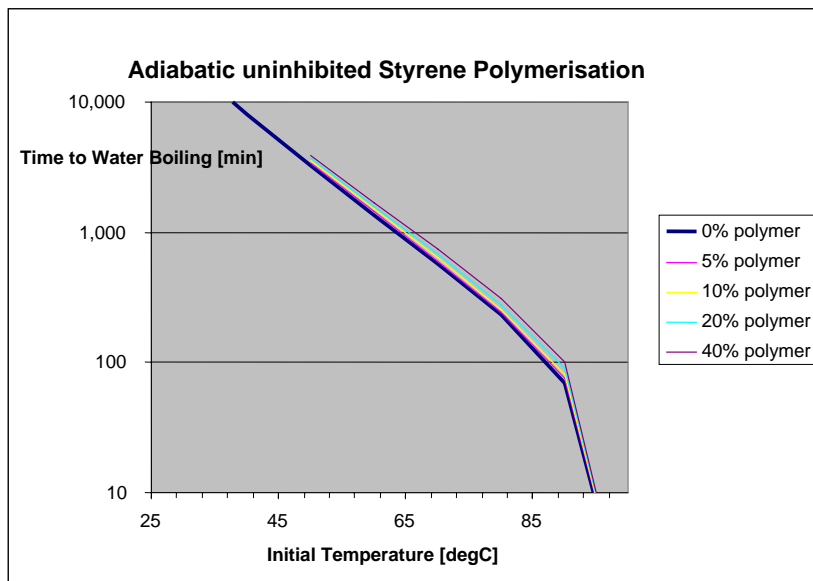
- That depends on the starting temperature. A better indication would be the temperature increase. A $2-3^{\circ}\text{C}/\text{day}$ temperature increase indicates the onset of runaway reaction.
- The actual runaway is very rapid. As soon as a temperature of 65°C has been reached, it takes about 20 minutes before a complete runaway.
- Starting at 20°C uninhibited styrene takes 25 days to show a 10°C temperature rise.
- Temperature is a better indication of a runaway than polymer levels. High polymer levels are not necessarily an indication for a runaway, but must just as well be taken seriously.

Make sure that the temperature reading is representative for the bulk temperature. Polymerization can be ongoing unnoticed in zones that are not near the thermocouple if the tank contents are not well mixed.

How much time do we have before the reaction enters the “runaway” mode?

The TWB (Time to Water Boiling) graph in Figure 8 can be used to make an evacuation decision: e.g. If is 85°C , the storage tank may rupture within 100 minutes.

Figure 8: Predicted moment of storage vessel failure



For normal storage tanks the design pressure will be exceeded during the runaway. The venting capacity is normally insufficient for a runaway.

The ultimate consequence of a runaway in a styrene storage tank therefore is a vessel rupture. It is possible to predict the moment of vessel rupture when the tank temperature is known. This knowledge can be used to make an informed decision on evacuation of (emergency) staff or notification of 3rd parties (authorities).

Assumptions:

- The tank is adiabatic
- The tank is well mixed (e.g. the temperature is measured correctly)
- The reaction is uninhibited
- The storage vessel has a design pressure of around 1 bara.
- The styrene is possibly contaminated with water.

Since the final part of the runaway has a very steep dT/dt curve the time at the vapour pressure reaches 1 bar is nearly identical for (1%) for water and styrene.

By the same reasoning, the time at which a 1 bar vapour pressure is reached is nearly identical to that of reaching a 1.5 bar pressure.

Therefore the time at which normal storage tank fails will - within engineering accuracy - not be determined by the presence of water or by the design pressure.

Furthermore, the build-up of polymers also has a negligible influence.

Figure 8 is conservative (i.e. "safe") unless:

1. The temperature measurement is not accurate (e.g. in a dead zone)
2. The reaction is accelerated due to radical forming components like hydroperoxides
3. The tank is heated through other mechanisms (solar radiation, high ambient temperatures, fires etc)

Figure 8 is over-cautious unless:

1. The reaction is inhibited
2. The tank is cooled
3. The polymerization has exceeded 50%

What is the colour of high polymer styrene compared to on-spec styrene?

Normally this is colourless (as is on-spec styrene), but various sources of contaminants can colour the product:

- Copper or copper-containing alloys can give a blue-green colour
- Styrene oxidation products can be highly coloured
- Iron (rust) can give a yellow colour
- Very high concentrations of polymer can colour the product yellowish.

Being off-spec is therefore not a strong indication of polymerisation.

At what polymer level does styrene become too viscous to pump?

It depends on the type of pump. In general a polymer level of 20-30% is likely to trip a pump that is not designed to move partially polymerised styrene on high amperage or high power consumption. The pump might not have such a trip and could damage the motor.

If the product is too viscous, it can be diluted (up to 50%) with e.g. toluene, xylene or Ethyl benzene.

Can we transport the product if polymer levels are rising?

There is a risk of exposing the public to an incident if this goes wrong. It would depend on the temperature and temperature rise of the styrene and the time required for transport. Loading road cars does have the advantage that the styrene product will be homogeneously mixed during loading and transportation. With sufficient p-TBC levels this could stop the polymerization reaction.

Will adding a nitrogen blanket slow down the polymerisation reaction?

No. Oxygen needs to be dissolved in the product in order for the p-TBC to work effectively. Without having a nitrogen blanket the oxygen in the air can be assumed to be in equilibrium with the oxygen that is dissolved in the product. With an inert blanket, an oxygen concentration of 6 vol.% needs to be maintained in the gas cap.

Oxygen is required for p-TBC to work effectively. Is there a risk of creating a flammable mixture?

Yes, there is. The flash point of styrene monomer is 31°C, so therefore there is a chance of creating a flammable mixture in warm climates if the storage vessel is not blanketed. A proper risk assessment should be made. Since oxygen is required for the p-TBC to work effectively a nitrogen blanket with 6-10 vol.% could minimize the risk of fire/explosion and avoid polymerisation. Static electricity or any other ignition source should be avoided at all cases.

What additional controls should be considered when transporting (high polymer) styrene?

- Inhibitor levels (Enough for duration of journey. Assuming the styrene is saturated with oxygen, the shelf life is 5-6 months with 12-15 ppm p-TBC)
- Materials of construction (similar to storage, e.g. stainless steel)
- Stowage plans (don't store styrene adjacent to heat or containers of polymerization initiators like peroxides, concentrated acids, ...)
- Cleaning of transportation medium (no traces of contaminants from cleansing agent or other products that had been stored)

Is there a preferred physical state for the inhibitor to be added (i.e. liquid, powder)?

Yes. p-TBC is supplied in solution (85% p-TBC in 15% methanol or water) in drums. For 10 ppm inhibitor in styrene, 0.2 kg of p-TBC solution should be added to 20 m³ of styrene.

Are there any standard processes/procedures for dosing TBC? (against which we could validate 3rd party capability).

Not really. If an inhibitor dosing system is present this can be used as described in the operating manual. Pouring a drum/bottle/can of p-TBC solution manually into the storage vessel/tank would do the trick as well. Appropriate personal protection should be applied and MSDS should be available to understand the risks.

What are the trigger points for product disposal of off spec/high polymer material? (Linked to this: Establish disposal options at danger levels. Guidelines for disposal)

- If the polymer levels are not extremely high, specific alternative customers can be found that are able to process the off-spec material.
- As an alternative, the off-spec product could be blended with on-spec product to reduce the polymer concentration and bring the product back on spec.
- When temperature and polymerisation are stable, the styrene needs to be removed from the tank before it solidifies. If it is already too viscous to pump, dilution might help.
- The product can be used as fuel.

Can a ship's cargo of off-spec/high polymer SM be overdosed with p-TBC such that the product arrives on spec due to the depletion rate of p-TBC

Practically not, but it depends on the destination of the product. Too much p-TBC can colour the product. If the product, although off-spec, can still be used as feedstock for other products, colour might be a problem and p-TBC dosing might be limited. This should be discussed with the potential customer (some customers can accept up to 100 ppm of p-TBC). The amount of p-TBC to add depends on the time it takes to arrive at the final destination. Also during the journey p-TBC can be dosed, but will not bring the product back on spec.

What are the hazards of p-TBC?

p-TBC is a polymerisation inhibitor and an antioxidant for Styrene. It forms hygroscopic crystals or flakes and is poorly soluble in water, but soluble in ether, alcohols and acetone. P-TBC is harmful if inhaled, ingested or absorbed through the skin. It is severely irritating to skin (some producers even classify it as corrosive), eyes, respiratory and gastrointestinal tract. It could cause allergies following skin contact. There is no evidence for carcinogenicity or genotoxicity, but effects on blood (formation of methemoglobin) have been observed. Due to its close to corrosive effects p-TBC might have negative effects on aquatic organisms.

What are the hazards of DNBP?

DNBP (4,6-Dinitro-2-sec-butylphenol) is used as a polymerization retarder for Styrene. At room temperature DNBP forms solid crystals, poorly soluble in water, but soluble in organic solvents. It is combustible and may explode, if heated in a closed system. DNBP is absorbed in the body after skin contact, ingestion or inhalation. It is a severe eye irritant. Hemolytic effects as well as necrosis of liver and kidney have been observed. From animal experiments it has been concluded that it is toxic, a developmental toxicant (category 2) and impairs male fertility (category 3). In humans DNBP has effects on the gastrointestinal tract and liver (jaundice) and causes hyperthermia. There is no evidence for carcinogenicity and genotoxicity. DNBP is very toxic to aquatic organisms. It is hazardous to environmental organisms, such as mammals, bee and birds and is classified as Marine Pollutant. It is bio-accumulative and persistent.

The use of DNBP as ingredient of crop protection products is banned because of birth defects, male sterility and acute effects in agricultural workers.

Can off-spec/high polymer be drummed?

It can be drummed, if the tank temperature and polymer concentration are stable. Drumming is however not preferred and not practiced within most companies. Pumping the off-spec product to tank cars is preferred.

Could the efficacy of p-TBC alter due to a change in supplier?

No. There is no reason to suspect differences in efficacy between various suppliers. p-TBC is delivered in 85% solution and added to the styrene product in concentrations of typically 10-15 ppm. Any contaminant would therefore be diluted to very low ppm levels and would not be likely to cause significant quality problems to the finished product.

Can p-TBC still be used if the shelf life has expired?

p-TBC is a very stable chemical. Proper storage conditions and a lab test before applying p-TBC to make sure it still meets the purchase spec should be sufficient.

Is there a p-TBC efficacy test if supplier is changed. (Note : Maintain a list of approved suppliers).

No. There is no reason to suspect differences in efficacy between various suppliers. Approval is determined by quality, delivery lead times, price, ...

Potential suppliers:

- Rhodia PPA in Siant Fons, France and Baton Rouge, LA, in the USA
- Borregaard Italy in Madone, Italy
- Dainippon Ink and Chemicals Incorporated in Ichihara, Japan
- Penta Manufacturing Company in Fairfield, NJ, USA

- Zhengmao Chemical Factory in Wuxi, Jiangsu province, PR China
- K.K. Poonja & Sons in Mumbai, India
- Pergan GmbH in Bocholt, Germany

Should the tank capacity and volume of styrene be considered in the event of high polymer levels being measured?

Yes, for obvious reasons. The more styrene that is available, the better an uncontrolled polymerisation can be sustained and the larger the loss of containment in case the tank is over-pressurised. More styrene also requires a larger volume of diluent to quench a reaction. The tank must have the capacity to contain the styrene product as well as four times that volume for adding a diluent.

What reference documents are available to support a styrene polymerisation emergency situation?

Product Safety Data Sheets

Definitions:

Inhibitor	Chemical that is added to another chemical to prevent an unwanted reaction (e.g. polymerisation).
Retarder	Chemical that is added to another chemical to slow down an unwanted reaction (e.g. polymerisation)
Runaway	Self-accelerating chemical reaction (e.g. polymerisation). During a runaway the temperature will rapidly increase.

APPENDIX 3: DESIGN AND CONSTRUCTION OF VESSELS AND BARGES

1. Introduction

As there is a considerable variety in the existing design of vessels and barges for styrene movements, each vessel/barge should be inspected prior to contracting and should conform to a checklist compiled from specific design requirements.

2. General Recommendations

In addition to the relevant IMO and ADNR requirements vessels and barges should have:

- Vapour return facilities.
- A closed ullage system and a system for overfill protection including an automatic alarm.
- Efficient stripping facilities.
- Double hull
- A communication system
- Stainless Steel preferred, otherwise lined mild steel (zinc silicate lining or Teflon coated)

For new vessels and barges, a computer system to control/measure tank contents on board is recommended.

APPENDIX 4: DESIGN AND CONSTRUCTION OF TANKS

General Tank Design Aspects

In addition to the precautions for flammable liquids, the maintenance of a uniform temperature, preferably below 25°C, is important. The internal surface of the tank, including safety devices, must be smooth to avoid adhesion of condensed styrene and thus build-up of polymer. For emergency situations, facilities must be provided, both to adjust the inhibitor content and to inject air or oxygen into the pump suction and/or circulation system. The use of inert gas implies that styrene vapours can be captured for treatment or recovery, but also that with TBC as polymerisation inhibitor, in line with a minimum of 10-15 ppm in the liquid phase, the oxygen content must in theory absolutely be maintained above 4-5%-vol. (note: when stored under air, the oxygen solubility in styrene is about 50 ppm; see Table 2). In other words, if pure nitrogen or other inert gas is used, air or oxygen must be injected into the liquid.

Because at higher doses TBC can form coloured complexes, the standard inhibitor content of 10-15 wt. ppm is sufficient for normal temperatures and storage time. Stagnant product must be avoided. Blocked lines and infrequently used valves are typical situations in which the proper conditions are not met. Therefore, to achieve protection in each corner, the tank contents must be circulated frequently. Experience has shown that efficient circulation is also important to avoid a temperature gradient in the tank. Inlet, outlet and recirculation connections are required and optionally, as explained later, a swing pipe.

Tanks should be designed and constructed in accordance with an appropriate and recognized standard of good engineering practice (e.g. British Standards, German Industry Norms (DIN) and American Petroleum Institute Standards) and take into account local climate conditions.

4.1. Construction materials and tank internals

The standard construction material is carbon steel or stainless steel. Aluminum is satisfactory but will not withstand a fire. Internal structures like beams and pipes should be minimised as these provide places for condensed styrene to accumulate and polymerise. The insulation of storage tanks especially in warm and hot climates is recommended. A white reflective exterior coating will increase the effectiveness of the insulation.

Copper will combine with the organic acids and oxidation products present in the monomer. Therefore, copper and copper alloys must be avoided. The resulting impurities will colour the monomer green and will inhibit polymerisation of styrene.

The roof openings above the normal liquid level should be large in diameter and kept to a minimum number. By sloping the tanks toward the drains, horizontal tanks can be drained more completely.

Floors of large vertical tanks may be tilted toward a small built-in sump with a bottom drain.

4.2. Pressure rating

The design pressure should be to API-620 or equivalent. This sets the specification for the relief system as well as minimising breathing losses during ambient temperature changes and enabling vapour conservation measures during filling. Containment of breathing losses during a temperature rise of the contents of 20°C should be considered. Preferably the vents should be connected to a vapour collection and recovery or treatment system and thus minimise hydrocarbon emission.

4.3. Fire protection

Considerations in site selection and tank spacing include proximity to other flammable material storage facilities, nearby sources of ignition, accessibility of fire fighting, and the impact of vapour cloud explosion on nearby areas. Fire monitors may be considered to provide cooling in the event of an external fire. Monitoring of oxygen levels within the vapour space inside the tank is one approach to ensure that oxygen levels remain below 8% at all times and thus an explosive atmosphere is avoided. A flame arrestor or pressure vacuum relief valve may be installed between the tank and any external opening if an explosive atmosphere within the vapour space is possible. Flame arrestors should be purged with nitrogen to prevent polymer formation. All safety equipment should undergo regular maintenance and replacement to avoid fouling/plugging by styrene polymerisation. See Table 3 for recommended inspection details. The installation of a foam chamber or sub surface injection connection is also recommended for automatic fire fighting, particularly on larger tanks.

4.4. Lining

Tank linings can help control or reduce polymer and stalactite formation, in particular in hot climates. A non-porous, non-wettable, and smooth tank lining prevents retention and attachment of the condensed (uninhibited) monomer droplets. As a result, the monomer drains quickly back into the pool of inhibited liquid monomer before polymerisation can take place. Both inorganic zinc silicate and epoxy linings can be used for storage tank surfaces as well as internal necks for safety features. The resistance characteristics of these should be checked, and information obtained from the manufacturer on their long-term performance for styrene storage. Rubber-based linings and polyamide-cured epoxies should not be used.

4.5. Uniform temperature control

Efficient mixing is important to achieve a uniform temperature. Therefore, inlet, outlet and re-circulation connections are usually located near the bottom of the tank and can be reversed so that the product is pumped from the bottom and discharged through the swing pipe below the liquid surface. If desired, cooling the content from the bottom up can be achieved via the swing pipe, i.e. styrene can be withdrawn below the liquid surface and returned to the bottom. It is stressed that return of product to the tank should always be below the liquid level, to prevent static electric charge build-up, and that a reliable siphon break should be provided in dip pipes. It goes without saying that in warm climates, a chiller will be a minimum requirement to maintain the desired storage condition.

4.6. Lines and valves

The following are recommended engineering practices for styrene:

1. Lines smaller than 25 mm in diameter should not be used,
2. A minimum of flanged connections is preferred because of leak potential,
3. Lines should not be buried because of the difficulty of checking for leakage,
4. All lines should be sloped so they can be completely drained for maintenance,
5. Newly installed lines should be pressure tested by an approved method before insulation.

Thermal expansion in blocked styrene lines exposed to the sun and without relief protection can cause high pressure, which can result in failure of gaskets, pump seals, and pump housings. Excessive temperatures in blocked lines can also cause polymerisation. If burial is preferred, the regulatory requirements to protect soil and ground water should be observed.

A dip pipe should extend to the bottom of the tank and be provided with a pinch hole (siphon break). The electrical continuity across connections should be checked to ensure grounding. Lines constructed of carbon steel are acceptable, but copper, bronze, or plastic should not be

used. Large lines are usually joined by welded flanges, for smaller lines threaded joints are satisfactory.

Styrene can dissolve pipe dope and thus cause product coloration and contamination. To avoid this, the pipe threads can be wrapped with PTFE [poly (per)tetrafluoroethylene] tape.

As with all transport equipment, caution should be taken with the choice of valve. All valves should be protected against climatic extremes, shock and mechanical stress. For rail tankers left standing in the sun, resultant high temperatures can promote polymerisation of styrene. A fusible airline or equally effective safety shutoff valve should be installed to close off lines in case of excessive external heat.

Emergency block valves for isolation of equipment by remote activation may be considered on storage tanks, unloading stations and long pipelines holding large amounts of styrene. Plug cocks and ball valves, lined with fluoro-elastomer, give excellent service with stainless steel balls. Gate valves are less satisfactory, but usually cheaper, and may be used. Lubricated plug cocks and non-lubricated ball-type valves are satisfactory. The piping system should use either ball valves or plug valves. However both types of valve can trap styrene that may polymerise, seize the valve and render it inoperative. Thus all valves should be regularly inspected according to the recommendation in Table 3. Gate valves may be considered for applications with infrequent use. The piping system should use plug valves rather than ball valves for all manually and infrequently operated valves. Ball valves may trap product that may polymerise, seize the ball and thus make it inoperative. To limit emissions from packed glands, bellow valves may be considered. Drain line valves should be provided with a cap or end-flange. Valves must be protected against freezing, heat shock, or mechanical stress.

4.7. Pumps

Most pumps are suitable for styrene, except those having copper, bronze, or plastic parts. Centrifugal pumps with enclosed impellers and mechanical seals are the most widely used, but displacement pumps and rotary pumps are satisfactory. A canned or magnetically driven pump may be considered to comply with tight fugitive emission regulations. All metal should be properly grounded to avoid static accumulation. Because deadheading will cause heat build up and lead to polymerisation, a minimum flow line should be installed.

The pump and circulation system should allow injection of instrument air, TBC stock solution, to inject foam to smother a fire, and a diluent, e.g. toluene or ethyl benzene, to reduce the viscosity of the tank content during a runaway polymerisation. In addition to mechanical reliability aspects, environmental performance parameters should be considered in the selection process for seals. For mechanical seal components it is recommended to specify the stationary face (e.g. tungsten carbide) and rotating face (e.g. carbon). Tandem seals with barrier fluid are recommended.

4.8. Tank pit

A containment system is a basic requirement for styrene storage to:

1. Limit the spreading of a product spill and thus limit the flammability and environmental hazard,
2. Control run-off during fire fighting,
3. Provide a barrier against soil and groundwater contamination,
4. Allow spilled product to be effectively covered with foam.

An under storage leak detection system is recommended. For containment the storage size, configuration and hydraulic load due to sprinkler water and rainwater and whether foam will be the standard medium/practice for fire extinguishing should be considered. To contain the styrene in such a situation, a siphon or under-flow weir may be considered.

4.9. Loading and unloading facilities

A remote impoundment for flammables could be considered.

4.10. Drainage

Installation design should allow for recirculation and complete drainage, and subsequently flushing with inert gas. This is especially important when styrene is stored for extended periods or when equipment is used intermittently.

4.11. Accessories

Gaskets and O-rings

For flanged connections at ambient conditions it is recommended to use gaskets of PTFE or graphite with a reinforced rim inside. O-rings in styrene service should be made from a co-polymer of fluorinated ethylene and fluorinated propylene. Rubber or other styrene soluble materials and PTFE encapsulated O-rings should be avoided. For gland sealing, graphite (optionally PTFE) is the material of choice.

Filters

Since small amounts of foreign matter may enter a storage tank from various sources, a filter in the transfer piping between tank and processing equipment is recommended. A replaceable cartridge or filter is recommended. Suitable materials are polyester and nylon. Especially for sealless pumps, an inline basket strainer is recommended. The strainer will have adjacent isolation valves and connections for blowing it clear, for safe removal and cleaning.

Flexible transfer hoses

To avoid product contamination, the most important aspects for transfer facilities are easy cleaning and product compatibility. Therefore lightweight aluminum pipe and swing joints, with seals of fluoro-elastomer are preferred.

Composite hoses, which are static-conductive, and flexible metal hoses (woven metal type) are satisfactory, but they require more care and attention to keep them properly clean and to prevent damage or breakage during use.

Hoses from fluoro-olefin elastomers give the best service and are the most widely used of the composite hoses.

Neoprene elastomer synthetic hoses do not have sufficient resistance to aromatics and are therefore not recommended for styrene service.

Multi-layered polypropylene and PTFE hoses are flexible and chemically resistant, and are therefore recommended materials.

Because styrene can attack the interior of a hose, it should never be allowed to stand in any of the composite hoses. All residual styrene should be drained, and all intermittently used transfer lines should be thoroughly cleaned to prevent formation of polymer and other undesirable reaction products. All transfer lines and hose connections should be properly grounded to prevent build up of static electricity. Regular preventive maintenance is recommended for flexible transfer lines.

APPENDIX 5: CHECK LIST FOR LOADING

1. Routine Inspection of Road Tankers and Tank Containers at Loading Terminals

If any of the following conditions are not met, the loading operation must be stopped and the situation rectified before loading is allowed to continue.

A) Before Loading:

1. Are there any visual safety deficiencies on the truck? (e.g. lights, tyres, windscreen, etc.)
2. Is there a valid ADR-Certificate for styrene?
3. Has the driver a valid ADR license for the transport of dangerous substances and means of identification which include his/her photograph?
4. Are all dangerous goods labels fitted with correct identification numbers (39/2055) attached and are the Tremcards in all required languages on board?
5. For combined ADR/IMO transport; are the IMO dangerous goods labels fitted?
6. Does the driver have all the necessary items of protective clothing and safety equipment?
7. Is the tare weight in your possession?
8. Is the road tanker pressureless?
9. Is there a valid cleaning certificate (name / address / stamp) or a confirmation that the last product was styrene?
10. Are all the valves closed upon arrival?
11. Is the tanker properly earthed?
12. Can all valves be operated?
13. Are hoses on truck clean and qualified for styrene (for possible later use at customer site)?
14. Check the maximum allowed filling degree.

B) Whilst Loading

1. Are controls against leaks and spillages done?
2. Remove old Dangerous Goods labels of former products
3. Are all Dangerous Goods labels fitted with correct identification numbers (39/2055) attached and are the Tremcards in all required languages on board?

C) After Loading

1. Remove earthing
2. Clean tank outside wall surface and equipment from spilled styrene if necessary
3. Clean bunded filling station from spilled styrene if necessary
4. Are all valves closed and blinded, with all bolts in place?
5. Is the maximum gross weight exceeded? (Check by weighbridge)
6. Is the maximum degree of filling exceeded? (Check by weighbridge)

2. Routine inspection of rail tank cars at Loading Terminals

The same inspection list as for road tankers should be used (except Points 1,2,3,5,6 and 8). Identification requirements exist for all mode of transport.

Note: Rail tank cars have to be inspected on both sides.

APPENDIX 6: CHECK-LIST FOR UNLOADING

The same elements as in Appendix 5, 1(A) and 1(B) should be used for the preparation of a checklist for the inspections of the transport equipment before and during unloading. When discharging at a customer's premises, the following additional points should be noted:

1. The conditions of discharge at customer's premises are the customer's responsibility

2. The customer is responsible for writing and keeping Operating Procedures up-to-date for product discharge at his premises and for the operation of the customer installation during discharge. The customer must ensure that all personnel in his employ who are engaged in such operations are aware of, and are trained in these procedures.

3. Immediately upon arrival the driver should report to the Customer's Representative, who will be responsible for:

- a) Identification and registration of driver and vehicle. Positive identification of the product
- b) Identifying the discharge point
- c) Confirming that the installation can receive the load

4. The driver should get instructions on how to act in case of an emergency. He should stay with his vehicle at all times.

Note: If the transport equipment is connected, the emergency plan shall include the contents of this equipment.

5. The following point should be highlighted in the operating procedures:

If any problems develop during discharging, the operation should be stopped and the tanker isolated preferably by shutting the external discharge valve(s).

6. Unloading checklist:

An unloading checklist is highly recommended to prevent operator's errors.

APPENDIX 7: RECEPTION AND STORAGE

1. Purpose

The checklist should be used for a self-audit by the customer. It can as well be used as a guideline for the safety service of the supplying company. See Section 6.1.4.

2. Scope

This scheme shall apply to the reception of styrene by road or rail at all customers.

The principal objective is to ensure that the transfer of styrene from the delivering vehicle to the storage tank can be carried out safely. However, because the storage system and procedures may affect the safety of the unloading operation, these also need to be considered.

The scheme should also be used to:

- a) Assess and record any changes in policy, attitudes or equipment since the previous check.
- b) Obtain customer's comments on the transport operation and equipment being used.

The attached guidance notes provide an explanation of the check-list, and recommended minimum standards in certain cases.

3. Styrene Unloading / Storage Checklist

CUSTOMER:

DATE:

ADDRESS:

PERSONS INTERVIEWED:

VISITED BY:

3.1. The Unloading Area

1. Ease of access
2. Housekeeping
3. Separation of other activities
4. Ability to mobilise road tanker/rail car in case of emergency
5. Facilities to isolate area and restrict access
6. Fire fighting systems
7. Electrical classification
8. Minimum safety distances should be 15 m. between the off-loading point and storage, ignition sources etc.
9. Hoses/unloading arms
10. Earthing point
11. Protection against pipe damage
12. Other vehicles and trucks movements
13. Are hoses on truck clean and qualified for styrene?
14. Spillage controls systems
15. Hazard labelling of unloading points
16. Visual and audible alarm

3.2. The Unloading Personnel and Equipment

1. The presence of customer's operator/ driver self-unloading
2. Operator's experience, training and seniority

3. Deputy availability
4. Hose testing and renewal policy
5. Fixed unloading arm testing and maintenance
6. Availability of suitable safety equipment
7. Communication system
8. Use of dedicated loading / unloading lines

3. 3 The Unloading Operations

1. Written procedures
2. Hose purging and leak testing
3. Sampling procedure
4. Atmospheric/personal monitoring
5. Method of unloading (for example nitrogen pressure, pump - pump preferred)
6. Safeguards for pump
7. Emergency response
8. Emergency stop

3.4 The Storage Tank

Site

1. Bunded?
2. Shared? If shared, with what ?
3. Separation distances
4. Emergency disposal facilities

Construction

1. Construction materials
2. Insulated
3. Uninsulated
4. Refrigerated
5. Fire fighting systems
6. Earthed
7. Agitation
8. Blanketing
9. Fire protection
10. Internal coating tanks
11. Design pressure
12. Maximum allowed working pressure
13. Date and type of last test, inspection
14. Dip inlet pipe

Relief Valves

1. Separate
2. Combined with interlock
3. Size
4. Venting to: (Stack, Scrubber, Other)
5. Flame arrestors
6. Nitrogen purge vents

Instrumentation

1. Nitrogen blanketing pressure
2. Control points:
 - Temperature
 - Pressure
 - Level
3. Are control and alarms independent?

Monitoring of Storage

1. Temperature
2. Pressure
3. Level
4. Piping
5. Pumps
6. Valves
7. Gaskets
8. Hoses

4. Storage Tank to Process

Precautions to prevent process streams contaminating storage vessels.

4.1 Procedures

There should be written procedures available for the following:

- o Unloading styrene
- o Testing, inspection and maintenance of equipment
- o Emergency procedures

5. Customers Comments

Guidance notes for styrene unloading/storage checklist:

The reference numbers shown below relate to items shown on the styrene unloading / storage checklist.

5.1. The Unloading Area

- 1.1. There should be sufficient space for easy access of vehicles
- 1.2. Unless it is connected to the unloading facilities, it should be possible for the vehicle to be removed from the unloading area in the case of an emergency
- 1.3. Barriers, warning notices are required. Special consideration may need to be given to prevent shunting close to the unloading area
- 1.4. A foam or powder-based system is recommended.
- 1.5. This should be in accordance with national regulations.
- 1.6. Unloading arms are preferred to hoses

1.7. The earthing point should be checked on a regular basis.

5.2. The Unloading Personnel and Equipment

2.1. The customer's operator must be present during off-loading and maintain control of the styrene unloading area. If the driver unloads the cargo, he should be trained and certified by the receiving party, to operate the installation according to the unloading procedures.

2.2. There should be at least two trained deputies to provide cover for illness and holidays

2.3. Consider general protective equipment. Goggles should be worn. A safety shower and eye fountain should be sited adjacent to the unloading area.

5.3. The Storage Tank

The sizing of styrene storage tanks should be the smallest compatible with shipping and receiving requirements.

Storage times in excess of 3 to 6 months should be avoided to minimize degradation of styrene quality.

5.4. Construction

Construction materials

Carbon steel and stainless steel are suitable for handling styrene.

No copper nor material containing copper as an alloy element should contact liquid.

(Copper can discolour the styrene and has been known to cause polymerisation in some applications).

Insulation and Refrigeration

Styrene storage tanks do not normally require insulation or refrigeration unless extremely high temperatures are likely to be encountered.

Blanketing

Blanketing of tanks for fire protection should be considered if ambient temperatures warrant this ($t > 30^{\circ}\text{C}$). However, exothermic polymer formation is prevented by oxygen, so a minimum level of 15 ppm of dissolved oxygen is recommended. P-TBC should be added at a level depending on the residence time, but minimum at all times to be 5 ppm, to prevent subsequent poly-peroxide formation.

Fire Protection

The provision of fire protection systems eg. foam should be considered where appropriate. This includes water spray systems to isolate from other fires near the tank.

Earthing

Adequate provision should be made to allow dissipation of static electricity.

Internal Coating

Internal coatings are not required for styrene storage tanks, but can help to minimise polymer formation. Inorganic zinc silicate linings can be used. If a tank lining is used, it is important to ensure that a satisfactory tank earthing arrangement is provided.

5.5. Relief Valves

There should be a rigorous procedure for regular checking for signs of polymer formation.

6. Instrumentation and Monitoring

Level indicators and level alarms are advised to prevent tanks overfilling. Consideration should be given to extra high level interlocks to shut off the tank feed.

Pressure and temperature indications are also advised and should be monitored regularly.

An interlock of high level alarm with unloading pump shutdown is recommended.

7. Piping

Carbon steel, stainless steel may be used.

All low points should be provided with drains. Blanks should be fitted to open ends.

8. Pumps

Centrifugal pumps are preferred for styrene service. For environmental considerations double mechanical seals with styrene-compatible antifreeze flush are preferred.

9. Valves

Gate, globe, angle or ball valves may be used in styrene service. Stem packing should be graphite-based coil, modified PTFE, or equivalent. Bonnet gaskets may be soft iron, flat asbestos or spiral-wound. For ball valves, Teflon seats are acceptable.

10. Hoses

The use of hoses should be avoided, but if needed for loading or unloading operations, they should be styrene-resistant line armoured austenitic stainless steel flex hose or equivalent. Hoses should be inspected by carrying out a pressure and conductivity test at least every 12 months.

APPENDIX 8: CEFIC Ericard

Emergency Response Information

ERIC 3-36

FLAMMABLE LIQUID

1. Characteristics.

- Can spontaneously lead to violent reaction.
- Hazardous to eyes and air passages.
- Flash point between 23°C and 61°C (or above 61°C but product carried above its Flashpoint).
- Immiscible or partly miscible with water (less than 10%), lighter than water.

2. Hazards.

- Heating of container(s) will cause pressure rise with risk of bursting and subsequent explosion (BLEVE).
- Exposure to heat, light, mechanical shock or contact with other chemicals lead to spontaneous rise in pressure or self ignition.
- Gives off toxic and irritant fumes when heated or burning.
- May form explosive mixture with air at elevated ambient temperature.
- The vapour may be invisible and is heavier than air. It spreads along the ground and may enter sewers and basements.
- Heat may destroy stabiliser. Seek specialist advice.

3. Personal Protection.

- Self contained breathing apparatus.
- Chemical protection suit if risk of personal contact.
- Consider wearing standard fire fighting clothing underneath the suit.

4. Intervention Actions.

4.1 General.

- Keep upwind.
- No smoking, eliminate ignition sources.
- Work from protected position to reduce risk to personnel. Use unmanned monitors or lances.
- Minimise number of personnel in risk area.

4.2 Spillage.

- Stop leaks if possible.
- Contain spillage by any means available.
- Check explosive limits.
- Use low sparking hand tools and intrinsically safe equipment.
- Absorb liquid in sand or earth or any other suitable material, or cover with foam.
- If substance has entered a water course or sewer, inform the responsible authority.
- Ventilate sewers and basements where there is no risk to personnel or public.

4.3 Fire (involving the substance).

- Keep container(s) cool with water.
- Extinguish with foam.
- Do not use water jet or fog (spray), or dry powder to extinguish.
- Use water spray to knock down fire fumes if possible.
- Avoid unnecessary run-off of extinguishing media which may cause pollution.

5. First Aid.

- If substance has got into eyes, wash out with water for at least 15 minutes and seek immediate medical attention.
- Persons who have been in contact with the substance or have inhaled fumes should get immediate medical attention. Pass on all available product information.
- In case of burns, immediately cool affected skin for as long as possible with cold water. Do not remove clothing adhering to skin.
- Remove contaminated clothing immediately and wash affected skin with soap and plenty of water.

6. Essential Precautions For Product Recovery.

- Ensure proper earthing of pumping equipment.
- Use flame proof pump(s). If electrically driven, minimum class T3.
- Use mineral oil resistant equipment.
- Recover spilled product in vented container fitted with absorption filter.

7. Precautions After Intervention.

7.1 Undressing.

- Drench contaminated suit and breathing apparatus with water/detergent before removing facemask and suit.
- Use chemical protection suit and self contained breathing apparatus while undressing contaminated co-workers or handling contaminated equipment.
- Contain decontamination run off.

7.2 Equipment Clean Up.

- Drench with water/detergent before transporting from incident.

APPENDIX 9: CEFIC TREMCARD

Cefic Tremcard - Instructions in Writing

Class - 3
PG - III
HI No - 339
UN - 2055

LOAD

Styrene Monomer, Stabilised

Name of substance(s):

- Usually colourless liquid - Perceptible odour.
- Immiscible with water.
- Lighter than water.

NATURE OF DANGER

- Flammable.
- May form explosive mixture with air, particularly in empty uncleaned receptacles.
- Risk of spontaneous violent reaction.
- May evaporate quickly.
- The vapour may be invisible. The vapour is heavier than air and spreads along ground.
- Heating will cause pressure rise, severe risk of bursting and subsequent explosion.

PERSONAL PROTECTION

- Protective gloves.
- Protective footwear.
- Eyewash bottle with clean water.

INTERVENTION EQUIPMENT

- Shovel.
- Broom.
- Sand or other absorbent.
- Alternatively, appropriate spill kit

GENERAL ACTIONS BY THE DRIVER

- Stop the engine.
- No naked lights. No smoking.
- Mark roads with self-standing warning signs and warn other road users or passers-by.
- Keep public away from danger area. Keep upwind.
- Notify police and fire brigade as soon as possible.

ADDITIONAL AND/OR SPECIAL ACTIONS BY THE DRIVER

- Any action only if without personal risk.
- Stop leaks if without risk.
- Contain or absorb leaking liquid with sand or earth or other suitable material.
- Avoid direct contact with substance.
- Prevent liquids entering water courses, sewers, basements and workpits.
- If substance has entered a water course or sewer or been spilt on soil or vegetation, inform police.

FIRE (information for the driver in case of fire)

- Do not attempt to deal with any fire involving the load.

FIRST AID

- If substance has got into the eyes, immediately wash out with plenty of water. Continue treatment until medical assistance is provided.
- Remove contaminated clothing immediately and wash affected skin with plenty of water.

SUPPLEMENTARY INFORMATION FOR EMERGENCY SERVICES

- Keep container(s) cool by spraying with water if exposed to fire.
- Extinguish with waterspray, foam or dry chemical.
- Do not use water jet.

Additional Information

EMERGENCY TELEPHONE:

APPENDIX 10: GLOSSARY OF ABBREVIATIONS

ADR Accord européen relatif au transport des marchandises dangereuses par route. European agreement concerning the international carriage of dangerous goods by road.

ADN Accord européen relatif au transport des marchandises dangereuses par voie de navigation intérieure. Regulations concerning the transport of dangerous substances in barges on inland waterways.

ADNR See ADN: R for Rhine

ANSI American National Standard Institute

ASME American Society of Mechanical Engineers

CAS Chemical Abstract System

CEFIC European Chemical Industry Council

CDI Chemical Distribution Institute

DIN German Industry Standard (Deutsche Industrie Norm)

DNBP di-nitro butyl phenol, styrene process polymerization retarder

EEC European Economic Community

EINECS European Inventory of Existing Commercial Chemical Substances

EMS Emergency procedures of ships carrying dangerous goods

GESAMP Group of experts on Scientific aspects of Marine pollution

IARC International Agency for Research on Cancer

IATA International Air Transport Association

IBC Intermediate Bulk Container

IBC Code International Code for the Construction and equipment of ships carrying dangerous chemicals in bulk

ICE International Chemical Environment (CEFIC)

IMDG Code International Maritime Dangerous Goods Code

IMO International Maritime Organization

ISO International Standards Organization

JSA Job Safety Analysis

LC50 Lethal concentration (50%)

LD50 Lethal dose (50%)

MAC Maximum accepted concentration

MARPOL 73/78 International convention for the prevention of pollution from ships initiated 1973, 5 annexes in 1978.

MPL Marine Pollutant label

MFAG Medical First aid Guide for use in accidents involving dangerous goods at sea.

NPF Nominal protection factor (respirators)

OSHA Occupational Safety and Health Administration (USA)

p-TBC Para Tertiary Butyl Catechol (=TBC), styrene product polymerization inhibitor

PTFE Polytetrafluoroethylene

PVRV Pressure vacuum relief valve

PVC Poly Vinyl Chloride

RID Règlement International concernant le transport de marchandises dangereuses par chemin de fer. Regulations concerning the international carriage of dangerous goods by rail.

RTC Rail tank car

RTECS Registry of Toxic Effects of Chemical Substances

SM Styrene Monomer

SQAS Safety and Quality Assessment System

STEL Short Term Exposure Limit

Tremcard Transport Emergency Card (ADR)

TBC Tertiary butyl catechol

TLV Threshold Limit Value

TWA Time Weighted Average

UN United Nations

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