

Styrene Monomer: Safe Handling Guide

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Styrene Association (SPA)

The Styrene Producers Association (SPA) is a Sector Group of PlasticsEurope's Styrenics Chain, which gathers representatives from the companies mentioned below.

PlasticsEurope would also like to thank these companies for their valuable contributions and peer review of this document:

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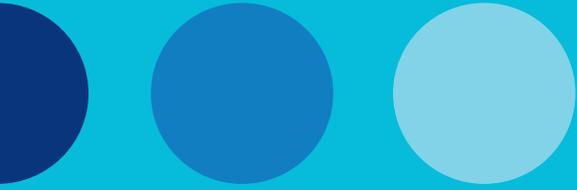
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Table of Contents

1. INTRODUCTION AND PURPOSE	8
2. PRODUCT INFORMATION AND CHARACTERISTICS	9
2.1. General Description and Hazardous Properties	9
2.2. Physical Properties of Styrene	10
2.3. Manufacturing and Use	11
2.4. Inhibition of Styrene (Chemistry, Mechanism and Levels)	11
2.4.1. Safety	11
2.4.2. Inhibition Chemistry	14
2.4.3. Standard Inhibitor Levels	15
2.4.4. Short Stop	15
2.5. Environmental Effects	15
2.6. Transport Classification (Europe)	15
2.7. European Regulatory Environment	16
2.7.1 REACH	16
2.7.2 Classification and Labeling	16
3. HEALTH ASPECTS	18
3.1 General Remarks	18
3.2 Acute Toxicity	18
3.3 Skin and Eye Irritation	18
3.4 Sensitization	18
3.5 Carcinogenicity / Genetic Toxicity	18
3.6 Conclusion	18
4. ENVIRONMENTAL ASPECTS	20
4.1 General	20
4.2 Partitioning to the Air Compartment	20
4.3 Partitioning to the Water Compartment	20
4.4 Partitioning to the Soil Compartment	20
4.5. Bioaccumulation, Movement and Partitioning	20
4.6 Degradation and Persistence	21
4.7 Aquatic Toxicity	21
4.8 Product Classification (Environmental Effects)	21
5. DESIGN AND CONSTRUCTION OF TRANSPORT AND STORAGE EQUIPMENT	22
5.1. Railcars (Rail Tank Wagons)	22
5.2. Tank Trucks (Road Tankers)	22
5.3. Tank Containers	22
5.4. Vessels and Barges	22
5.5. Storage Tanks	22
5.6. Loading and Unloading Facilities	22
6. TRANSPORT, STORAGE AND HANDLING OPERATIONS	24
6.1. Training	24
6.2. Operating instructions and Regulations	24
6.3. Inspections	24
6.4. Loading operations for rail and road transport	25
6.5. Unloading operations for rail and road transport	25

6.6. Vapour control	25
6.7. Previous cargoes, cleanliness and stowage	25
6.8. Blanketing	26
6.9. ROAD Specific Operations	26
6.9.1. Shipper's responsibility	26
6.9.2. Haulier's responsibility	26
6.9.3. Review	26
6.9.4. Routing	26
6.9.5. Drivers working hours and speed limits	26
6.9.6. Safe Parking	26
6.9.7. Severe weather conditions	26
6.9.8. Delays and transport accidents	26
6.9.9. Subcontracting	26
6.9.10 Instructions in writing	26
6.10. Intermodal transport	27
6.11. Ferries selection	27
6.12. RAIL Specific Operations	27
6.12.1. Transport responsibilities	27
6.12.2. Rail Operators	27
6.13. Barges and Sea Operations / Cargo separation for safety purposes	27
6.13.1. Reactive Products	27
6.13.2. Separate Systems	27
6.13.3. Temperature	27
6.13.4. Heating coils	27
6.13.5. Edible products	27
6.14 Barge Specific Operations	27
6.14.1. Barge selection	27
6.14.2. Loading/unloading procedures	27
6.14.3. Board-to-board trans-shipments	27
6.15. SEA Specific Operations	28
6.15.1. Parties involved	28
6.15.2. Certification	28
6.15.3. Vessel loading and unloading procedures	28
6.15.4. Vessel selection	28
6.16. Tank Storage Operations	28
6.16.1. Certification	28
6.16.2. Inhibitor control	28
6.16.3. Loading / unloading lines	28
6.17. Customer Collection	28
7. EMERGENCY PROCEDURES	29
7.1. Emergency Planning	29
7.1.2. CEFIC ICE	29
7.1.3 Response Plan	29
7.1.4. Fire	29
7.2. Measures in the event of a release of styrene	29
7.2.1. Emergency Response Team	29
7.2.2. ERICards	29
7.2.3. Spills and Leaks	29
7.2.4. Accidental Release	30
7.2.5 Drums leaks	30

7.3. Firefighting	30
7.3.1 Exothermic reaction	30
7.3.2 Fire Suppression	30
7.3.3 Foam	30
7.3.4. Water Spray	31
8. PERSONAL PROTECTION, FIRST AID AND MEDICAL TREATMENT	32
8.1 Introduction	32
8.1.1. Exposure to styrene	33
8.1.2 Occupational Health Aspects	33
8.2 Personal protection	33
8.2.1 Personal Hygiene	33
8.2.2 Protective Equipment	33
9. FIRST AID & MEDICAL TREATMENT	35
9.1 Acute intoxication with styrene - symptoms and treatment	35
9.1.1 Eye	35
9.1.2 Skin	35
9.1.3 Inhalation	35
9.1.4 Ingestion	35
9.2 Acute intoxication with inhibitor (TBC) - symptoms and treatment	35
9.2.1 Eye	35
9.2.2 Skin	35
9.3 Signs and symptoms of prolonged exposure to styrene	35
APPENDIX 1: CEFIC and Responsible Care®	38
1. Responsible Care® – A Public Commitment	38
2. Transport Accident Prevention and Response (ICE)	38
3. Safety and Quality Assessment for Sustainability (SQAS)	38
APPENDIX 2: STYRENE POLYMERISATION IN STORAGE	40
APPENDIX 3: DESIGN AND CONSTRUCTION OF VESSELS AND BARGES	46
APPENDIX 4: DESIGN AND CONSTRUCTION OF TANKS	74
APPENDIX 5: CHECK-LIST FOR LOADING	51
APPENDIX 6: CHECK-LIST FOR UNLOADING	52
APPENDIX 7: RECEPTION AND STORAGE	53
APPENDIX 8: GLOSSARY OF ABBREVIATIONS	57



Main chapters

1. Introduction and purpose

The purpose of this document is to review the environmental, health and safety aspects of 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 PlasticsEurope/Styrenics Chain, encourages customers and potential users of styrene to review their applications from the standpoint of human health and environmental quality.

A key document in this respect is the Safety Data Sheet (SDS) provided by your supplier. The SDS 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.

SPA considers the volume and the distribution pattern of styrene as a commodity chemical to warrant specific emphasis on the application of Responsible Care¹ 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 that 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 vessels, barges and tank containers is taken into account covering all aspects of the transport activity from the loading to the 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 Monomer: Safe Handling Guide is 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.

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)
Short Stop	A free radical scavenger that can be added to a polymerizing system to temporarily halt the polymerization. When the short stop is consumed the polymerization will continue.
Runaway	Self-accelerating chemical reaction (e.g. polymerisation). During a runaway the temperature will rapidly increase.

¹ See Appendix 1

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), is also commonly known as ethenylbenzene, phenylethylene, phenylethene, vinylbenzene, cinnamene or styrene monomer. Under ambient conditions, it 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 and consequently the acute hazard of spilled styrene will be limited for most aquatic species. According to the Standard European Behaviour Classification (Bonn Agreement), styrene is classified as a “floater evaporator”.

Styrene is a monocyclic alkenyl aromatic compound with a molecular weight of 104. Being rather volatile and having a flash point of 31°C, styrene is classified as a flammable substance, which in use may form flammable/explosive vapour-air mixtures. For other typical parameters, the reader is referred to Table 1: 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

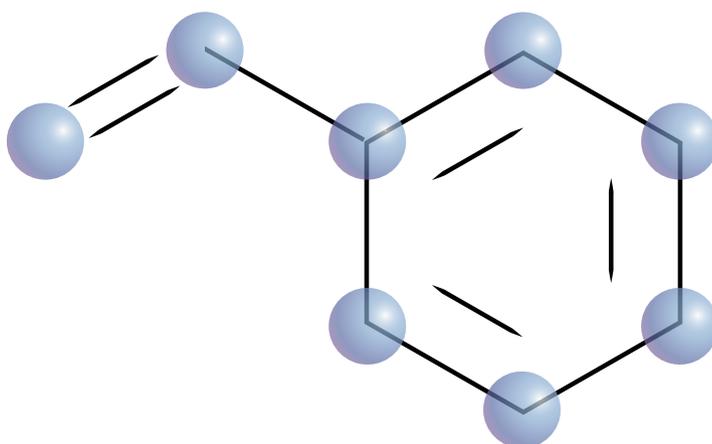
Aspects” for more details). Styrene is currently (June 2018) classified for flammability, skin / eye irritation, acute toxicity, hearing damage and is suspected of reproductive toxicity.

The characteristic unpleasant smell and low odour threshold (0.1 ppm; 0.43 mg/m³) allows 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 uncontrolled. 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 polymerisation 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 according to CLP as acutely toxic, as a skin and eye corrosive, a skin sensitizer, and hazardous to 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).

Figure 1: Chemical Structure of Styrene



2.2. Physical Properties of Styrene

Table 1: *Physical Properties of Styrene.*

Property	International System Value & Unit
Physical Form	Colourless, oily liquid
Colour (acc. ASTM D 2827)	15 max. / Pt-Co scale
Odour	Sweet, aromatic (if pure) sharp, penetrating, unpleasant (commercial grades)
Odour threshold	Water: 0.73 mg/L Air: 0.1 ppm (0.43 mg/m ³)
Relative molecular mass	104.14 g/mol
Density at 20°C (acc. ASTM D 4052)	0.9059
Boiling point at 1013 hPa	145°C
Melting point/Freezing point	-31°C
Kinematic viscosity at 25°C	0.77 mm ² /s
Vapor density (air =1)	3.6
Vapor pressure at 20°C	6.67 hPa
Henry's law constant (H) at 20°C	232 Pa m ³ /mol
Conductivity, thermal at 20°C	0.16 W/m°C
Flash point (ABEL; acc. IP 170)	31°C
Auto ignition temperature	490°C
Saturation concentration in air at 20°C	25.6 g/cm ³ (5 923 ppm vol.)
Explosion limits in air	0.9 - 6.8% vol.
Miscibility in water	Immiscible
Solubility in water at 20°C	300 mg/L (0.03% wt.vol.)
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	-4265.64 kJ/mole
Heat of formation, H _f , gas at 25°C	147.46 kJ/mole
Heat of formation, H _f , liquid at 25°C	103.50 kJ/mole
Heat of polymerisation, H _p at 25°C	-70.67 kJ/mole

2.3. Manufacturing and Use

The conventional method for producing styrene involves two steps: the alkylation of benzene with ethylene to produce ethylbenzene, followed by dehydrogenation of the ethylbenzene 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 of ethylbenzene and finally of styrene along with design changes to conserve and utilize the energy, in particular from the exothermic alkylation step. The traditional aluminium chloride catalyst used in this alkylation is now (2018) almost completely replaced by zeolite catalyst technology. Currently, the predominant route for the commercial production of styrene is by dehydrogenation of ethylbenzene in the presence of steam over a catalyst (iron oxide) in fixed bed adiabatic or, in some cases, tubular isothermal reactors. Another route involves co-production of styrene and propylene oxide via hydroperoxidation of ethylbenzene. Limited scale extraction from steam cracker pyrolysis gasoline is also practised.

The specification and analytical methods for styrene monomer have changed through the years. The majority of manufacturers have defined their specifications according to the standard D2827 “Standard Specification for Styrene Monomer” of the American Society for Testing and Materials (ASTM). Key parameters of rev. 13 of D2827 specification are:

- a minimum purity of 99.8 wt. %
- a maximum colour of 15 on the Platinum-Cobalt (Pt-Co) scale
- inhibitor (TBC) concentration between 10-15 ppm
- Polymer content of maximum 10ppm

The impurities and their concentrations depend upon the manufacturing route employed, along with plant performance characteristics. The inhibitor content specified in the standard is 10-15 ppm TBC (4-tert-butylcatechol), to meet minimum shipping

requirements. Higher levels may be defined in the customer specification to increase stabilization (shelf life), depending on the expected transport/storage duration and temperature.

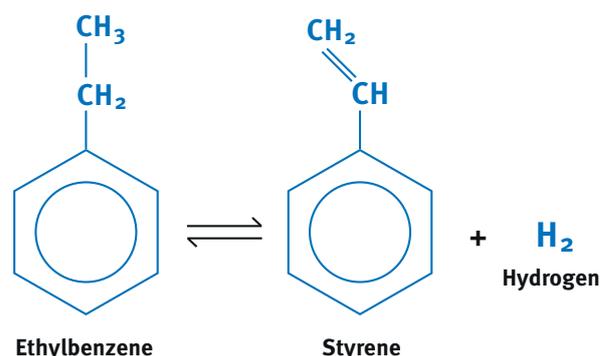
Styrene is predominately used in the manufacture of plastics and synthetic rubber, such as polystyrene, EPS, engineering plastics like ABS, and styrene-butadiene rubber. It's one of the most versatile and widely-used monomer building blocks with ability to be polymerised by free radical, cationic, anionic, thermal, group transfer, and redox techniques. Furthermore, it copolymerises readily with other vinyl-based monomers, such as acrylonitrile, butadiene, acrylates, and maleic anhydride. Polymers made with styrene ultimately find end-uses in packaging, medical, appliance, automotive, electronics, construction, and others.

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

2.4.1. Safety

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. Polymer formation occurs slowly even at ambient temperatures and becomes rapid at elevated temperatures. To maintain the monomer content for quality as well as safety reasons, the polymerisation reaction is retarded or inhibited 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). 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.

Figure 2: Dehydrogenation of Ethylbenzene to Styrene



An inhibitor must be maintained at certain minimum levels to prevent polymer formation. The presence of dissolved oxygen is required for the inhibitor to function properly, therefore styrene needs to be stored under air or inert gas with sufficient oxygen levels.

Storing and transporting styrene is better at low temperatures. This slows down the polymerisation reaction. In addition to using TBC, temperature control and proper selection of storage and transport environment should ensure shelf life with the necessary quality specifications. See appendix 2 for more detail.

Styrene should never be handled under an oxygen-free atmosphere. Air is preferable to support the inhibitor mechanism. If ambient temperatures are above flash point, it might be desirable to use a nitrogen/oxygen gas mixture to avoid flammability. However, the atmosphere above styrene monomer should contain a minimum oxygen level to maintain inhibitor effectiveness.

A study on the inhibition chemistry confirmed that oxygen is consumed as part of free radical scavenging mechanism. Thus, the atmosphere above styrene

monomer in a closed system should be periodically replenished with air or a nitrogen/oxygen gas mixture. Based on the experiences of SPA members, a minimum oxygen level of 3 vol% in the vapour phase is regarded as being sufficient for inhibition of the liquid phase, provided that all other parameters (temperature, polymer content, TBC content) are within recommended ranges. More than 8 vol% of oxygen in the vapour phase can lead to a flammable mixture (see figure 3). The recommended optimum oxygen level is 5% volume. The solubility of gases in styrene is shown in table 2.

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 that could result in the plugging of pressure-relief valves.

Figure 3: Flammability Diagram for “Styrene/Oxygen/Nitrogen”

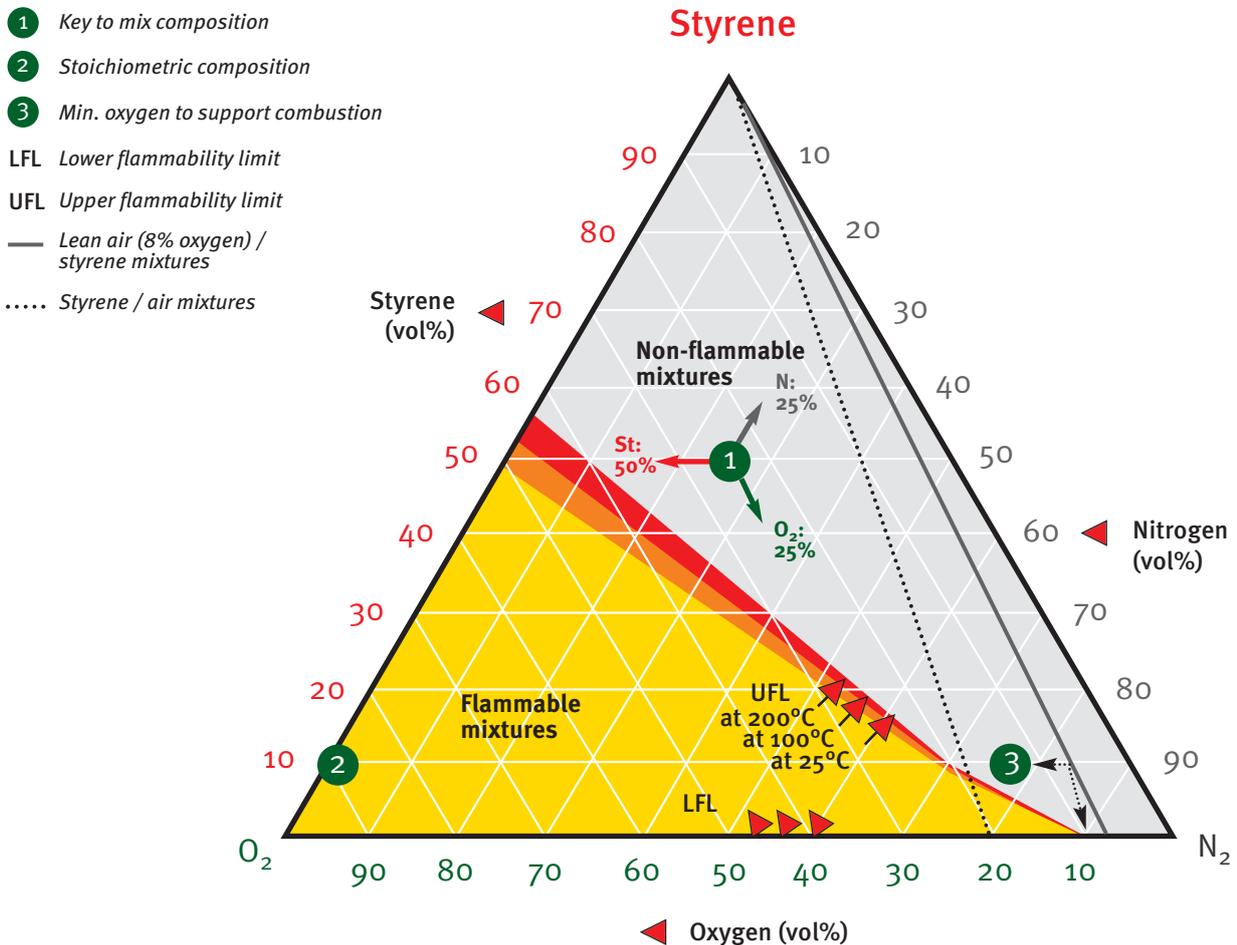


Table 2: Solubility of Gases in Styrene at 25°C

Gas	CC Gas/CC Styrene	Ppme 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 Styrene Storage Testing

Checkpoint	Interval	Remarks
Inhibitor Analysis	1 time weekly	If below 15 °C
	2 – 3 times weekly	If between 15 and 25 °C
	Daily	If above 25 °C
Polymer Analysis	1 time weekly	If below 15 °C
	2 – 3 times weekly	If between 15 and 25 °C
	Daily	If above 25 °C
Monomer Temperature	Daily	
Monomer Vapour Temperature	Daily	
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 compared to the polymer formation with styrene (r2). In the subsequent step, if inhibitor (TBC) is present, the peroxide radicals are scavenged via quinone formation (r3); whereas, if no 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 and oxygen molecules until the

oxygen is completely depleted. The poly(peroxides) are soluble in styrene and will not concentrate. 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 3), the IMO-related Safety Of Life At Sea (SOLAS) Convention has defined an atmosphere with < 8 vol-% oxygen as inert gas for styrene.

For the proper functioning of TBC, oxygen in vapour phase should be minimum 3 vol-%, which is equivalent to 8 ppm of dissolved oxygen in liquid phase (Figure 4).

Figure 4: Equilibrium of oxygen concentration in gas phase and liquid styrene at 25°C and 1bar

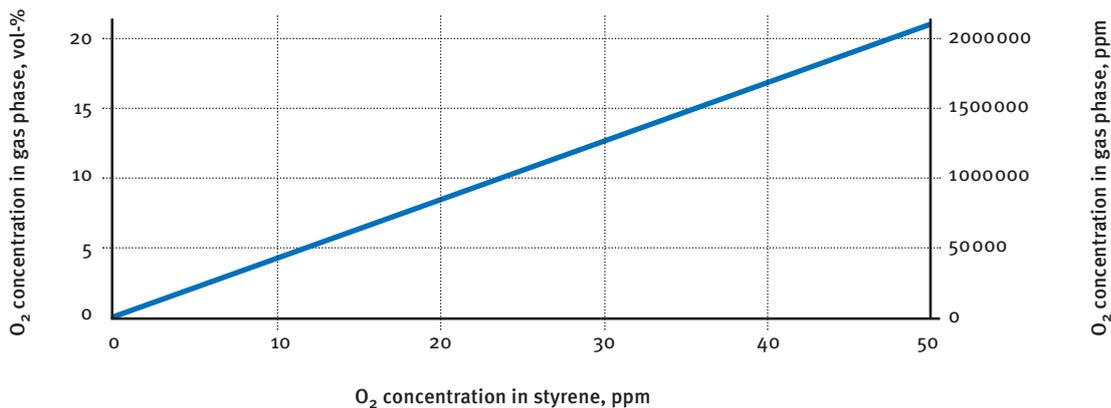
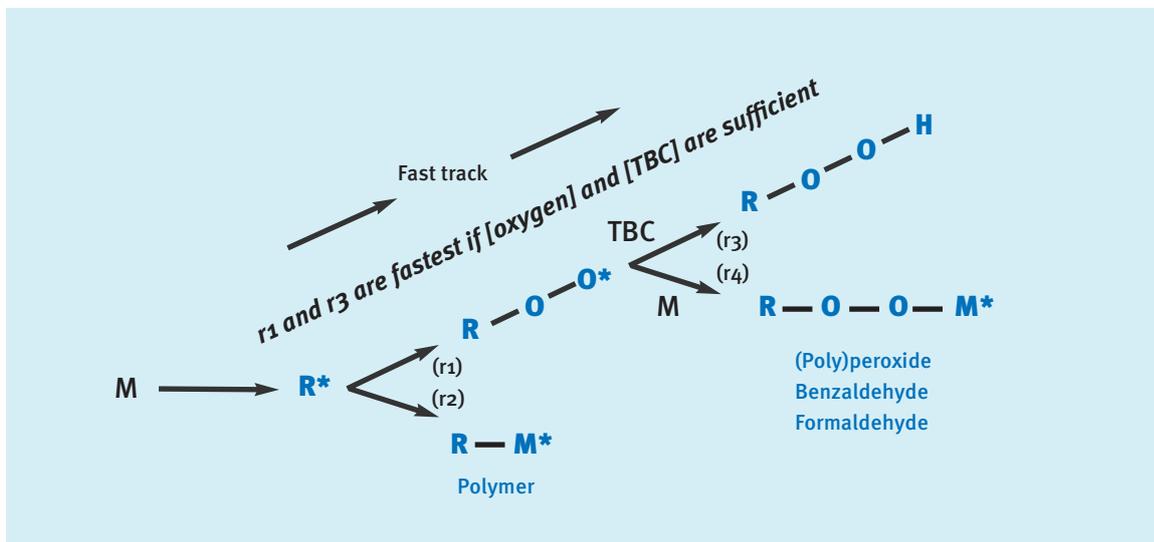


Figure 5: Inhibition Mechanism



2.4.3. Standard Inhibitor Levels

The required inhibitor (TBC) concentration to prevent polymerisation depends on temperature and residence time in the tank.

The recommended practice is to maintain the inhibitor (TBC) levels between 10-15 ppm, but higher inhibitor levels may be required depending on the storage conditions, process or specific user requirements. Typical protection in days for styrene, when inhibitor levels are at the recommended levels in the presence of air, are shown in Table 4.

Styrene users are advised to have a TBC concentrate/solution on-site to restore the TBC below the recommended concentration.

The depletion of oxygen in styrene is not only dependent on the temperature, but also on the TBC level added. At low TBC levels, oxygen depletion is rapid and the inhibition system will quickly become ineffective. Lower oxygen levels will lower the shelf life at the moment it comes below 3 vol-%.

2.4.4. Short Stop

If polymerisation has started and the temperature in the tank or transport is rising, it is possible to reduce the polymerisation rate significantly by adding a free radical scavenger (Short Stop). After adding Short Stop, the styrene has to be re-processed or discarded. Inhibitors suitable for Short Stop are **DEHA** (a free radical scavenger Diethylhydroxylamine CAS Registry Number: 3710-84-7 CA Index Name: Ethanamine, N-ethyl-N-hydroxy-), **4-Hydroxy-TEMPO** (a stable free radical, CAS Registry Number: 2226-96-2 CA Index Name: 1-Piperidinyloxy, 4-hydroxy-2,2,6,6-tetramethyl-) and **4-Oxo-TEMPO** (a stable free radical, CAS Registry Number: 220-778-7, CA Index Name: 2,2,6,6-Tetramethyl-4-oxopiperidinoxy).

Other free radical scavengers can also be suitable.

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

Temperature	Depletion Days/1 ppm	TBC Content		Shelf Life
°C t		[initial] ppm	[end]	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.

² http://otif.org/fileadmin/new/3-Reference-Text/3B-RID/RID_2017_E.pdf

³ https://www.unece.org/trans/danger/publi/adn/adn2017/17files_eo.html

⁴ http://www.unece.org/fileadmin/DAM/trans/danger/publi/adr/adr2017/ADR2017e_web.pdf

2.5. Environmental Effects

EU Risk Assessments have concluded that styrene is not bio-accumulative, meets the criteria for ready biodegradation and thus does not require classification for environmental effects. See Section 2.7- European Regulatory Environment.

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

More details on styrene's environmental effects can be found in Section 4 "Environmental Aspects".

2.6. Transport Classification (Europe)

For current Transport Classifications, please refer to the following sources:

Rail transport: Convention concerning International Carriage by Rail (COTIF) Appendix C – Regulations concerning the International Carriage of Dangerous Goods by Rail (RID, 2017)²

Inland waterways: European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways (ADN)³

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

Marine transport of packaged goods: International Maritime Dangerous Goods Code (IMDG Code, 2016).

Road transport: The European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR 2017)⁴

Air transport: International Civil Aviation Organisation Technical Instructions (ICAO TI 2017)

2.7. European Regulatory Environment

2.7.1 REACH

Styrene was previously regulated as a priority High Production Volume (HPV) Chemical under the Council Regulation (EEC) 793/93 Existing Substances Regulation (ESR).

An EU risk assessment for styrene was conducted by the United Kingdom in 2002. The Risk Assessment Report (RAR) concluded only on the environmental aspects, and that there was no need for further information and/or testing or for risk reduction measures beyond those that are already being applied.⁵

In June 2008, the United Kingdom published an update to the EU risk assessment addressing potential risks of styrene to human health and the environment. This Assessment concluded that there remained a need for further risk management in downstream industries, where high styrene exposures were identified, and in consumer use of styrene-containing resins.

In November of 2008, The UK submitted an ANNEX XV “Transitional Dossier” for styrene⁶. The document confirmed the contents of the 2002 environmental risk assessment and the 2008 human health risk assessments.

On 1 June, 2007, the EU Directive on Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) came into force. REACH assesses the hazards and risks of all uses of chemical substances to determine their impacts on human health and the environment. REACH replaced the existing ESR regulations and Council Directive 67/548/EEC for “new” chemical substances by providing a comprehensive new framework for the regulation of chemical substances. REACH involves a phased implementation whereby existing substances were to be registered by May 31st 2018. The European Chemicals Agency (ECHA)⁷ manages the technical aspects of REACH.

Styrene was registered in 2010, in a joint registration for tonnages above 1,000 tonnes per annum. A public version of the dossier is viewable on the ECHA website⁸.

In 2015, consumer uses of styrene were removed from the registration dossier. Thus, in effect, consumer uses of styrene are no longer supported under the REACH Joint Registration.

2.7.2 Classification and Labeling

The Classification, Labelling and Packaging (CLP) of substances and mixtures Regulation (EC) 1272/2008 entered into force in January 2009.

The CLP regulation introduces throughout the EU a new system for classifying and labelling chemicals based on the United Nations’ Globally Harmonized System (UN GHS). It also replaces over time two Directives to which the UP resin industry has historically complied: The Dangerous Substances Directive 67/548/EEC (DSD) and the Dangerous Preparations Directive 1999/45/EC (DPD).

Under CLP, it is the task of industry to establish the hazards of substances and mixtures before they are placed on the market, and to classify them in line with the identified hazards. In case a substance or a mixture is hazardous, it has to be labelled so that workers and consumers know about its effects before they handle it. A Safety Data Sheet (SDS) describing both hazards and Risk Management Measures is also provided to the customer allowing him to handle the substance/mixture safely, within a life cycle approach.

There are certain timelines for industry to classify, label, and package substances and mixtures according to CLP. The classification and labelling according to CLP for substances applied since 1 December 2010 and for mixtures applied from 1 June 2015.

Styrene currently (June 2018) has a harmonised CLP classification for flammability, skin / eye irritation, acute toxicity, hearing damage and is suspected of reproductive toxicity⁹.

The harmonised classification is listed in Annex VI to the CLP Regulation and should be applied by all manufacturers, importers or downstream users of such substances and of mixtures containing such substances.

⁵ <https://echa.europa.eu/documents/10162/a05e9fc2-eaf7-448e-b9b2-d224d28173co>

⁶ https://echa.europa.eu/documents/10162/13630/trd_uk_styrene_en.pdf/b2244ec9-74e6-4450-9556-9c1556e7e16e

⁷ <https://echa.europa.eu>

⁹ <https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/25673>



Signal Word: Danger

Flam. Liq. 3

Skin Irrit. 2

Eye Irrit. 2

Acute Tox. 4

STOT RE 1 (hearing organs)

Repr. 2

Additional to this official harmonized classification, the Styrene Joint Registration dossier¹⁰ adds further hazard statements for effects on aquatic organisms and for aspiration hazard:

H304: May be fatal if swallowed and enters airways.

H335: May cause respiratory irritation.

H412: Harmful to aquatic life with long lasting effects.

Hazard statements:

H226: Flammable liquid and vapour.

H315: Causes skin irritation.

H319: Causes serious eye irritation.

H332: Harmful if inhaled.

H361d: Suspected of damaging fertility or the unborn child Suspected of damaging the unborn child.

H372: Causes damage to organs (Hearing organs) through prolonged or repeated exposure.

¹⁰ <https://echa.europa.eu/registration-dossier/-/registered-dossier/15565/1>

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 Safety Data Sheet (SDS).

3.2 Acute Toxicity

The oral toxicity of styrene 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. However, aspiration into the lungs may cause chemical pneumonitis, which can be fatal.

Inhalation studies in rats indicate that styrene generally has a moderate acute toxicity (4 hour LC₅₀ is 11.8 mg/L). Some strains of mice (B6C₃F₁) 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 dermal irritation. Human experience indicates that liquid styrene can cause defatting of the skin and frequent contact might cause dermatitis. Liquid styrene has been reported to produce moderate eye irritation, with dose-dependent increases in severity of eye irritation at increasing styrene vapour concentrations in animals. 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 skin sensitiser and has no significant asthmogenic potential.

3.5 Carcinogenicity / Genetic Toxicity

The carcinogenic risk to humans after long-term exposure to styrene concentrations below recommended Occupational Exposure Limits (ranges from 2.4 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 reviewed the evidence for styrene carcinogenicity several times. In 1987, IARC upgraded styrene's classification from a Group 3 "not classifiable" to a Group 2B "possibly carcinogenic to humans." This reclassification resulted from revisions of the IARC's classification scheme and considerations of styrene oxide, an intermediate formed during styrene metabolism. In 1994 and 2002, IARC again reviewed styrene and did not change the Group 2B classification.

Styrene was reviewed most recently in March 2018 during which the classification was changed to Group 2A "probably carcinogenic to humans". The decision to assign styrene to group 2A resulted from the re-evaluation of existing studies, where the interpretation of the evidence in experimental animals changed from "limited" to "sufficient". The evidence based on human data did not change. This decision is not supported by new scientific evidence, but rather could be due to a change in the IARC technical guidelines. For example, effects seen in both male and female animals in a single study can be considered as two separate studies, numerically increasing the weight of evidence. Further, IARC discounted the "mode of action" evidence for the animal cancer findings showing potential tumorigenic concern was only observed in specific strains of mice. Experimental data published since 2002 demonstrates differences between mice and humans and hence the irrelevance of the carcinogenic concern to humans.

Case-control studies with occupationally exposed humans investigating styrene exposure and cancer incidence show equivocal evidence, but the risks are generally considered to be low. A recent epidemiological study of over 75,000 Danish workers in the FRP industry found no increased cancer risk associated with styrene exposure¹¹.

In vitro mutagenicity tests generally 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 that is summarised in the REACH Joint Registration dossier¹² 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 (narcosis). Under certain conditions of co-exposure with high noise levels, there may be a risk of damage to hearing.

The carcinogenic and reproductive toxicity risks to humans are very low if recommended occupational exposure levels will not be exceeded.

¹¹ Christensen et al. (2017) "Cancer incidence in workers exposed to styrene in the Danish reinforced plastics industry 1968-2012", *Epidemiology* 2017;28:300-310

¹² <https://echa.europa.eu/registration-dossier/-/registered-dossier/15565/1>

4. Environmental aspects

4.1 General

Persistence of styrene in the environment is very limited. Because of styrene's relatively high vapour pressure and low to moderate water solubility (volatilisation from water to the atmosphere is an important distribution process for styrene).

Styrene is readily biodegradable and does not bioconcentrate in aquatic or terrestrial species.

Styrene may have toxic effects on aquatic invertebrates and algae, but exposure time will be limited due to rapid removal from water through volatilisation, therefore the risks are considered low.

4.2 Partitioning to the Air Compartment

The relatively high Henry's Law Constant indicates that the primary removal mechanism of styrene from water and soil is volatilisation to the air.

Styrene does not substantially adsorb solar radiation at wavelengths greater than 300 nm, therefore degradation of styrene in air and water by direct photolysis is unlikely.

Styrene is rapidly degraded in the atmosphere through reaction with hydroxyl radicals and tropospheric ozone. A half-life in air of about 8 hours is estimated. Styrene contains no hydrolysable groups.

4.3 Partitioning to the Water Compartment

In the event of a spill, styrene will slowly volatilise.

The Henry's law constant value, calculated from vapour pressure and water solubility, indicates rapid volatilisation of styrene from surface waters. The concentration to which aquatic organisms will be exposed will therefore depend on the air and water temperature and particularly water turbulence. Under laboratory conditions, the rate of depletion of styrene from water will be greatly accelerated when stirred. Styrene is therefore expected to degrade more slowly in groundwater than in surface waters.

The volatilisation half-life of styrene from a body of water one-metre-deep, with a current velocity of 1 m/s and a wind velocity of 3 m/s, is calculated to be about 3 hours.

Almost complete removal of styrene is achieved in industrial wastewater treatment plants as well as in municipal wastewater treatment plants after microbial adaptation.

4.4 Partitioning to the Soil Compartment

The half-life for volatilisation of styrene from soil surfaces was estimated to be approximately 1 minute with the rate of volatilisation decreasing with increasing depth. Volatilisation from soil is slower than from water, with 26% volatilisation from a 1.5 cm depth of soil in 31 days.

The movement of styrene in a sand aquifer was found to be approximately 80 times slower than that of a non-adsorbing tracer.

Styrene is expected to adsorb to solids, the degree of which is related to the organic matter content. Sorption seems to have little effect on the rate of biodegradation.

Based on its low water solubility and the magnitude of its organic carbon partitioning coefficient (estimated $K_{oc} = 352$), the mobility of styrene in soil is considered to be moderate to low.

4.5 Bioaccumulation, Movement and Partitioning

The value for octanol-water partition coefficient ($\log K_{ow}$), which is considered a good predictor for bioconcentration potential, is 2.96 @ 25 C.

A bioconcentration factor (BCF) for styrene of 74 was predicted using the $\log K_{ow}$ value. This value suggests that the compound probably does not accumulate in aquatic organisms.

Styrene will be quickly metabolized and excreted by aquatic organisms, therefore bioaccumulation is unlikely. Similar substances such as toluene, xylene and ethylbenzene also do not accumulate to any great degree in aquatic organisms.

As styrene will be rapidly removed from water and soil by volatilisation, the potential for exposure of aquatic species will be limited.

Although mobility of styrene in soil is considered to be moderate to low, styrene will be quickly removed from soils through biodegradation, solubilisation disturbance by infiltrating water and, in shallow soils, volatilisation.

4.6 Degradation and Persistence

Styrene is shown to be readily biodegradable under aerobic conditions in screening and simulation tests on water and soil.

Although the availability of nutrients, i.e. nitrogen and phosphorous will be the determining factor, styrene is, in principle, degradable under anaerobic conditions.

Degradation in the atmospheric environment is expected within minutes to hours.

4.7 Aquatic Toxicity

Styrene is considered to have toxic effects in aquatic species by a non-specific mode of action (non-polar narcosis).

Following the evaluation of several acute toxicity studies with exposure periods of 72-96 hours, it has been concluded that the lowest LC₅₀ (Lethal Concentration) for fish is 4 mg/l. For waterflea (Daphnia) species exposed for 48 hours, the lowest EC₅₀ (acute immobilisation) value that has been found is 4.7 mg/l. For green algae, the lowest EC₅₀ for green algae is 4.9 mg/l.

It must be noted that protocols to assess aquatic toxicity require that the exposure concentration is

maintained during the test and that the real-world situation of styrene depletion from water through volatilisation is not always being considered in toxicity tests. Therefore, these values can be reasonably construed to represent worst-case scenarios. Volatilisation, rapid (bio)degradation and the low partition coefficient (log K_{ow}) of styrene (2.96 @ 25 C) indicate that secondary poisoning is unlikely.

The Predicted No Effect Concentration (PNEC) for styrene in freshwater (PNEC_{aqua}), calculated in the REACH dossier, is 0.028 mg/L. For marine water, the PNEC is 0.014 mg/L.

PNEC Soil is calculated as 0.2 mg/kg soil dw, while the PNEC for Sewage Treatment Plants (STP) is 5 mg/L.

4.8 Product Classification (Environmental Effects)

Styrene is not bio-accumulative and meets the REACH criteria for ready biodegradation.

Available studies show that styrene can be considered acutely toxic to aquatic organisms. The acute toxicity concentrations in fish, daphnia and algae are between 1 mg/L and 10 mg/L; however, because styrene is readily biodegradable, no environmental classification for acute effects is required.

Styrene is classified in the REACH joint registration dossier as aquatic chronic 3, which is triggered by the EC₁₀ of 0.28 mg/L for algae.¹³

¹³ <https://echa.europa.eu/registration-dossier/-/registered-dossier/15565/1>

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 be designed and constructed in accordance with the recommendations as described in the CEFIC transport logistics best practice guidelines¹⁴.

In addition to the CEFIC Guidelines, it is recommended that carbon steel railcars be coated to prevent polymerisation of the styrene. Zinc silicate coating is commonly used.

5.2. Tank Trucks (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.

For tank trucks, it is recommended to have full walkways on the top. In addition to the above requirements, it is recommended that tank trucks are designed and constructed in accordance with the recommendations as described in the CEFIC transport and logistics guidelines.

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 (ADR, RID, IMDG), depending upon the specific transport modes utilised.

For tank containers/potable tanks, it is recommended to have full walkways on the top. In addition to the above requirements, it is recommended that tank containers are designed and constructed in accordance with the recommendations described in the CEFIC transport & logistics best practice guidelines¹⁵.

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 “European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways” (ADN).

In addition to the above requirements, it is recommended that the vessels and barges used 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 4 exemplifies the best general practice that is followed within the styrene manufacturing industry, and should be used provided they do not conflict with any specific legal obligation.

^{14, 15} <http://www.cefic.org/Industry-support/Transport--logistics/Best-Practice-Guidelines1/General-Guidelines-/>

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, including protective devices to allow safe access to the top of transport equipment such as platforms or harness. Closed loading and unloading systems (i.e. vapour return, incineration or vapour absorbing systems) should be considered.

6. Transport, storage and handling operations

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 - ADN - IMO - IMDG 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.

Table 5: Storage Inspection Points

Check Point	Interval
Air Vent	At least quarterly
Foam reservoir	Within 5 years
Internal roof seal, Sides and floor	When technically possible
PVRV (Pressure Vacuum Relief Valve)	At least quarterly
Flame Arrestor	At least quarterly
Vapour return line	At least quarterly

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.

Table 6: Road and Rail Inspection Points

Check Point	Interval
Air Vent	At least quarterly
Foam reservoir	Within 5 years
Internal roof seal, Sides and floor	When technically possible
PVRV (Pressure Vacuum Relief Valve)	At least every half year

6.6. Vapour control

Because of the flammability hazard (in certain circumstances) and, to prevent exposure to environment and people, all loading/unloading activities should preferably be carried out via closed vapour return systems.

6.7. Previous cargoes, cleanliness and stowage

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

Some coatings, such as epoxy, can absorb prior cargoes into the coating and release those materials once a new cargo is loaded. The vessel owner is responsible for insuring that the coating offered for the cargo is suitable and will not release any materials that could contaminate the cargo.

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.

Table 7: Previous cargoes that must be avoided

Prior Cargo	Justification
Caustic soda	Reactivity with TBC
Benzene and Benzene-containing products such as Pyrolysis gasoline	Product quality
Fuel oils	Product quality
Lube oils	Product quality

Because of the effect of the application of heat to styrene, steam cleaning of tanks to adjacent compartments which contain styrene or styrene residues is strictly not allowed. Heated adjacent cargoes should be avoided, even if separated by cofferdams.

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 3-8 volume percent of oxygen in the vapour phase is recommended. TBC should be added at a level depending on the residence time, to prevent subsequent poly-peroxide formation.

6.9. ROAD Specific Operations

6.9.1. Shipper's responsibility

All SPA 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 Management System, such as ISO 9000, in place and have carried out an SQAS assessment (see Appendix 1).

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 that is lit at night. It is strongly recommended that receivers of styrene provide secure parking spaces for vehicles that 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. In the case of severe weather conditions, 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 Instructions in writing

One of the specific requirements of ADR not applicable to other modes of transport for the consignor is to provide single standard "Instructions in Writing" (liW) 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.

Instructions on how to obtain the liW in various languages are found on the UNECE website¹⁶.

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 transporting rail company (rail undertaker) is responsible for the safe transport of styrene by rail from the dispatch location to the final reception location. 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 Management 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 even if separated by cofferdam. Heating styrene 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. The inspection reports are readily available to participants of the European Barge Inspection Scheme (EBIS)¹⁶

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.

¹⁶ http://www.unece.org/trans/danger/publi/adr/adr_linguistic_e.html

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

Since oxygen is required for the TBC to work effectively, a nitrogen blanket with 3-8 oxygen volume% could minimize the risk of fire/explosion and avoid polymerisation. 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

When collecting empty vessels from customers, 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. (See Appendix 1).

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. See Appendix 1 for more details.

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, Seveso Directive requirements must also be taken into account,
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.

Pre-plan fire response preparedness (training, resources, etc.) corresponding to the major accident scenarios.

7.2. Measures in the event of a release of styrene

7.2.1. Emergency Response Team

Firefighting 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 polymerisation 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 the supplier Safety Data Sheet (SDS) 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. The ERICard for styrene can be found at www.ericards.net.

7.2.3. Spills and Leaks

Because styrene is only slightly soluble in water and a flammable liquid and vapour, 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 harmful to aquatic life with long lasting effects and therefore entry into drains, sewers and watercourses must be prevented if at all possible.

Since flammability is the main hazard, 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. Therefore, it may travel a considerable distance to a source of ignition and then flashback.

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 the addition of water can be avoided by installing an underflow weir or siphon. Advise the Local 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. Firefighting

7.3.1 Exothermic reaction

If styrene vapour ignites and the temperature of the liquid reaches 52°C, the stabilising effect of the inhibitor (TBC) 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 they may simply spread the fire, given that styrene is both immiscible with water and lighter than water. Burning styrene may produce carbon, carbon monoxide, carbon dioxide and large quantities of thick black smoke. Firefighters should wear breathing apparatus.

Take necessary actions to avoid static electricity discharge (which might cause ignition of organic vapours).

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 layers 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; however, 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, as styrene is classified as harmful to aquatic life with long lasting effects. 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.

The REACH registration for styrene identifies Derived No-Effect Levels (DNELs), which are human exposure limits that should not be exceeded. The DNEL is a threshold for health effects and is used to establish operating conditions and risk management measures that define the safe use of a substance for specific exposure scenarios attached to the supplier's extended safety data (eSDS).

The styrene DNEL for long-term worker inhalation exposure is 20 ppm for an 8-hour TWA. The styrene DNEL for short-term worker inhalation exposure is 68 ppm.

Additionally, in most European countries, strict limits are set over occupational exposure to dangerous chemicals. There is not yet a European standard for occupational exposure limits. The Scientific Committee on Occupational Exposure Limits (SCOEL) is working on proposals for the standardization of these limits.

Table 8 gives an overview of styrene OELs across Europe. Styrene vapour concentrations are shown in parts per million (ppm) as an 8-hour Time-Weighted Average (TWA), Short-Term Exposure Limit (STEL), or Ceiling (C) limit. The TWA is measured or estimated over an 8-hour working period.

Table 8: Occupational Exposure Limits (OELs) applying to styrene in the EU

Country	8-hour TWA (ppm)	15 min STEL (ppm)
Austria	20	80 (4x15 mins)
Belgium	25	50
Bulgaria	20	50
Czech Republic	24	94*
Denmark	–	25*
Estonia	2.4	7
Finland	20	100
France	23.3	46.6
Germany	20	40 (4x15 mins)
Greece	100	250
Hungary	12	12
Ireland	20	40
Italy	20	40
Latvia	2.4	7
Lithuania	20	50
Luxembourg	20	40 (30 mins)

* Ceiling limit

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Country	8-hour TWA (ppm)	15 min STEL (ppm)
Netherlands	25	50
Norway	25	37.5
Poland	12	47
Portugal	20	40
REACH DNEL	20	68
Romania	12	35
Slovakia	20	40*
Slovenia	20	80
Spain	20	40
Sweden	10	20
Switzerland	20	40 (4x10 mins)
United Kingdom	100***	250

* Ceiling limit

***Obligation to reduce as much as possible

To cover emergency situations, single exposure values have been developed for styrene. For example, the USEPA uses a lower Acute Exposure Guideline Levels (AEGs) for styrene of 20 ppm to 230 ppm for a single inhalation exposure¹⁷.

8.1.2 Occupational Health Aspects

Occupational Exposure Limits in European countries range from 2.4 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.
4. Personal Protective Equipment (PPE), including suitable respirators, as discussed below.

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

The inhalation of styrene vapour should be avoided; therefore, exposure limits should be viewed as maximum guideline values. It is a legal requirement to conduct risk assessments to determine the potential for worker exposure to styrene liquid and vapours.

Based on the risk assessments, due attention should be paid to providing adequate ventilation, including specific engineering controls such as ventilation hoods, wherever styrene exposure is possible.

Effectiveness of risk management measures should be confirmed through monitoring of styrene vapours. There are a number of different monitoring and analytical test equipment on the market that can measure and record

¹⁷ <https://www.epa.gov/aegl/styrene-results-aegl-program>

8-hour average concentrations; e.g. active carbon badges, Tenax tubes, or portable Photo-Ionisation Detection (PID) systems may be considered. Consult an Industrial Hygienist for recommendations.

For specific conditions of use and for meeting relevant workplace-related legislation, suitable respiratory protective equipment (RPE) should be selected.

Each RPE type and class is categorised by an Assigned Protection Factor (APF). The APF is a numerical rating that indicates how much protection that RPE is capable of providing. For example, RPE with an APF of 10 will reduce the wearer's exposure by at least a factor of 10 if correctly fit-tested and used. The wearer will, theoretically, only breathe-in one-tenth or less of the amount of substance present in the air. With modern equipment, protection efficiency is often much higher.

For protection against styrene vapours, generally an APF 20 or APF 40 filtered/powered respirator should be used, and then only for short-term exposures of <1 hour. If there is the potential for aerosol mists to be generated, then a combined organic and particulate filter is required. Particulate filters should meet EN143. P3 types are recommended. Typically, filters should meet at least EN14387:2004.

For activities longer than 1 hour, an air-supplied hood offering APF of 40 or APF 200 is highly recommended. APF 40 would imply a 97.5% efficiency as a lower bound (powered masks, combined particulate filter). APF 200

would imply a 99.5% efficiency as a lower bound (hood with constant flow airline).

In general, tight-fitting masks can only be recommended for short periods of use (<1 hour). Heat and sweat can cause discomfort to the operator, leading to the need for readjustment, and this provides opportunities for direct incidental exposures.

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

8.2.2.3 Eye Protection

Chemical splash goggles are always recommended.

8.2.2.4 Skin 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.

9. First aid & medical treatment

9.1 Acute intoxication with styrene – symptoms and treatment

9.1.1 Eye

Liquid styrene 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.

9.1.2 Skin

Liquid styrene 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.

9.1.3 Inhalation

Styrene 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.

9.1.4 Ingestion

Styrene liquid 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. When 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).

9.2 Acute intoxication with inhibitor (TBC) – symptoms and treatment

9.2.1 Eye

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

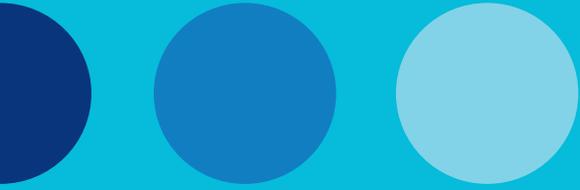
9.2.2 Skin

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

9.3 Signs and symptoms of prolonged exposure to styrene

Headache, fatigue, drowsiness, insomnia, anorexia and weight loss, pain in limbs, nervousness, or impairment of memory can be symptoms of prolonged exposure. 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 effects of styrene, please refer to Section 3 “Health Aspects”.



Appendices

Appendix 1.

CEFIC and Responsible Care®

1. Responsible Care® – A Public Commitment

Responsible Care® is the global chemical industry's unique initiative to improve health, environmental performance, sustainability, enhance security, and to communicate with stakeholders about products and processes.



A key element of this initiative is that chemical companies shall demonstrate their commitment to continuously improve all aspects of performance which relate to protection of health, safety and the environment, and report openly on performance, achievements and shortcomings.

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, as these ensure conformance with the principles of Responsible Care.

MORE INFORMATION:

CEFIC Responsible Care:
<http://www.cefic.org/Responsible-Care/>

2. Transport Accident Prevention and Response (ICE)

Under the Responsible Care programme, the chemical industry makes every effort to transport goods to and from its manufacturing sites and storage locations safely and in full accordance with relevant regulations and codes of practice.

ICE (Intervention in Chemical Transport Emergencies) is a co-operative programme, set up by the European chemical industry to achieve this goal. In each European country, it seeks to create a framework for providing assistance in an effective way.

The ICE Emergency Response programme aims to minimise the consequences of transport incidents involving chemicals by providing uniformly competent assistance in each European country, and by coordinating Emergency Response particularly across national boundaries.

Each national ICE scheme applies only to distribution incidents (i.e. those that occur outside manufacturing sites) and is formalised in a protocol between the national chemical industry federation and the national competent authorities.

A national ICE scheme is a voluntary initiative, normally open to all manufacturers and distributors of chemical products.

The focal point of a national ICE scheme is the national ICE centre, which emergency authorities can call in case of an accident. When needed, the national ICE centre can provide emergency response advice in the local language, alert the producing company, and obtain further information (possibly via other national ICE centres) or mobilise mutual assistance. The centre is manned 24 hours a day by at least one person who, in addition to the local language(s), can also speak English to facilitate communication between the national ICE centres.

A similar MAR-ICE network was established between CEFIC and the European Maritime Safety Agency (EMSA) to provide information and expert advice on chemicals involved in maritime emergencies.

Safety data sheets (SDS) are the primary source of substance and product emergency information.

Participating companies therefore must ensure the SDS for their own products are accessible at all times at the locations identified as company contacts in the national ICE scheme.

MORE INFORMATION:

ICE: <http://www.cefic.org/Industry-support/Transport—logistics/Transport-Emergency-Scheme/>

MAR-ICE:
<http://www.cefic.org/Documents/IndustrySupport/Transport-and-Logistics/EMSA-MAR-ICE-Information-service-for-use-in-marine-chemical-emergencies.pdf>

Transport & Logistics - CEFIC Best Practice Guidelines:
<http://www.cefic.org/Industry-support/Transport—logistics/Best-Practice-Guidelines1/General-Guidelines/>

3. Safety and Quality Assessment for Sustainability (SQAS)

SQAS is CEFIC's Safety and Quality Assessment for Sustainability system for evaluating the safety, security, health, quality, environmental and Corporate Social Responsibility (CSR) standards of their logistics service providers.

SQAS is a standardised assessment to evaluate the quality, safety, security and environmental performance of logistics service providers and chemical distributors centrally managed by CEFIC.

SQAS assessments are carried out by a European network of accredited independent third-party assessors using a standard questionnaire. This ensures consistency and avoids duplication of assessments.

SQAS covers all key service providers in the land-logistics chain: road transport companies, intermodal operators and terminals, rail carriers, rail tank car maintenance workshops, packaged goods warehouses and tank cleaning stations.

Since 1995, more than 2000 assessments of road transport companies have been carried out covering most European countries. The list of assessed transport companies is available on the SQAS Transport Service website.

The assessment reports are stored on a central database, accessible only to chemical companies that are member of the CEFIC SQAS Service Group.

MORE INFORMATION:

CEFIC SQAS:
<http://www.cefic.org/Industry-support/Transport—logistics/SQAS2/>

SQAS Questionnaires and Accredited Assessors:
<http://www.cefic.org/Industry-support/Transport—logistics/SQAS2/SQAS-Transport-Service/>

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.

Q1: 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 polymerisation. The temperature needs to be monitored continuously.
- TBC levels (target >10 ppm wt). At temperatures below 15°C in the tank/container, weekly sampling

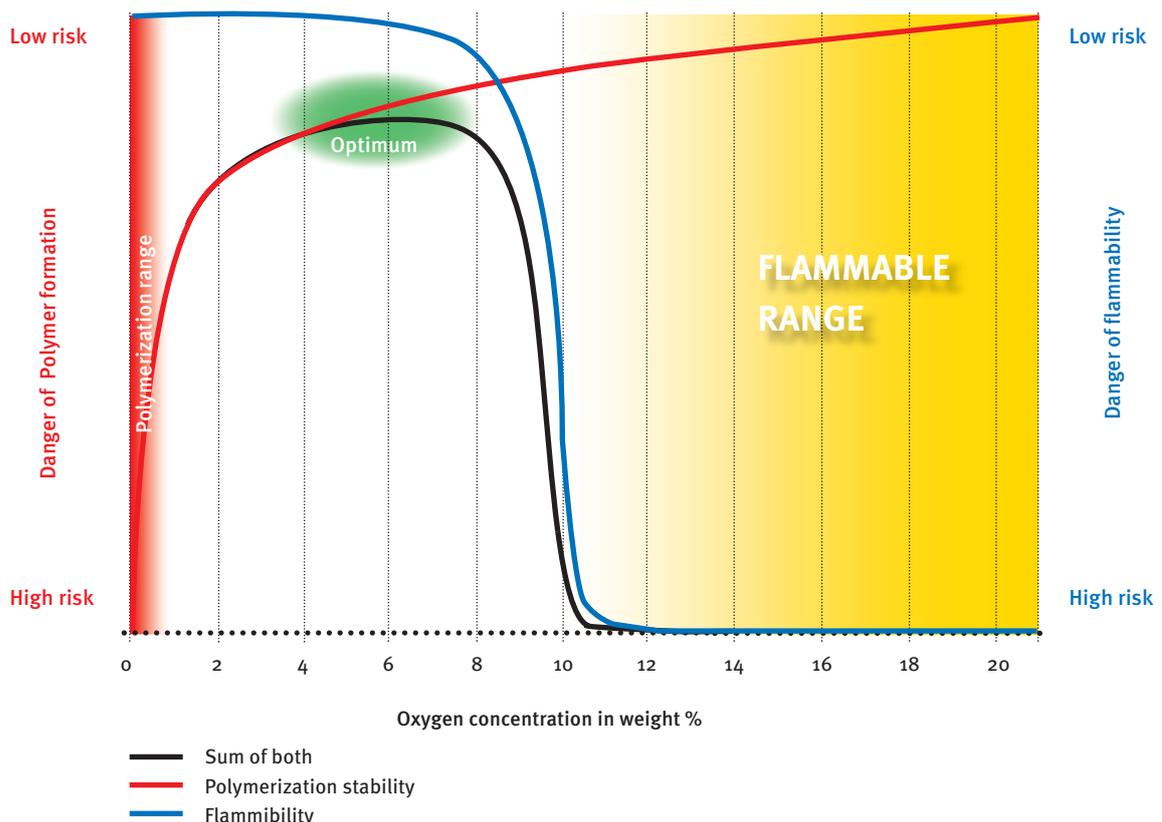
should be sufficient; above 25°C daily sampling is recommended. Normal TBC levels are between 10 and 15 ppm (for some applications higher concentrations are required). Below 10 ppm TBC polymer levels can slowly increase; below 4 ppm the TBC is not effective and accelerated polymerisation will occur. Lower TBC levels can be accepted when the temperature is low and the residence time is short.

- Oxygen levels (3-8 volume % in the vapour phase).

Q2: What is the recommended range of oxygen in the vapour phase of a styrene storage tank?

3-8 volume % oxygen in the vapour phase. Less than 3 vol% is not recommended because the increased risk of polymerization leading to a shorter shelf life. Higher than 8% will lead to an atmosphere above the lower explosion limit. Extra measures have to be taken to prevent sparks.

Figure 6: Optimum oxygen concentration in vapour space of storage tank.



Q3: What exactly do we define as polymer content – polystyrene or dimers, trimers, oligomers?

The ASTM D2827-04 standard specification of styrene monomer prescribes that the polymer content is analysed 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.

Q4: How often should the styrene be analysed for polymer levels?

Under normal storage conditions: typically 2-3 times/week for product quality.

If product temperature is above 25°C daily. If storage temperature below 15 °C once per week is sufficient.

Q5: How can we ensure thorough mixing of the inhibitor and oxygen 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 pumps
- Try circulation with existing equipment like transfer pumps, minimum flow lines, sample loops
- Connect temporary pump (e.g. compressed air driven)
- Bubbling air (also has the advantage that oxygen is present to enable TBC 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.

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

Q6: 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. When temperature of the tank is above 60 °C, start with low water flow in order to prevent a vacuum in the tank by styrene condensation.
- Remove insulation.
- Increase inhibitor levels by dosing TBC (up to 100 ppm is acceptable for some customers), aerate the tank contents, and mix bulk contents to make sure that the inhibitor and oxygen are effectively mixed.
- At higher polymerisation rates (i.e. possible HSE risk), mitigate by adding a large enough volume (4:1) of cold inert material (Ethylbenzene (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), TBC is not an active inhibitor (reaction rates and therefore TBC consumption are high). A Short Stop agent can be added. DEHA and O(H)TEMPO can be used as Short Stop. Be aware that short stop makes the styrene unfit for use by customers and refinishing or discarding is necessary.

Q7: 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 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 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: TBC levels and temperature will remain constant).

Q8: Can there be a runaway reaction if there is inhibitor and oxygen present in the styrene?

Not under normal storage conditions, but it is possible in some circumstances that must be avoided, such as:

- Presence of contaminants (e.g. due to insufficient/in-correct cleaning of storage/transportation medium) that initiate polymerisation and overwhelm the inhibition effects of TBC. Known contaminants that initiate polymerisation are acids, peroxides and iron chlorides.
- Presence of rust (particles) inside the tank can form fertile seeds to initiate polymerisation.
- High enough (local) temperature (~ > 40-50°C) (e.g. exposure to heat from an adjacent tank fire). 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 TBC and oxygen in the tank contents: If the TBC concentration is low at certain zones in the tank, this could lead to runaway zones in the bulk contents.

Q9: 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 polymerising a 2-3°C temperature increase is observed per 1% SM polymerisation.

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

Q10: 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°C/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. Polymerisation can be ongoing and unnoticed in zones that are not near the thermocouple, if the tank contents are not well-mixed.

Q11: How much time do we have before the reaction enters the “runaway” mode?

The TWB (Time to Water Boiling) graph in Figure 7 can be used to make an evacuation decision: e.g. if is 85 °C, the storage tank may rupture within 100 minutes.

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.

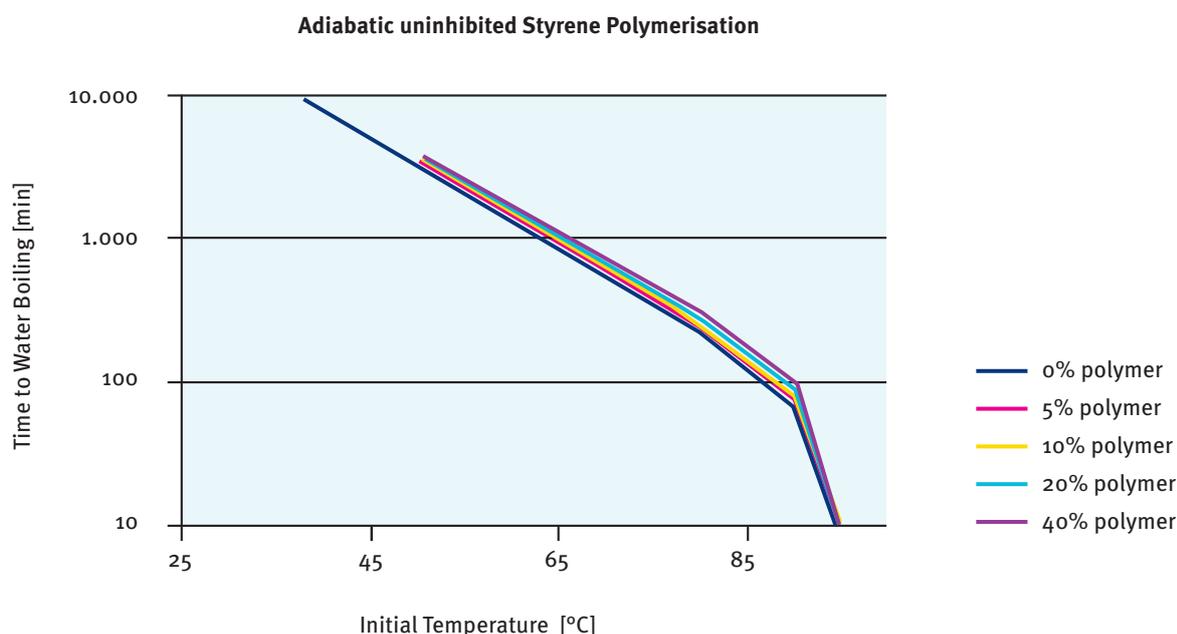
It is possible to predict the moment of vessel rupture when the tank temperature is known. This knowledge can be used to make an informed decision on evacuation of (emergency) staff or notification of third parties (authorities).

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 bar.
- The styrene is possibly contaminated with water.

The decision to evacuate should be based on the onset of an uncontrollable runaway reaction. The graph below is indicative only and can be useful in the evaluation of evacuation plans. It should NOT be used as a basis to delay evacuations.

Figure 7: Predicted moment of storage vessel failure



Since the final part of the runaway has a very steep dT/dt curve, the time at which 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 7 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 6 is over-cautious if:

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

Q12: 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.

Q13: 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% is likely to trip a pump that is not designed to move partially polymerised styrene to a 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 toluene, xylene or Ethylbenzene.

Q14: 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 TBC levels, this could stop the polymerisation reaction.

Q15: Will adding a nitrogen blanket slow down the polymerisation reaction?

No. Oxygen needs to be dissolved in the product in order for the 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 3 - 8 vol.% needs to be maintained in the gas cap.

Q16: Oxygen is required for 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 TBC to work effectively, a nitrogen blanket with 3-8 volume% of oxygen could minimize the risk of fire/explosion and avoid polymerisation. Static electricity or any other ignition source should be avoided in all cases.

Q17: What additional controls should be considered when transporting (high polymer) styrene?

- Materials of construction (similar to storage, e.g. stainless steel)
- Stowage plans (do not store styrene adjacent to heat or containers of polymerisation initiators like peroxides, concentrated acids, ...)
- Cleaning of transportation medium (no traces of contaminants from cleansing agent or other products that had been stored)

Q18: Is there a preferred physical state for the inhibitor to be added (i.e. liquid, powder)?

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

Q19: Are there any standard processes/procedures for dosing TBC? (against which we could validate third 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 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.

Q20: 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.

Q21: Can a ship's cargo of off-spec/high polymer SM be overdosed with TBC such that the product arrives on spec due to the depletion rate of TBC?

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

Q22: What are the hazards of TBC?

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. 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 TBC might have negative effects on aquatic organisms.

Q23: *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.

Q24: *Could the efficacy of TBC alter due to a change in supplier?*

No. There is no reason to suspect differences in efficacy between various suppliers. 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.

Q25: *Can TBC still be used if the shelf life has expired?*

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

Q26: *Is there a 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.

Q27: *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.

Q28: *What reference documents are available to support a styrene polymerisation emergency situation?*

Product Safety Data Sheets (SDS), ERICard
www.ericards.net

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 ADN 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,
- IMO ship type 3, 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 carbon steel tanks a suitable coating (e.g. zinc silicate, baked phenolic or modified epoxy coating) is recommended. For emergency situations, facilities must be provided, both to adjust the inhibitor content and to inject air 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 should be maintained between 3-8% vol. Proper circulation of the liquid styrene is necessary for a sufficient distribution of the oxygen.

Refrigeration of the styrene and short residence time during storage will reduce the need for oxygen.

The standard inhibitor content of 10 – 15 wt. ppm is sufficient to protect against unwanted polymerisation at normal temperatures and storage times. At higher doses TBC can form colour complexes. 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.

To avoid stagnant product in blocked pipes, valves, or standby pumps, they should be purged with stabilized styrene on a regular basis, at least once a week.

Nozzles above the liquid level are prone to be blocked by condensing and polymerising styrene monomer containing no TBC. To avoid condensation, it is recommended to purge them, as well as all dead ends, continuously with nitrogen or to apply outside electrical heat tracing.

For vertical storage tanks, a double bottom construction with vacuum monitoring is recommended.

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. Aluminium 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. Vertical storage tanks should be constructed with a self-supporting or exterior-supported domed roof without internal bracing.

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 firefighting, 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 frequency of inspection can be adjusted based on experience or based on climatic conditions. The installation of a foam chamber or sub surface injection connection is also recommended for automatic firefighting, particularly on larger tanks.

4.4. Lining

Tank linings can help control or reduce polymer and stactite 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. 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, except for frequently used sampling points. Preferred line size should be 50 mm (2 inch) and up,
2. A minimum of flanged connections is preferred due to leak potential,
3. Lines should not be buried due to 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, but their usage should be minimized in favour of welded lines.

Styrene can dissolve pipe dope and thus cause product colouration 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 ethylbenzene) 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. Secondary Containment

A secondary 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 firefighting,
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/Clearing

Installation design should allow for recirculation and complete drainage, and subsequently flushing and purging 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 bag 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 aluminium 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 cargo transport unit?
3. Has the driver a valid ADR license for the transport of dangerous substances and means of identification which include his/her photograph?
4. Remove old dangerous goods labels of former products
5. Are all dangerous goods labels placards (model number 3) attached?
6. Are the orange-coloured plates fitted with the correct hazard identification number and UN number (39/2055)
7. Are the written instructions on board?
8. For combined ADR/ IMDG transport, are the IMDG code dangerous goods placards and marks fitted?
9. Does the driver have all the necessary equipment for personal and general items of protection?
10. Is the tare weight in your possession?
11. Is the road tanker pressure-less?
12. Is there a valid cleaning certificate ECD (name / address / stamp) or a confirmation that the last product was styrene?
13. Is the container suitable for loading styrene (no overdue on periodic testing, Minimum Tank-code LGBF / UN T2)?
14. Are the valves closed upon arrival? appropriate gaskets? temperature less than 30°C?
15. Is the tanker properly earthed?
16. Can all valves be operated?

17. Are hoses on truck clean and qualified for styrene (for possible later use at customer site)?
18. Check the maximum allowed filling degree.
19. Check if the engine is switched off and if disconnected, is the battery master-switch open?
20. Check if handbrake/wheel blocks are applied.

B) Whilst Loading

1. Are controls against leaks and spillages done?

The driver should remain in the vicinity of truck loading and be easily reachable by loading station personnel.

C) After Loading

1. Remove loading/unloading arms/hoses,
2. Remove earthing,
3. Clean tank outside wall surface and equipment from spilled styrene if necessary,
4. Clean bunded filling station from spilled styrene if necessary,
5. Are all valves closed and blinded, with all bolts in place? Labelling correct?
6. Verify equipment is loaded according to regulations (maximum gross weight not exceeded?),
7. Is the maximum degree of filling exceeded? Check by weighbridge?

2. Routine inspection of rail tank cars at Loading Terminals

Guidelines in the form of checklist issued by the CEFIC is available from the following link:

<http://www.cefic.org/Documents/RESOURCES/Guidelines/Transport-and-Logistics/Best%20Practice%20Guidelines%20-%20General%20Guidelines/Checklists-avoiding-leaks-filling-discharging-rail-tank-wagons.pdf>

Identification requirements exist for all mode of transport.

NOTE: Rail tank cars should 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. The driver should remain in the vicinity of truck unloading and be easily reachable by unloading station personnel.**

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 also be used as a guideline for the safety service of the supplying company. See Section 6.

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. Firefighting systems,
7. Electrical Area classification and Electrical classification of equipment,
8. Define the minimum safety distances between the off-loading point, storage, and ignition sources.
9. Hoses/unloading arms,
10. Earthing point,
11. Protection against pipe damage,
12. Other vehicles and trucks movements,
13. Are hoses on the truck clean and qualified for styrene?
14. Spillage controls systems with styrene resistant surface and sufficient containment volume,
15. Hazard labelling of unloading points,
16. Visual and audible alarm,
17. Declaration of suitability, approval by local authorities if legally required.

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. Antifall guard or fall arrestors for work on top of the vehicle,
8. Communication system,
9. 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, flow velocities to prevent static build-up),
6. Safeguards for pump,
7. Emergency response,
8. Emergency stop,
9. Sufficient tank venting capacity.

3.4 The Storage Tank

Site

1. Secondary containment (bund),
2. Shared? If shared, with what?
3. Separation distances,
4. Emergency disposal facilities.

Construction

1. Construction materials,
2. Insulated,
3. Uninsulated,
4. Refrigerated,
5. Firefighting 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 with siphon breaker,
15. Circulation loop for air, TBC, temperature distribution.

Relief Valves

1. Separate,
2. Combined with interlock,
3. Size,
4. Venting to: (stack, scrubber, flare, other),
5. Vacuum relief valves,
6. Flame arrestors,
7. Nitrogen purge vents.

Instrumentation

1. Nitrogen blanketing pressure,
2. Control points:
 - a. Temperature,
 - b. Pressure,
 - c. 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:

1. Unloading styrene,
2. Testing, inspection and maintenance of equipment,
3. 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. There should be sufficient space for easy access of vehicles.
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.
3. Barriers, warning notices are required. Special consideration may need to be given to prevent shunting close to the unloading area.
4. A foam or powder-based system is recommended.
5. This should be in accordance with national regulations.
6. Unloading arms are preferred to hoses.
7. The earthing point should be checked on a regular basis.

5.2. The Unloading Personnel and Equipment

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. There should be at least two trained deputies to provide cover for illness and holidays.
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 ($T > 30^{\circ}\text{C}$). Exothermic polymer formation is prevented by oxygen, so a minimum level of 3-8% volume of oxygen in the vapour phase is recommended. 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. The liquid should be circulated for proper distribution of both oxygen and TBC.

Fire Protection

The provision of fire protection systems, e.g. 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.

A certified lightning protection system must be installed.

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 regularly 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, canned motor pumps or magnetically driven pumps could be considered.

Double mechanical seals with styrene-compatible antifreeze flush are also possible.

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, graphite 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.

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

CAS Chemical Abstract System

CEFIC European Chemical Industry Council

CDI Chemical Distribution Institute

DIN *Deutsche Industrie Norm.* German Industry Standard

IARC International Agency for Research on Cancer

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

LC50 Lethal concentration (50%)

LD50 Lethal dose (50%)

OEL Occupational Exposure Limit

OSHA Occupational Safety and Health Administration (USA)

TBC Para Tertiary Butyl Catechol (=TBC), styrene product polymerisation 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

SM Styrene Monomer

SQAS Safety and Quality Assessment System

SPA Styrene Producers Association

STEL Short Term Exposure Limit

TWA Time Weighted Average

UN United Nations

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