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Styrene Monomer: Safe Handling Guide

Styrene Producers Association (SPA)

OCTOBER 2024

Styrene Producers Association (SPA) Member Companies:

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

- BASF SE
- INEOS Styrolution Europe GMBH
- LyondellBasell
- Repsol Química S.A.
- Shell Chemicals Europe B.V.
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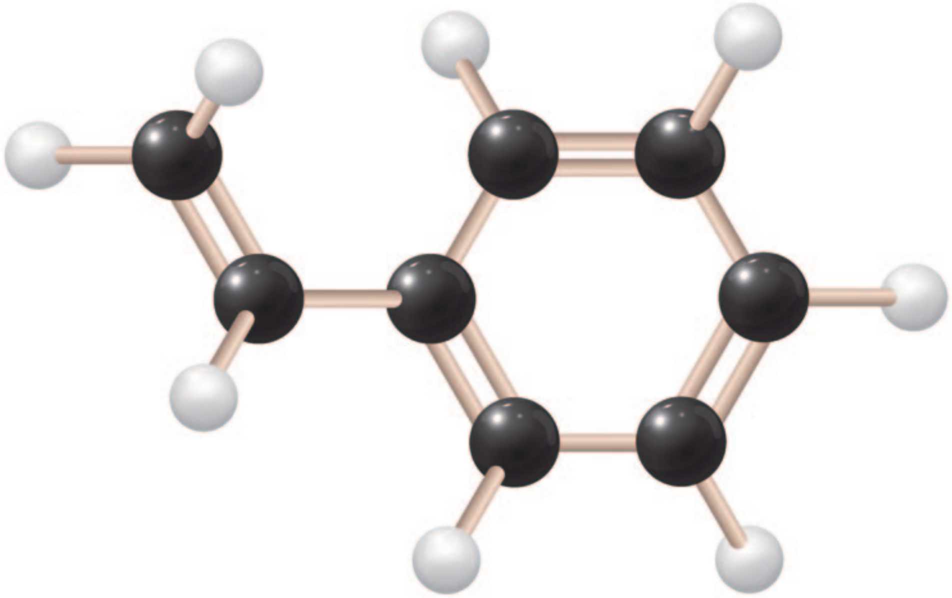

MAIN CHAPTERS

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 Plastics Europe/Styrenics Chain, encourages customers and potential users of styrene to review their applications from the standpoint of human health and environmental quality.

Although this document is written primarily for the European audience, the basic principles of inhibition chemistry and flammability risk management are relevant for all regions of the world where styrene is manufactured, stored, handled, and distributed.

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 Care[1] 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, ships, 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 Environmental, Health, Safety and Distribution Guidelines are adopted by all parties involved in the transfer of styrene, including commercial transaction partners for product swaps, toll or trade agreements along with customer collection arrangements. The latter arrangements should adhere to the same distribution safety principles as if conducted by the manufacturing supplier.

Additional valuable resources on styrene: *Styrene Information and Research Center*

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[1] See Appendix 1

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	An exothermic reaction can lead to thermal runaway, which begins when the heat produced by the reaction exceeds the heat removed. The surplus heat raises the temperature of the reaction mass, which causes the rate of reaction to increase. This in turn accelerates the rate of heat production. An approximate rule of thumb suggests that reaction rate – and hence the rate of heat generation – doubles with every 10 °C rise in temperature. Thermal runaway can occur because, as the temperature increases, the rate at which heat is removed increases linearly but the rate at which heat is produced increases exponentially. Once control of the reaction is lost, temperature can rise rapidly leaving little time for correction. The reaction vessel may be at risk from over-pressurisation due to violent boiling or rapid gas generation. The elevated temperatures may initiate secondary, more hazardous runaways or decompositions. An over-pressure may result in the plant failing catastrophically resulting in blast or missile damage. A release of flammable materials from the process could result in a fire or an explosion in the workroom. Hot liquors and toxic materials may contaminate the workplace or generate a toxic cloud that may spread off-site.

2. PRODUCT INFORMATION AND CHARACTERISTICS

2.1 General Description and Hazardous Properties

Styrene (C6H5-CH=CH2, CAS RN:100-42-5; EC No.: 202-851-5, EEC Annex I Index No.: 601-026-00-0), also known as ethenyl benzene, phenyl ethylene, phenyl ethene, vinyl benzene, cinnamene or styrene monomer, under ambient conditions is a colourless clear liquid with a distinctive sweetish aromatic odour. It is miscible with most organic solvents in any ratio and is a good solvent for synthetic rubber, polystyrene, and other high molecular weight polymers. From the environmental impact point of view, it is only slightly soluble in water 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 (§ 2.2): Typical Physical Properties of Styrene.

Short-term exposure to styrene in humans' results in respiratory effects such as throat irritation and lung constriction, irritation to the eyes, and neurological effects such as dizziness (see Section 3 "Health Aspects" for more details). Under CLP, Styrene is currently (October 2024) classified for flammability, skin / eye irritation, acute toxicity, hearing damage, aspiration hazard, specific target organ toxicity, long-term (chronic) aquatic toxicity and is suspected of reproductive toxicity.

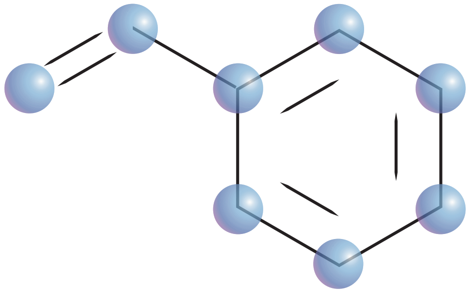


Figure 1: Chemical Structure of Styrene

The characteristic unpleasant smell and the low odour threshold (0.1 ppm; 0.43 mg/m^3) 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).

2.2 Physical Properties of Styrene

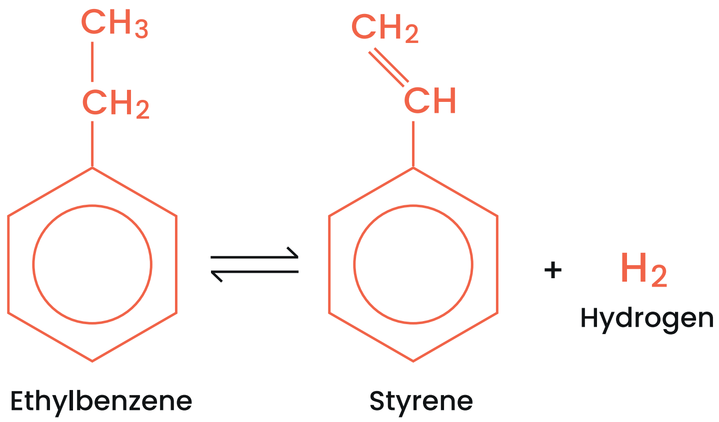
Property	International System Value & Unit
Physical Form	Colourless, oily liquid
Colour (acc. ASTM D 2827)	15 max. / Pt-Co scale
Odour	Sweet, aromatic (if pure) Sharp, penetrating, unpleasant (commercial grades)
Odour threshold	Water: 0.73 mg/L • Air: 0.1 ppm (0.43 mg/m^3)
Relative molecular mass	104.14 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
Conductivity, electrical at 25°C	10 pS/m
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	0.979×10^{-3} /°C
Specific heat at 20°C	1.73 kJ/kg °C
Heat of combustion, Hc at 25°C	-4265.64 kJ/mole
Heat of formation, Hf, gas at 25°C	147.46 kJ/mole
Heat of formation, Hf, liquid at 25°C	103.50 kJ/mole
Heat of polymerisation, Hp at 25°C	-70.67 kJ/mole

Table 1: Physical Properties of Styrene

2.3 Manufacturing and Use

The conventional method for producing styrene involves two steps: the alkylation of benzene with ethylene to produce ethyl benzene followed by dehydrogenation of the ethyl benzene to produce styrene (refer to Figure 2). Over the almost fifty years of practicing the conventional two-step process, refinements have constantly been made to improve conversion and selectivity of ethyl benzene 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 (2024) almost completely replaced by zeolite catalyst technology. Currently the predominant route for the commercial production of styrene is by dehydrogenation of ethyl benzene in the presence of steam over a catalyst (iron oxide) in fixed bed adiabatic or, in some cases tubular isothermal reactors. Another route involves co-production of styrene and propylene oxide via hydroperoxidation of ethyl benzene. Limited scale extraction from steam cracker pyrolysis gasoline is also practised.

Figure 2: Dehydrogenation of Ethyl benzene to Styrene



The specification and analytical methods for styrene monomer have changed through the years. Most 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[2]
- Polymer content of maximum 10 ppm

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.

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[2] Note that Reproducibility of ASTM D4590 (spectrophotometry) is rather poor around 15 ppm TBC. This can affect the precision of reporting performed at different labs on different samples. GC/MS based methods may provide greater accuracy, but this is not included in ASTM D2827.

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.

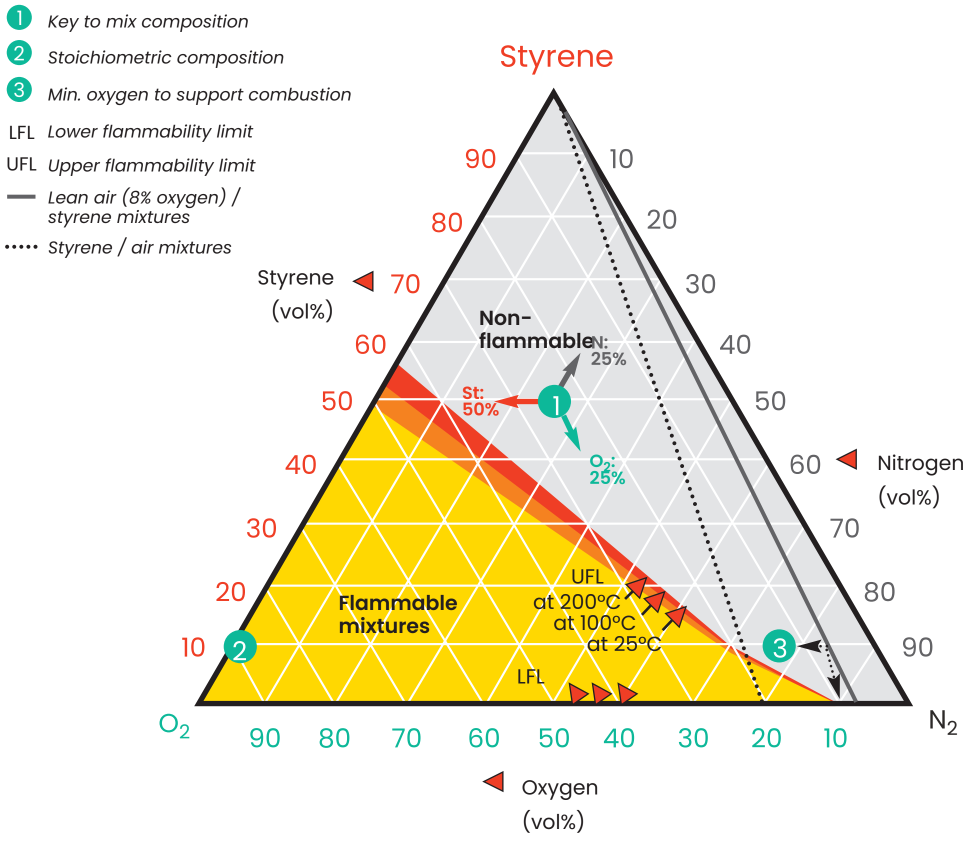
Inhibitor must be maintained at certain minimum level to prevent polymer formation. The presence of dissolved oxygen is required for the inhibitor to function properly; therefore, styrene needs to be stored under air or inert gas with sufficient oxygen levels.

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.

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



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

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

GAS	CC GAS/CC STYRENE	Ppm by wt.
Oxygen	0.4	581
Nitrogen	0.08	102
Air	0.15	198
O_2 from air*	0.032	50

* amount of oxygen when saturated with air

In warm climates, consideration can be given to applying a coating on the internal surfaces of tanks, thereby preventing discolouration of the styrene from oxidised iron and minimizing polymer build-up in the headspace.

It is recommended that the testing schedule for storage of styrene be followed as indicated in Table 3.

It is also recommended to keep a running log of product turn-over which should include date of last filling, volume before filling, volume after filling.

Table 3: Schedule for Styrene Storage Testing

Checkpoint	Interval		
	=> 25 °C	> 20 °C < 25 °C	=< 20 °C
Inhibitor Analysis	Daily	2 - 3 times weekly	Weekly
Polymer Analysis	Daily	2 - 3 times weekly	Weekly
Monomer Temperature	Daily	Daily	Daily
Monomer Vapour Temperature	Daily	Daily	Daily

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 < 8vol-%. 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

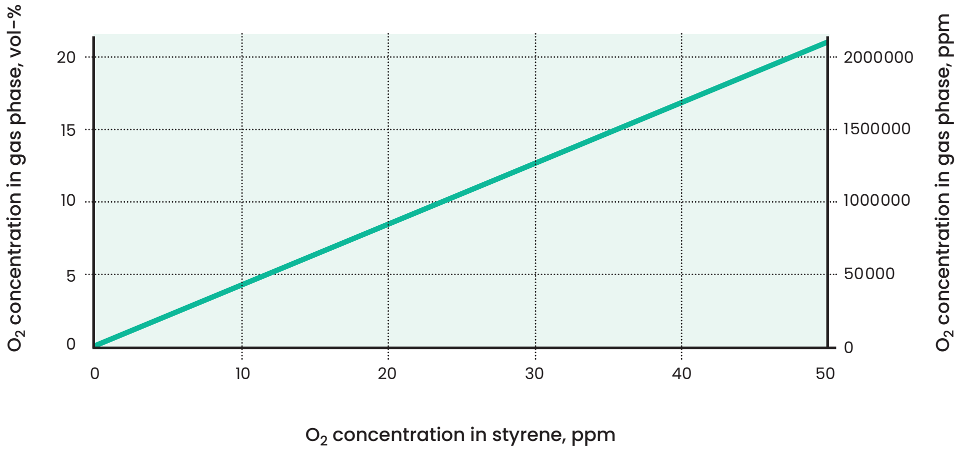
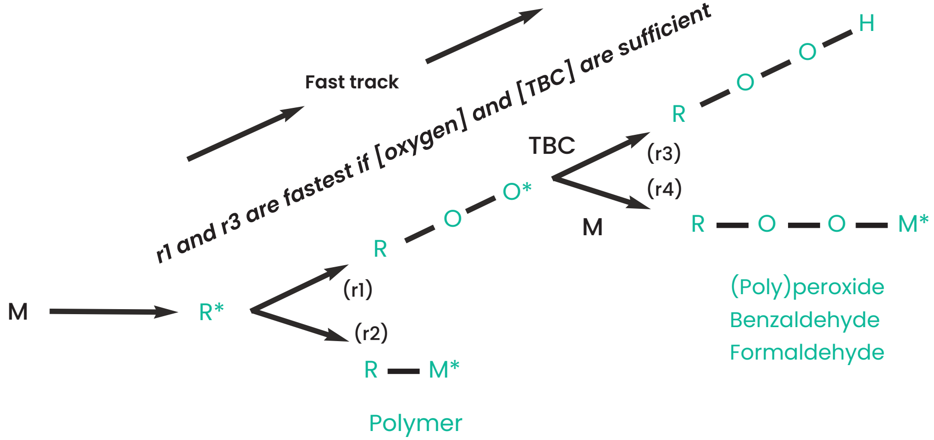


Figure 5: Inhibition Mechanism



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 presence of air is shown in table 4.

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

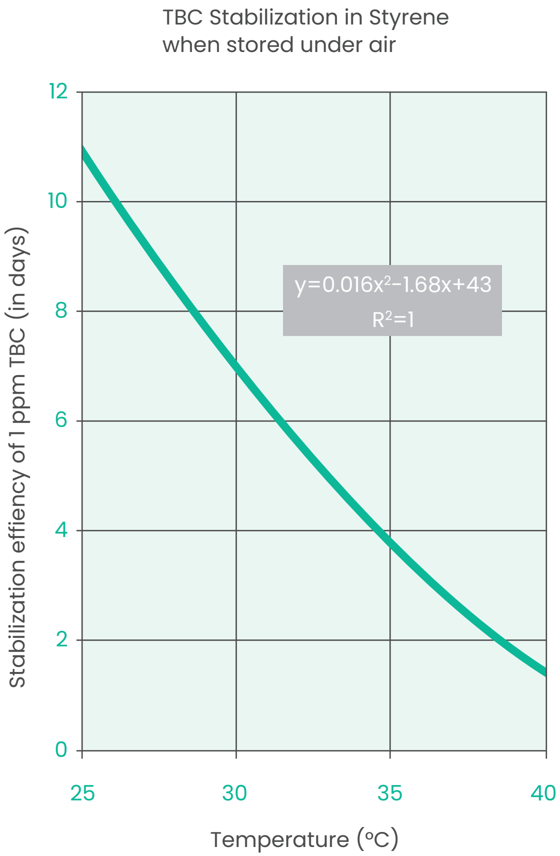
Temperature	Depletion Days/1 ppm	TBC Content		Shelf Life
°C t		[initial] ppm	[end]	Assured days
25	11	15	10	55
30	7	15	10	35
40	1.5	15	10	7

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

It is possible to calculate the TBC Depletion days for temperatures in between 25-40°C using Table 4 fitted exponentially (Figure 6).

Figure 6: TBC depletion in Styrene if stored under air

Temperature	Depletion Days/1 ppm
°C	Days/1 ppm
25	11.0
26	10.1
27	9.3
28	8.5
29	7.7
30	7.0
31	6.3
32	5.6
33	5.0
34	4.4
35	3.8
36	3.3
37	2.7
38	2.3
39	1.8
40	1.5



The depletion of oxygen in styrene is not only dependent on the temperature, but also on the TBC level added. If blanketing with lean oxygen systems (Nitrogen/Oxygen mix), provisions must be made to restore the oxygen level at 3 vol% minimum as otherwise the TBC will become ineffective. Lower oxygen levels will lower the shelf life at the moment it comes below 3 vol%.

Styrene users are advised to have a TBC concentrate/solution on-site to restore the TBC below the recommended concentration. 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 m^3 of styrene.

2.4.3.1 Inhibitor Levels for Extended Transport / High Temperature Environments

For shipments of styrene involved in extended transport, or in higher temperature environments, inhibitor levels in excess of typical manufacturer specifications may be required. This may be typical in tanker ship or barge transport.

The consignor, charter party or other entity responsible for transport (such as Incoterm Group E, F and some C & D group purchasers) must review the trip / voyage plan and determine the quantity of TBC appropriate for safe transport. In some instances, the manufacturer has little to no specific knowledge of transport details and typical inhibitor specifications may be insufficient.

“Contingency”

This is a factor which is intended to account for voyage plan variability. Some voyage durations may be extended due to schedule, inclement weather or other circumstances. The potential for voyage plan variance should be discussed and selected in consultation with the carrier / shipping company. For more details see Q4 in Appendix 2

Another factor to consider is if the voyage is through warm (tropical) seas or oceans. This can lead to warmer storage temperatures and require higher TBC concentrations.

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 an adequate amount (> 1000 ppm) of free radical scavenger (Short Stop). The short stops must be added when the monomer content is still mobile and not viscous. 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[3] (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-oxopiperidinooxy).

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

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).[4]

Inland waterways: European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways (ADN).[5]

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[3] As per US5880230, the 0.1 millimoles-10 millimoles of 4-Hydrooxy-TEMPO is preferred

[4] ID 2021 (otif.org)

[5] https://unece.org/sites/default/files/2021-01/ADN%202021%20English.pdf

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).[6]

Road transport: The Agreement concerning the International Carriage of Dangerous Goods by Road (ADR).[7]

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

2.6.1 Special Provision 386

Styrene Monomer is a self-reactive substance of Class 3 (Flammable liquids) listed in the Dangerous Goods regulations as UN 2055, Styrene monomer stabilized.

For the precautions necessary to prevent polymerization during transport, Special Provision 386 (respectively A209 as per IATA-DGR and 387 as per 49 CFR) must be observed. Shippers must ensure that the level of stabilization is sufficient to prevent the substance in the packaging, IBC or tank from dangerous polymerization at a bulk mean temperature of 50 °C and of 45 °C for portable tanks.

Suppliers can assess compliance to Special Provision 386 using suitable hot storage tests.[8] Such tests must take into consideration the inhibitor levels as offered for the journey of the packed goods, the duration of the voyage and the capacity and geometry of the packaging/tank container.

Special Provision 386 does not apply to bulk shipment in ships or barges. For these shipments a Certificate of Protection (see section 6.11.2) is required to ensure that the level of stabilization is sufficient for the conditions and duration of the journey.

2.6.2 Self-Accelerating Polymerization Temperature (SAPT)

In the 19th edition of the UN Recommendations on the Transport of Dangerous Goods (2015), a new physical hazard polymerization (Class 4, Division 4.1 "polymerizing substances") was introduced, in order to take account of the characteristic physico-chemical hazards of this substance group.

By analogy with self-reactive substances of Division 4.1 "self-reactive substances", polymerizing substances are classified as dangerous goods in Division 4.1. The classification criteria for this read as follows:

- Self-accelerating polymerization temperature SAPT ≤ 75 °C (as intended for transport with or without chemical stabilization) under the conditions and in the packaging, IBC or tank as intended for transport.
- Reaction energy exceeding 300 J/g; and
- No hazards requiring classification into one of the dangerous goods classes 1-8*).

SAPT is defined as the lowest temperature at which (self-accelerating) polymerization may occur with a substance in the packaging, IBC or portable tank as offered for transport.[9] The SAPT must be determined in accordance with the test procedures established for the self-accelerating decomposition temperature for self-reactive substances in accordance with Part II, Section 28 of the Manual of Tests and Criteria.

Testing for SAPT is used to determine whether a substance that polymerizes but has not been previously classified under Classes 1-8 meets the standard for classification as a Class 4.1 self-polymerization substance (UN3531, 3532, 3533, 3534). Styrene monomer is specifically listed by name in the IMDG DG as a Class 3 Flammable Liquid and already has transport stowage and handling provisions assigned to it in that it must be stored on deck and kept away from sources of heat. Therefore, as per interpretation of SPA members, it is not necessary to specify an exact SAPT for styrene.

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[6] IMDG Code (imo.org)

[7] https://unece.org/transportdangerous-goods/adr-2021-files)

[8] Manual of Tests and Criteria- seventh edition

[9] Microsoft Word - 00ERev17_Intro_Volume1.doc (unece.org)

For styrene monomer, even slow polymerization below 45°C (if not intervened with measures such as chemical stabilization, short stops or temperature control), has the potential to accelerate into a runaway reaction.

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.[10]

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 until 2018. The European Chemicals Agency (ECHA) manages the technical aspects of REACH.

Styrene was registered in 2010, in a joint registration for tonnages above 1,000 tpa. A public version of the dossier is viewable on the ECHA website.[11]

In June of 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 was still some 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 Styrene.[12] The document confirmed the contents of the 2002 environmental risk assessment and the 2008 human health risk assessments.

Consumer concerns were addressed in 2015 by removing the identified consumer uses from the Styrene registration. Thus, in effect, consumer uses of styrene are no longer supported under the REACH Joint Registration.

Concerns over professional uses focused on the possibility of increased cancer risk among professional workers in the Danish Fibre Reinforced Plastics industry, and chiefly because this was identified as the worker population with the highest potential exposures to styrene. An epidemiological study of over 75,000 Danish workers in the FRP industry found no increased cancer risk associated with styrene exposure.[13]

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).

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[10] https://echa.europa.eu/documents/10162/a05e9fc2-eaf7-448e-b9b2-d224d28173c0

[11] https://echa.europa.eu/registration-dossier/-/registered-dossier/15565

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

[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

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 must 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 is currently classified for flammability, skin / eye irritation, acute toxicity, hearing damage and is suspected of reproductive toxicity.[14]

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 dossier adds precautionary statements for effects on aquatic organisms.

Hazard statements

H412: Harmful to aquatic life with long lasting effects.

H226: Flammable liquid and vapour.

H332: Harmful if inhaled.

H319: Causes serious eye irritation.

H335: May cause respiratory irritation.

H315: Causes skin irritation.

H361: Suspected of damaging fertility or the unborn child <state specific effect if known> <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>.
Suspected of damaging the unborn child.

H372: ses damage to organs <or state all organs affected, if known> through prolonged or repeated exposure <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>.

H304: May be fatal if swallowed and enters airways.

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[14] https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/25673

3. HEALTH ASPECTS

3.1 General Remarks

This section covers repeat the effects of exposure to styrene, i.e., acute toxicity, skin and eye irritation, sensitization 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, however, aspiration into the lungs may cause chemical pneumonitis. 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 are particularly sensitive to styrene in that deaths occurred following inhalation exposure at 500 ppm (6Hrs).

In humans, exposure to 300 ppm styrene elicited eye and nasal irritation, along with CNS depression. As the smell (odour threshold = 0.04 to 0.32 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 dermal irritation. Human experience indicates that dermal contact with styrene can cause dermatitis. Liquid styrene has been reported to cause dose-dependent increases in severity of eye irritation at high styrene vapour concentrations in animals. Human studies indicate that vapour exposures have produced slight eye irritation (100 ppm; 20minutes) with greater incidence of eye irritation at 400 ppm.

3.4 Sensitization

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

3.5 Ototoxicity

Animal and human studies suggest a risk for adverse effects on hearing, following styrene exposure, which are exaggerated by co-exposure to elevated sound (≥85 dB).

In 2019, the Styrene Research and Information Center (SIRC) completed and published an updated comprehensive human health risk assessment as a capstone to their 30-year research program and to update their 2002 Harvard risk assessment. The assessment concluded that hearing impairment is a concern for certain workplace exposures; moreover, simultaneous exposure to noise and styrene appears to increase potential adverse effects. Noise protection is important for workers exposed to styrene.

3.6 Carcinogenicity / Genetic Toxicity[15]

The **International Agency for Research on Cancer** in Lyon, France, reviewed styrene in 1987, 1994, 2002, and most recently in 2018. IARC classified styrene as Group 2A, “probably carcinogenic to humans.” A final **monograph** was published in September 2019.

Unmetabolized styrene is not genotoxic; however, its metabolite (styrene-7,8-oxide) has exhibited mutagenicity/clastogenicity in vitro. Studies evaluating the bio-kinetic behaviour in humans, rats and mice indicate that mice have the greatest capacity to metabolize styrene to styrene-7,8-oxide, while humans exhibited the lowest of the species tested. These findings potentially suggest reduced sensitivity in humans to genotoxic effects resulting from styrene exposure.

In the 2019 SIRC[16] human health risk assessment, it was concluded that there are no strong/consistent indications that styrene causes cancer in humans. Although some studies suggest styrene-exposed workers may be at increased cancer risk, the human evidence for styrene carcinogenicity is inconclusive.

3.7 Conclusion

Liquid styrene is an irritant to skin and eyes, while higher vapour concentrations may be irritating to the eye and respiratory tract.

Under certain conditions of co-exposure of styrene with high noise levels, there may be a risk of damage to hearing.

Based on existing studies, an association between styrene exposure and cancer development in humans is inconclusive.

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[15] Styrene and Human Health

[16] Styrene Risk Assessment

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 three 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 one 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 Koc = 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 Kow), 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 Kow 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.

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 has been determined at 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 Kow) of Styrene (2.96 @ 25 C) indicate that secondary poisoning is unlikely.

The Predicted No Effect Concentration (PNEC) for styrene in freshwater (PNECaqua), 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 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.[17]

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[17] 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 guidelines.[18]

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. If a coating is applied, it is important to ensure that adequate tank earthing is maintained.

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 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 Europe, tank trucks must be designed and constructed in accordance with the requirements of ADR 2023 (Chapters 6.8).[19]

5.3 Tank Containers / Portable tanks

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, which are to be utilised.

For tank containers/portable tanks, it is recommended to have full walkways on the top.

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[18] https://cefic.org/guidance/transport-and-logistics

[19] ADR2023_Vol2e.pdf (unece.org)

In Europe portable tanks must be designed and constructed in accordance with the requirements of ADR (Chapters 6.7) note 21 or the IMDG-code (Chapter 6.7)

Tank containers must be designed and constructed in accordance with the requirements of ADR (Chapters 6.8) note 21.

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.

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

This section describes the operation of transport, storage, and handling equipment. The general comments below apply to all forms of transport.

6.1 Training

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

6.2 Operating instructions and Regulations

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

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

6.3 Inspections of customers reception and storage facilities

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 recommendations of the scheme included in Appendix 7.

It is recommended for the owner of a styrene storage tank to do inspections according to Table 5, which includes auxiliaries such as vapour return lines and safety valves.

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.

It is recommended for the owner of rail and road transport equipment that is used for styrene to do inspections according to Table 6, which includes auxiliaries such as vapour return lines and safety valves.

Table 6: Road and Rail Inspection Points

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

Tanks or compartments should be in dedicated service for styrene monomer or adequately cleaned, along with a list of the last three cargoes prior to loading. Styrene monomer quality and reactivity can be adversely affected by low levels of any contaminant present.

As a general principle, a tank that carries Styrene Monomer should not have carried the following substances as any of the last two cargoes:

Table 7: Previous cargoes

Prior Cargo	Justification
Strong acids and bases	Reactivity
Strong oxidizing and reducing agents	Reactivity
Peroxides	Reactivity
Benzene and Benzene-containing products such as Pyrolysis gasoline	Product quality
Heavy Fuel oils	Product quality
Lube oils	Product quality
Dyed CPPs, due to azo compounds	Product quality

Exceptions to the above list are possible. Manufacturers may have approved science-based cleaning and testing methods to assure that Styrene monomer is allowed to be loaded following the list of cargoes mentioned above. Please contact your supplier for detailed information.

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 ensuring that the coating offered for the cargo is suitable and will not release any materials that could contaminate the cargo or contribute to depletion of TBC either by reaction or adsorption.

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.

6.8 Road Specific Operations

6.8.1 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 hailers.

6.8.2 Haulier's responsibility

The measures taken by the styrene supplier 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.

6.8.3 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.

6.8.4 Routing

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

6.8.5 Drivers working hours and speed limits

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

6.8.6 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.

6.8.7 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).

6.8.8 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.

6.8.9 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.

6.8.10 Instructions in writing

One of the specific requirements of ADR for the carrier is to provide single standard "Instructions in Writing" (IiW) "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 IiW in various languages are found on the UNECE website.[20]

6.9 Intermodal transport

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

6.10 Rail Specific Operations

6.10.1 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 (see Appendix 6).

6.10.2 Rail Operators

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

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[20] http://www.unece.org/trans/danger/publi/adr/adr_linguistic_e.html

6.10.3 Instructions in writing

One of the requirements of RID is for the carrier to provide single standard "Instructions in Writing according to RID" (IiW) "to the drivers. These instructions, for which the format and required content have been established, should enable the 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 and shall be readily available.

6.10.4 Stationary railcars

Apart from transportation times, it is not recommended to store styrene in railcars for an extended period. Railcars should be promptly offloaded upon arrival. If, for unforeseen reasons, railcars remain stationary for an extended duration, the schedule for styrene storage testing (section 2.4.1 - Table 3) is recommended as a guidance to monitor and maintain product integrity.

6.11 Barges and Ship Operations

This section provides guidelines for the safe carriage of styrene in marine bulk onboard ship and barges. If locally operated ship/barges are not governed by the SOLAS convention, equivalent arrangement should be in place.

6.11.1 Ship / barge assurance

It is recommended that the parties involved in the arrangement of transport of styrene undertake inspections of ship/barges or participate in a common inspection scheme to assess and assure themself that the ship/barges nominated have been positively vetted for safe operations.

6.11.2 Loading inhibited cargoes

Care shall be taken to ensure that Styrene is sufficiently protected with inhibitor to prevent an unwanted reaction. At no times during the voyage the inhibitor levels should drop below 10 ppm. The voyage in this case is defined as the period from the commencement of loading to the completion of unloading.

Ships carrying Styrene shall be provided with a Certificate of Protection meeting the requirement under IBC Code 15.13.3, from the manufacturer/supplier and be kept onboard during the voyage. An “Example of a Certificate of Protection for products requiring oxygen-dependent inhibitors” is set by IMO as Annex to IBC Code.

If onboard dosing with inhibitor, following should be considered but not limited to:

- should be a non-routine operation that involves dealing with numerous hazards. It should be carefully planned, and risk assessed in accordance with latest industry practices.
- should be an agreed dosing plan with ships responsible officer that include management of the identified hazards.
- should be carried out in closed condition, without any free fall of liquid in a non-inerted atmosphere.
- To achieve best possible mixing, dosing is preferable done with liquid inhibitor which is added in first foot early in loading. In addition, ship should circulate cargo to ensure adequate mixing upon completion.
- To avoid human error, there should be a validation that each tank has been dosed with inhibitor and to the intended level, either by sampling and testing or other means.

If styrene cargo samples are to be stored onboard:

- there should be a company procedure for monitoring, which includes maximum period for storage on-board and periodic inspection of the samples.
- Samples should be stored in a locker outside of accommodation which is designed to prevent sample bottles moving at sea and constructed with a styrene resistant material and has adequate ventilation arrangements.
- Incompatible samples should not be stowed close to each other.
- Company procedure should also include safe and regulatory compliant disposal of samples and recordkeeping.

6.11.3 Styrene temperature

Styrene cargo temperatures exceeding 30°C or ambient conditions without an external heating source, indicate unwanted elevated temperatures and should be avoided. Actions to identify cause and corrective actions should be considered, ref 6.11.14.

To minimise styrene exposure to excessive heat from the environment, the following should be considered:

- Styrene should not be carried in deck tanks (fixed installation of an independent tank on deck of a chemical tanker).
- Cargo deck lines should be drained empty after each cargo operation, including after re-circulation.

6.11.4 Adjacent spaces temperature

Styrene has an IBC Code 16.6.1 notation and should not be exposed to excessive heat. Styrene should be loaded and carried adequately segregated from adjacent spaces with temperatures exceeding 35°C. For this purpose, adjacent spaces include but not limited to, adjacent cargo tanks, void spaces, cofferdams, pumprooms, slop tanks and water tanks.

For corner-to-corner tanks, styrene stowage should be such that at no time its adjacent space temperature exceeds 35°C.

When cleaning of tanks adjacent to styrene, or styrene residues, tank cleaning methods involving elevated temperatures that could result in overheating of adjacent bulkheads should be avoided.

6.11.5 Separation from heated cargoes

Cargoes, or residues of cargoes carried in adjacent tanks to styrene should not be heated.

Stowing of heated cargoes on the same vessel can result in a dynamic situation in which degree of heat transfer may be complex and difficult to predict.

Owner's stowage should take into consideration that one tank separation to a heated cargo may not be sufficient; stowage should be such that at no time the adjacent space temperature exceeds 35°C.

6.11.6 Separation from cargoes which can cause a hazardous reaction or initiate self-polymerisation

Products which are known to either react in a hazardous manner or initiate a self-polymerisation of styrene monomer are mentioned in Table 7. When carrying such cargoes there should be an adequate separation from the containment system for styrene monomer with two or more barriers.

United States Coast Guard (USCG), Code of Federal Regulations 46, Part § 150.130 provides further clarification on two barriers.

6.11.7 Heating coils

Heating coils to tanks carrying styrene shall be blanked off.

6.11.8 Means for measuring cargo temperatures and alarms

Means should be provided to measure cargo temperatures with remote reading capability, with adequate number of sensors in each tank based on the depth of the tank.

Each tank carrying styrene should be fitted with an individual tank temperature monitoring and alarm system[21] with capability to always provide audible and visible warning during carriage. The alarm should be set to give adequate warning before reaching the critical temperatures as per this guide.

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[21] IBC Code 7.1.5.4

6.11.9 Pump rooms

Carrying Styrene in tanks serviced by cargo pumprooms comes with associated risks, including exposure to elevated temperatures

6.11.10 During voyage

During the voyage, the vessel shall record following data at least twice a day, at least 8 hours apart.

- Styrene tank(s) temperatures
- adjacent space (empty or full) temperature.
- air and sea water temperatures.
- oxygen content and pressure in vapour space of Styrene tanks

Placing additional TBC on board ships may be beneficial during long voyages but should be carefully evaluated, including export controls, local requirements, and availability of adequate hazardous waste disposal facilities, should it not be used.

Ship has normally no capability to test inhibitor levels onboard during voyage and should there be any concern on effective levels, the ship should, if necessary be diverted to a port with testing capabilities.

Inhibitor (TBC) tends to sink to the bottom over time, recirculation at least twice a week may be beneficial and would also minimise build-up of polymers in lines and localised heating.

6.11.11 Stationary barges

Apart from transportation times, it is not recommended to store styrene in barges for an extended period. Barges should be promptly offloaded upon arrival. If, for unforeseen reasons, barges remain stationary for an extended duration, the schedule for styrene storage testing (section 2.4.1 - Table 3) is recommended as a guidance to monitor and maintain product integrity.

6.11.12 Inerting

Styrene monomer inhibitor TBC is oxygen-dependent, therefore IBC Code 15.13.5, inerting requirement for cargoes protected by oxygen-dependent inhibitors must be complied with.

If inerting, while maintaining oxygen level between 3-8 vol%, only nitrogen should be used as inert gas for safety and product quality purposes.

6.11.13 Critical temperature and oxygen conditions

Below critical oxygen and temperatures conditions at which actions should be considered:

- 1 °C rise of cargo temperature per day, over 3 consecutive days.
- 2 °C rise of temperature within any 24 hours.
- Cargo temperature at any level raises above > 30°C Cargo temperature exceeding ambient conditions
- Adjacent spaces temperature >35°C
- Oxygen content in any tank vapour space <3%

6.11.14 Actions in the event styrene tanks falling outside of temperature and oxygen limits

A ship/barge technical operator should identify credible and specific actions if temperature and oxygen limits given in this guide are exceeded, or are close to, be exceeded. Following are some actions that should be considered.

- Issue instructions to crew when, how and who to notify if limits are exceeded, or are close, to be exceeded, both for Styrene tanks and/or adjacent spaces,

- Notify and consult charterer,
- Identify how qualified Styrene product expert advice are made available and are engaged as necessary,
- Increase frequency of monitoring temperatures of styrene and adjacent spaces.

If mitigations are necessary, following are some that should be considered:

- Identify source of heat and eliminate the same as far as reasonably practicable,
- Continuous cooling of deck with water spray, day and night,
- Cooling by filling ballast in adjacent tanks, if permitted,
- Recirculate cargo as inhibitor (TBC) tends to sink to the bottom over time. Recirculation also minimises build-up of polymers in lines and localised heating,
- Validate inhibitor (TBC) levels by sampling and testing. Diverting the ship to suitable location with testing capabilities if necessary and possible,
- If ship is at sea, consult with qualified Styrene product expert to identify if any test can be conducted with the available equipment onboard to identify polymer level,
- In agreement with charterer add more inhibitor (TBC), if available and applicable,
- Increase oxygen level in vapour space till 3 – 8 vol%, if the oxygen level in vapour space has fallen below the criteria in this guide,
- Consider aeration by recirculation or other methods as inhibitor is oxygen dependant and consumes dissolved oxygen in the process,
- If ship is fitted with a cargo cooling system, use it to cool styrene and/or adjacent cargoes,
- Transfer of styrene from the affected tank(s) into several tanks where possible. This to increase exposed area for cooling from ballast tanks, move styrene away from any sources of heat and would facilitate cooling by dilution if necessary.

If all mitigation measures above are ineffective reaching a point where safety of the crew and ship becomes at risk, it may become necessary to consider:

- Cooling styrene by dilution, by adding a large enough volume of seawater or other cold inert material as specified in this guide, if sufficient space in tanks available,
- Add a free radical scavenger (Short Stop) as specified in this guide, if polymerisation has started and the temperature in the tank is rising significantly,
- Jettisoning of cargo, as a final resort.

6.12 Transportation in portable/transport tanks

This section applies to transport in tanks, such as ISO tank containers, and other types of portable and transport tanks.

6.12.1 Tank construction

Tanks should be insulated with a white outer jacket and fitted with external temperature reading to measure the temperature of Styrene inside the tank.

When practicable, tanks should be fitted with remote temperature solutions that are able to monitor real-time temperature developments of Styrene.

The tank construction, provisions and labelling must also comply with the regulations for the intended mode of transport.

6.12.2 Tank inspection

An inspection of tanks should be carried out by the loading terminal staff before, during and after loading. Inspection checkpoints detailed in Appendix 5 (2) are recommended at a minimum.

6.12.3 Shipper’s Responsibility

Styrene monomer is chemical stabilized controlled by using an inhibitor. Shipper should ensure that Styrene is sufficiently protected with inhibitor to prevent an unwanted reaction. At no times during transportation should the inhibitor levels drop below 10 ppm. If this cannot be ensured, the transport of such products should not be conducted. Transportation in this case is defined as the period from initial loading until final unloading, regardless of mode.

In addition to the Certificate of Analysis, the inhibitor expected duration of effectiveness, and temperature limitations qualifying the inhibitors effective lifetime, should be provided to the carrier. This could be in form of a Certificate of inhibition or stabilisation.

Where Tanks are transported by road hauliers, Shippers should meet the applicable guidance in 6.8.1.

Where tanks are transported by maritime vessel, Shippers should use vessels that are certified by the Administration of the vessel flags state for carrying Styrene Monomer as dangerous goods.

6.12.4 Haulier’s responsibility in Road and Rail Transport

The measures taken by the styrene supplier 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 final delivery.

Road Hauliers transporting portable tanks should meet applicable guidance in 6.8.2 – 6.8.10.

Rail operators transporting portable tanks should meet applicable guidance in 6.10.

Verify inhibitor’s expected duration of effectiveness is valid for the anticipated duration of the transport, and conditions which must be maintained for inhibitor function.

6.12.5 Transportation by maritime vessel (Ship/barge)

The International Maritime Dangerous Goods (IMDG) Code applies for transportation onboard international trading vessels for Styrene Monomer Stabilized with UN 2055, including requirements such as to be stowed away from sources of heat and on deck only.

Prior to shipment Shipper should conduct a risk assessment including factors such as, but not limited to:

- duration of voyage, and likelihood for delays extending duration beyond the inhibitor expected duration of effectiveness. Transporting Styrene on long voyages are discouraged,
- expected ambient temperatures conditions typically encountered on the voyage, considering also the season of the year,
- tank insulation capacity,
- styrene monomer loading temperature,
- expected temperature of styrene monomer not exceeding 30°C,
- the effective inhibitor levels needed for the voyage duration and expected temperatures. If effective inhibitor levels cannot be ensured throughout the intended voyage, the transport of such products is prohibited under IMDG Code.
- oxygen levels in vapour space being effective for inhibitor for the duration of the voyage,
- specific instructions to Carrier for stowage onboard for accessible temperature readings,
- specific instructions to Carrier for temperature monitoring, twice day minimum 8 hrs apart,
- instruction to Carrier of actions to take, should the length of voyage exceed the inhibitor duration of effectiveness or if Styrene temperature limits in this guide are exceeded, or close to be exceeded.

6.12.6 Actions in the event of Portable Tanks falling outside of temperature limits

A Carrier should identify actions if temperature limits given in this guide are exceeded or are close to be exceeded. The following are actions that should be considered:

- issue instructions to crew when, how and who to notify if limits are exceeded, or are close, to be exceeded,
- notify and consult shipper / charterer,
- identify how qualified Styrene product expert advice are made available and are engaged as necessary,
- increase frequency of monitoring temperatures of styrene,
- identify, and if possible, eliminated any sources of heat,
- consider options to test for inhibitor and polymer levels.

If mitigations are necessary, following are some that could be considered:

- continuous cooling of Tank(s) with water spray, day and night
- in agreement with shipper/charterer, add more inhibitor (TBC), if available and possible,
- Inhibitor is oxygen dependant, consider action to verify oxygen level and aeriation if necessary, and can be conducted safely,
- if it is suspected polymerisation has started and the temperature in the tank is rising, consider adding Short Stop scavenger as per guidance in section 2.4.4,
- if the temperature increase cannot not be stopped, there is a risk of runaway polymerisation with accelerated temperatures, volumetric expansion, boiling liquid, rupture of tank, fire and explosion. In such scenario
  - if possible, facilitate cooling by dilution of styrene with any cold inert material,
  - consider options to remove styrene from tank, including jettisoning of cargo overboard, or
  - if possible, open tank hatch to avoid tank overpressure and explosion, protect people by evacuation to safe distances, and prepare firefighting capabilities.

6.13 Tank Storage Operations

6.13.1 Certification

All bulk storage and handling operations must meet the requirements of the relevant national regulations. There are industry schemes such as CDI Terminal (CDI-T) to inspect terminals to give an assessment of the terminal at the time of inspection, with the assessment of the report resting with each chemical company.

6.13.2 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.

Without recirculation, polymerization inhibitor (TBC) added tends to sink to the bottom. A recirculation pump is not essential but highly recommended. Recirculation helps to minimize build-up of polymer in lines. Localized heating is minimized. Recirculation decreases the effect of temperature cycling, so reduces styrene vaporization and condensation and subsequent build-up of polymer in the head space.

6.13.3 Loading / unloading lines

The use of dedicated loading and unloading lines is recommended

6.14 Collection – Road transport

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 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 considered,
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 consider 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.

Preplan 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. The vapour can travel long distances (see Appendix 9 – LG Polymers incident)

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 vapor, 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 possible.

Since flammability is the main hazard is, it is important to eliminate all sources of ignition in the area of the spill. Styrene vapour is invisible, heavier than air and spreads along the ground. 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 addition of fire 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 release of styrene, all non-essential personnel should be evacuated, and all sources of ignition extinguished immediately. After the appropriate personal protective equipment has been issued, the spill can be covered with fire-fighting foam as quickly as possible to minimise emissions and the potential of fire hazards. The released liquid must then be recovered and transferred to sealable tanks or drums. Any remaining quantities of styrene should be absorbed into suitable materials such as sand and transported in closed drums to a suitable processing installation. The recommended method of disposal is by incineration.

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

7.2.5 Drums leaks

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

7.3 Fire Fighting

7.3.1 Exothermic reaction

If styrene vapour ignites and the temperature of the liquid reaches 52°C, the stabilising effect of the inhibitor 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 these may simply spread the fire, styrene being both immiscible with water and lighter than water. Burning styrene may produce carbon, carbon monoxide, carbon dioxide and large quantities of thick black smoke. Fire fighters should wear breathing apparatus.

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; 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 sheet (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. ECHA and its Committee for Risk Assessment (RAC) have been supporting the European Commission's Directorate-General for Employment, Social Affairs, and Inclusion (DG EMPL) by providing scientific opinions on OELs since 2019. This work was previously carried out by DG EMPL's Scientific Committee on Occupational Exposure Limits (SCOEL).

The different OELs for styrene can be found on the suppliers SDS

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 8-hour average concentrations, for example 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 the 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 Sign and symptoms of prolonged exposure to styrene

Headache, fatigue, drowsiness, insomnia, anorexia and weight loss, pain in limbs, nervousness, 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.

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MORE INFORMATION:

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

Responsible Care®
OUR COMMITMENT TO SUSTAINABILITY

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) in 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 that 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: https://www.ice-chem.org

MAR-ICE: https://www.ice-chem.org/_files/ugd/bb9d72_c00a3a28b0f34689bf10a83f75110861.pdf

Transport & Logistics - CEFIC Best Practice Guidelines:
https://cefic.org/guidance/transport-and-logistics

Spill Respose Guide - Cedre

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 an 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: https://sqas.org

SQAS Questionnaires and Accredited Assessors:
https://sqas.org/resources/

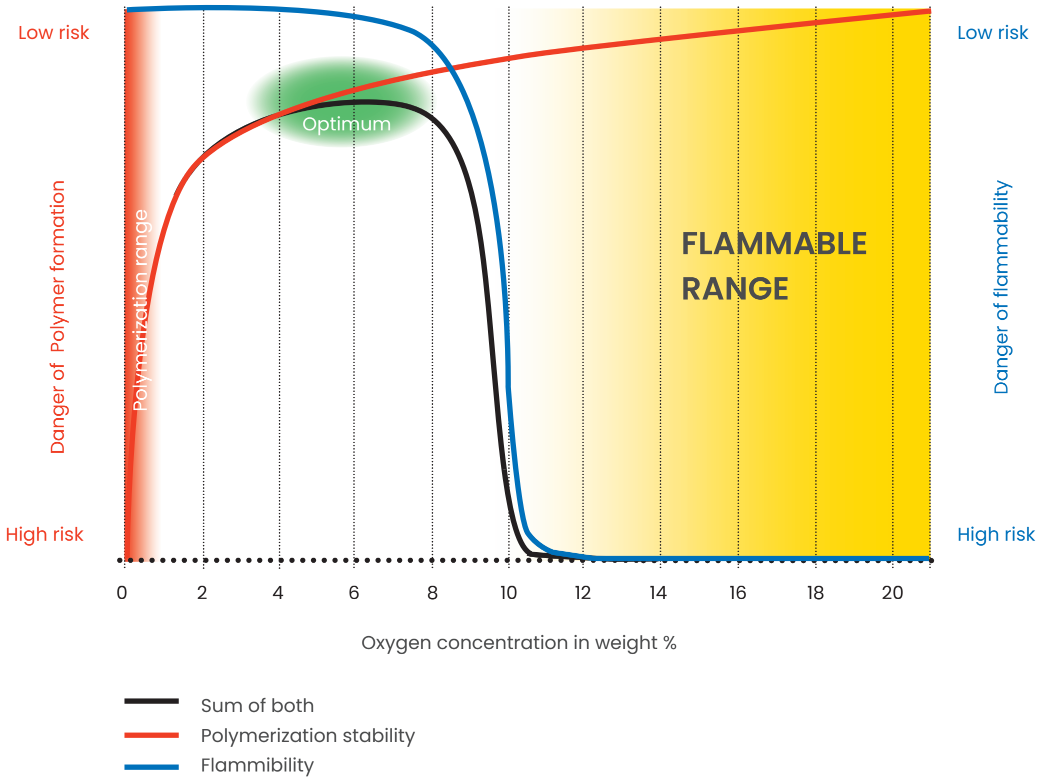
APPENDIX 2: STYRENE POLYMERISATION IN STORAGE

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).

Figure 7: Optimum oxygen concentration in vapour space of storage tank.



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.

Q3: If lean oxygen/Nitrogen mix is used as blanket, what actions should to taken to prevent oxygen content in vapor falling below the recommended minimum?

If an inert gas blanket such as nitrogen is used, provisions should be made to aerate the monomer once a week for approximately 30 minutes, or until the oxygen level again reaches saturation. An alternative is to recirculate product and inject air at a rate of approximately 0.06-0.12 m^3/hr/million kg of styrene monomer until the oxygen level in the liquid reaches saturation again.

Q4. Is it possible to estimate the inhibitor concentration based on the duration of the journey and anticipated cargo temperatures?

Yes, this is possible using inhibitor depletion models presented in Table 4.

NOTE:

- That cargo temperatures are influenced by sea-water temperatures and stowage plan.
- The accuracy of the results might be poor if extrapolated to temperatures not covered in the model and especially above 40°C.
- Oxygen content of the vapor space should be higher than 3 vol%

Approach #1: Percentage Based Contingency

$$\text{TBC} = \text{Min. Inhibitor Conc.} + \left(\left(\frac{\textit{Anticipated Voyage Duration (days)}}{\textit{Planning Temperature TBC Depletion rate (from Table 4)}}\right) * \textit{Contingency}\right)$$

“Minimum Inhibitor Concentration”:_The minimum recommended inhibitor level for styrene is 10 PPM.

“Planning Temperature”: This is the typical maximum temperature for a specific transport route. For most voyage plans, 30°C is recommended. In areas of higher ambient temperatures, a higher value may be required. Conversely, lower values may be used if transport is restricted to cooler routes / winter months. This value should be selected in consultation with the carrier / shipping company.

The temperature selected as the planning temperature must be communicated to the carrier / shipping company as a not to exceed value. Controls such as temperature alarms, routine inspection of cargo temperature or other administrative controls are necessary to identify any periods where storage during transport exceeds the planning temperature.

“Anticipated Voyage Duration”: This is the planned voyage duration in days. This should be selected in consultation with the carrier / shipping company.

“Contingency”: This is a factor which is intended to account for voyage plan variability. Some voyage durations may be extended due to schedule, inclement weather, or other circumstance. The appropriate factor (> 100%) should be discussed and selected in consultation with the carrier / shipping company and product quality considerations.[22]

Example #1	
Min. Inhibitor concentration	10 ppm
Anticipated voyage duration	30 days
Planning temperature	30 °C
Planning temp. TBC depletion rate	7 days/1ppm
Contingency	110%
TBC required	15.5 ppm

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[22] Too much TBC could be detrimental for some end-uses

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.

Q3: If lean oxygen/Nitrogen mix is used as blanket, what actions should to taken to prevent oxygen content in vapor falling below the recommended minimum?

If an inert gas blanket such as nitrogen is used, provisions should be made to aerate the monomer once a week for approximately 30 minutes, or until the oxygen level again reaches saturation. An alternative is to recirculate product and inject air at a rate of approximately 0.06-0.12 m^3/hr/million kg of styrene monomer until the oxygen level in the liquid reaches saturation again.

Q4. Is it possible to estimate the inhibitor concentration based on the duration of the journey and anticipated cargo temperatures?

Yes, this is possible using inhibitor depletion models presented in Table 4.

NOTE:

That cargo temperatures are influenced by sea-water temperatures and stowage plan.

- The accuracy of the results might be poor if extrapolated to temperatures not covered in the model and especially above 40°C.
- Oxygen content of the vapor space should be higher than 3 vol%

Approach #1: Percentage Based Contingency

$$\text{TBC} = \text{Min. Inhibitor Conc.} + \left(\left(\frac{\text{Anticipated Voyage Duration (days)}}{\text{Planning Temperature TBC Depletion rate (from Table 4)}}\right) * \text{Contingency}\right)$$

“Minimum Inhibitor Concentration”:_The minimum recommended inhibitor level for styrene is 10 PPM.

“Planning Temperature”: This is the typical maximum temperature for a specific transport route. For most voyage plans, 30°C is recommended. In areas of higher ambient temperatures, a higher value may be required. Conversely, lower values may be used if transport is restricted to cooler routes / winter months. This value should be selected in consultation with the carrier / shipping company.

The temperature selected as the planning temperature must be communicated to the carrier / shipping company as a not to exceed value. Controls such as temperature alarms, routine inspection of cargo temperature or other administrative controls are necessary to identify any periods where storage during transport exceeds the planning temperature.

“Anticipated Voyage Duration”: This is the planned voyage duration in days. This should be selected in consultation with the carrier / shipping company.

“Contingency”: This is a factor which is intended to account for voyage plan variability. Some voyage durations may be extended due to schedule, inclement weather, or other circumstance. The appropriate factor (> 100%) should be discussed and selected in consultation with the carrier / shipping company and product quality considerations.[22]

Example #1	
Min. Inhibitor concentration	10 ppm
Anticipated voyage duration	30 days
Planning temperature	30 °C
Planning temp. TBC depletion rate	7 days/1ppm
Contingency	110%
TBC required	15.5 ppm

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[22] Too much TBC could be detrimental for some end-uses

Q7: 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. Styrene mixing by external circulation through a refrigeration system is key factor when long storage time (several weeks or more) occurs. Also, return piping in the tank should force mixing of all liquid content, thus preventing stratification of liquid induced by natural convection.[23]
- 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 by e.g., over-pressuring the tank.

Q8: 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 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:
- Mixing of 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 (Ethyl benzene (EB), xylenes, toluene) to dilute and cool the styrene. The resulting product cannot be sold and needs to be re-worked or burned as fuel.

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

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

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[23] The High Power Commitee Report.pdf (indiaenvironmentportal.org.in)

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 at customers and refinishing or discarding is necessary.

Q9: 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).

Q10: 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 under uncommon, favourable conditions:

- Contaminants (e.g., insufficient/incorrect 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.
- Rust (particles) inside the tank can form fertile seeds to initiate polymerisation.
- At high temperature (e.g., exposure to heat from adjacent tank fire) the TBC depletion rate is quickly increasing and >52°C TBC is not an active inhibitor.
- 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.

Q11: 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 do only measure local temperatures and are misleading (they read correctly but at the wrong spot) when the content is not well mixed!

When stratification occurs the temperature in the top layer where polymerisation takes place will be rising while the lower content of the tank will remain at normal storage temperature. The rise in temperature can only be measured if a thermocouple is present at that height.

Q12: What polymer and temperature levels are indicative of a runaway reaction?

- Polymerization of styrene is exothermic. If the reaction heat generated cannot be dissipated by cooling, the liquid temperature will rise. When this reaction becomes self-propagating at a high rate it is called a runaway reaction.

- Temperature is a better indication of the onset of a runaway reaction than polymer levels. High polymer levels are not necessarily an indication for a runaway but must just as well be taken seriously.
- An even better indication would be the temperature increase. A 2-3°C/day temperature increase indicates the onset of runaway reaction requiring continuous monitoring of the temperature.
- Starting at 20°C, uninhibited styrene takes approximately 25 days to show a 10°C temperature rise.

It is imperative that the temperature reading(s) is (are) representative for the bulk temperature of the liquid in the tank. Polymerization can be ongoing unnoticed in zones that are not near the thermocouple if the tank contents are not well mixed (be aware of the stratification potential).

Presence of contaminants may contribute to further acceleration of the styrene polymerization reaction

A runaway reaction (uncontrolled polymerization) may lead to violent eruption of vapour from vents and if these are plugged sufficient pressure can be created to rupture the container/storage tank. Even slow polymerization has the potential to later accelerate into a runaway reaction.

Initiate emergency procedures if temperature increases 2-3°C/day and no source of external heat has been identified. As soon as a temperature of 65°C has been reached, the situation is critical (evacuate the area) and a runaway reaction will occur unless the temperature can be lowered by cooling and the heat generated by the polymerization reaction can be sufficiently removed to stop the reaction from self-propagating. For further information about styrene polymerization in storage please refer to Chapter 2.

Q13: 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.

Q14: Can high levels of TBC impart colour to the end product?

Yes, under certain circumstances, too much TBC can colour the end product. This should be discussed with the potential customer (some customers can accept up to 100 ppm of TBC). There are process means to reduce the impact of high TBC such as activated Alumina-bed.

Q15: 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 e.g., toluene, xylene or Ethyl benzene.

Q16: 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.

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 hot cargoes 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: 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. An inert gas blanket (nitrogen) will contribute to depletion of the oxygen dissolved in the SM liquid.

Q19: 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 effectively work 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 at all cases.

Q20: 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 methaemoglobin) have been observed. Due to its close to corrosive effects TBC might have negative effects on aquatic organisms.

Q21: 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 m^3 of styrene. TBC flakes or bars are also convenient and come pre-packaged for easy addition to a cargo.

When using TBC and water solution in colder climate the melting point of the solution should be taken into account, typically + 4 °C to + 10 °C. Crystallisation can start at higher temperatures, typically between 12 – 15 °C.

Q22: Are there any standard processes/procedures for dosing TBC?

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 SDS should be available to understand the risks.

Q23: Can a ship's cargo of off-spec/high polymer SM be overdosed with TBC such that, due to the depletion rate of TBC, the product will arrive within the TBC spec?

Practically not, but it depends on the destination of the product. , 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. The product, although off-spec, can still be used as feedstock for other products

Q24: Can a ship's cargo of off-spec/high polymer SM be overdosed with TBC such that, due to the depletion rate of TBC, the product will arrive within the polymer spec?

No, TBC will prevent the formation of new polymer molecules, but it will not reduce the amount of the already formed polymer.

Q25: What are alternative outlets for 1) off spec 2) high polymer material? (Linked to this: Establish disposal options at danger levels. Guidelines for disposal)

1. 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.
2. 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.

Q26: 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.

Q27: 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.

Q28: 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.

Q29: 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.

Q30: 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 SHIPS AND BARGES

1. Introduction

As there is a considerable variety in the existing design of ships and barges for styrene movements, prior to contracting it should be ensured the required specific design requirements are met.

2. General Recommendations

In addition to the relevant IMO and ADN requirements ships and barges carrying Styrene should have:

- Vapor return facilities
- A closed ullage system, including an independent visual and audible high-level alarm
- Stainless Steel preferred, otherwise Carrier to verify suitability of coating. Coated tanks to be in very good condition with minimal blistering or breakdown. After application coatings may contaminate cargo in its early lifetime and applicable precautions should be taken. Mild steel, uncoated, is not recommended
- Pumps, lines, and fittings to be of stainless steel
- Remote cargo temperature reading capability should be provided, with adequate number of sensors in each tank based on the depth of the tank.
- An individual cargo tank temperature monitoring and alarm system which monitors the temperature with capability to always provide audible and visible warning during carriage.
- Due to risk of polymer build up, vent lines should be fitted with remote pressure monitoring system for each cargo tank vapour space, providing audible and visible alarm in the event of over/under pressurisation

APPENDIX 4: DESIGN AND CONSTRUCTION OF TANKS

1. 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. 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 twice 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 change (day – night cycle) 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 always remain below 8% 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 Coating

Tank coatings can help control or reduce polymer and stalactite formation, in particular in hot climates. A non-porous, non-wettable, and smooth tank coating 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 coatings can be used for storage tank surfaces as well as internal necks for safety features. If a tank coating is applied, it is important to ensure satisfactory tank earthing is provided. 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.

The thickness of non-conductive coating may be increased to less than 2 mm if there is a contact point to earth for the liquid at the bottom of the container.

In all other cases the following additional precautions should be taken:

a) the coating should be in good contact with the wall (i.e., no separation or delamination);

b) there should be a conductive path between the liquid and earth. This may be an earthed conductive dip tube projecting to the lowest point of the tank, a foot valve or a conductive plate at the base of the tank;

c) if the tank can be entered by a person (e.g., for cleaning) precautions should be taken to prevent persons and hand tools from being charged. This can be achieved by ensuring the person is earthed by wearing dissipative shoes and providing an earthed conductive or dissipative walkway at the tank bottom (e.g., by providing dissipative coatings in the area where people may walk), or by other means.

4.5 Uniform temperature control

Efficient mixing is important to achieve a uniform temperature. Inlet, outlet, and re-circulation connections are usually located near the bottom of the tank and often on the same side of the tank. This will not support mixing. Mixing the whole content is critical and needs to be taken care of in order to avoid stratification.

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 because of leak potential,
3. Lines should not be buried because of the difficulty of checking for leakage,
4. All lines should be sloped so they can be completely drained for maintenance,
5. Newly installed lines should be pressure tested by an approved method before insulation.

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

A dip pipe should extend to the bottom of the tank and be provided with a pinch hole (siphon break). The electrical continuity across connections should be checked to ensure grounding. Lines constructed of carbon steel are acceptable, but copper, bronze, or plastic should not be used. Large lines are usually joined by welded flanges, for smaller lines threaded joints are satisfactory, but their usage should be minimized in favour of welded lines.

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

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. A fusible airline or equally effective safety shutoff valve should be installed to close off lines in case of excessive external heat.

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 valves can trap styrene that may polymerise, seize the valve, and render it inoperative. Thus, all valves should be regularly inspected according to the recommendation in Table 3. Gate valves may be considered for applications with infrequent use. The piping system should use plug valves rather than ball valves for all manually and infrequently operated valves. Ball valves may trap product that may polymerise, seize the ball and thus make it inoperative. To limit emissions from packed glands, bellow valves may be considered. Drain line valves should be provided with a cap or end-flange. Valves must be protected against freezing, heat shock, or mechanical stress.

4.7 Pumps

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

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

4.8 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. ISO tank inspection

In addition to any required vehicle inspections an ISO Tank may be connected to, prior to loading, an external visual inspection must be performed of:

- Tank inspection dates are compliant.
- Tank specification to ensure it meets requirements.
- The shell, piping, valves and other equipment for corroded areas, dents, defects in welds and other defects such as missing, damaged, or leaking gaskets.
- All flanged connections or blank flanges for missing or loose nuts and bolts.
- Data plate to ensure it is present and legible.
- Tank frame to ensure it is free of impacts, cracks or structural damage.
- Tank thermometer ensuring it is installed and functional.
- All emergency devices for corrosion, distortion, or any damage or defect that could prevent their normal operation.
- All Valves and openings to ensure they are closed and sealed.

3. Routine inspection of returning rail tank cars

Returning rail cars should be inspected for content upon arrival. If a heel is detected the railcar should be sampled and weight before deciding on the path forward. Guidelines in the form of checklist issued by the CEFIC is available from the following link:

CEFIC Checklist - Filling and discharging of rail tank-wagons

Identification requirements exist for all modes 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. In particular RTCs should be inspected before departure to rule out the risk of polymerization caused by non-empty return.

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 always stay with his vehicle. 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. Among others, such checklist should include controls to identify "non-empty" tank cars that are shipped as empty on paperwork.

APPENDIX 7: RECEPTION AND STORAGE

1. Purpose

The checklist should be used for a self-audit by the customer. It can as well be used as a guideline for the safety service of the supplying company. See Section 6.

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 checklist 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 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
6. 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°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. The 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.

CAS Chemical Abstract System

CEFIC European Chemical Industry Council

CDI Chemical Distribution Institute

CLP Classification, Labelling and Packaging

DIN German Industry Standard (Deutsche Industrie Norm)

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 Organisation

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

APPENDIX 9: MAJOR INDUSTRY INCIDENTS

This appendix is meant to recapitulate some of the major industry accidents with styrene monomer which occurred during last couple of years and for which a comprehensive report is publicly available.

Case studies - Industry Incidents

On 28 September 2019, a cargo tank containing styrene monomer on board the Cayman Islands registered chemical tanker Stolt Groenland ruptured causing an explosion and fire. The tanker was moored alongside a general cargo berth in Ulsan, Republic of Korea and the Singapore registered chemical tanker Bow Dalian was moored outboard. The ignition of the styrene monomer vapour resulted in a fireball, which reached the road bridge above. Both vessels were damaged, and two crew suffered minor injuries. Fifteen emergency responders were injured during the firefighting, which lasted for over 6 hours. Report

In May 2020, LG Polymers India Pvt. Ltd. (LG Polymers) located in Visakhapatnam, Andhra Pradesh, India, had an uncontrolled release of styrene vapor from one of their styrene feedstock storage tanks. The styrene vapors spread beyond the site, affecting the neighboring villages. There were a total of 12 fatalities, 585 hospitalizations, and significant environmental damage. Summary, Report

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