



**Safe Handling and Storage of  
Styrene Monomer**



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August 20, 2009

## ***Operational Excellence Policy***

We will strive each day to conduct our business in a safe, secure, injury-free, and environmentally responsible manner. We are committed to comply with all laws and regulations applicable to our facilities and business activities and to comply with all voluntary programs to which we elect to subscribe. We will strive to make optimal use of the resources we consume and minimize emissions and waste. We will strive to limit the risks of our products throughout their lifecycle. We are committed to reducing risks in our operations to safeguard our employees, contractors, and the communities where we operate and engage in business activities. We will openly communicate our results and welcome the input of our employees and contractors, regulatory agencies, our communities, our customers, and other interested stakeholders.

We will accomplish this by integrating safety, security, health, environmental, reliability, and quality into our management processes using our Operational Excellence System (OE). OE will be used worldwide to: set goals for improvement; provide alignment of activities and resources; assess and manage risks; gain stakeholder input; and, rigorously audit our performance against operational objectives and compliance requirements.



G. C. Garland

President & CEO

Chevron Phillips Chemical Company LLC

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## **PRODUCT STEWARDSHIP**

Chevron Phillips Chemical Company LP ("Chevron Phillips Chemical Company") is committed to being a good Product Steward of the products we produce. We want anyone who comes in contact with one of our products to have access to information that will help them to understand its potential risk and how to use it safely. The thrust of our Product Stewardship program is the implementation of an Operation Excellence Management System (OEMS) initiative, which makes health, safety and environmental protection an integral part of our products. Successful implementation of this system must include a shared responsibility of all those who come in contact with a product throughout its life cycle. Chevron Phillips Chemical Company will continue to work with customers and others to help ensure that all who use and handle our products follow safe and environmentally sound practices.

**The information contained in this technical bulletin is not intended to, nor does it, amend or replace the Material Safety Data Sheet for Styrene (MSDS No. 10000068536). The most current Material Safety Data Sheet can be obtained from Chevron Phillips Chemical Company by calling (800) 231-1212 and should be carefully examined prior to working with this product.**

## INTRODUCTION

Chevron Phillips Chemical Company LP markets styrene monomer at its joint venture plant in Jubail, Saudi Arabia. Styrene is one of the most important monomers produced by the chemical industry today. Styrene monomer is a basic building block of the plastics industry. The conventional method of producing styrene involves the alkylation of benzene with ethylene to produce ethylbenzene, followed by dehydrogenation of ethylbenzene to styrene.

Styrene undergoes polymerization by all the common methods used in plastics technology to produce a wide variety of polymers and copolymers. Styrene is readily polymerized and copolymerized by both batch and continuous mass polymerization, emulsion, suspension, and solution processes. The most important products are polystyrene (PS), rubber-modified high impact polystyrene (HIPS), styrene butadiene latex (SBL), styrene-acrylonitrile copolymer (SAN), acrylonitrile-butadiene-styrene/terpolymer (ABS), and styrene-butadiene copolymer (SBR, synthetic rubber). An approximate breakdown of styrene's markets are polystyrene 54%, expandable polystyrene 12%, ABS 10%, SBR 7%, SBL 6%, and other 11%. Other important uses of styrene are in styrene-polyester resins, latexes, and styrenated oils and alkyls.

Polystyrene is primarily used in packaging, disposables, and low cost consumer products. Expandable polystyrene beads (EPS) are primarily used in food and beverage packaging, insulation and cushion packaging. Improved grades of resins are used in higher performance applications, such as home electronics and appliances. ABS and SAN have many uses in the consumer durables market. Styrene-based polyesters have lifetimes of over thirty years in both indoor and outdoor applications, e.g., polyester boats typically last longer than boats made from conventional materials. Thermoplastic elastomers are directly replacing natural and traditional synthetic rubbers in many established applications and entering new markets. Other applications include carpet backing (SB Latex), production of tires (SB Rubber) and castings for textiles and paper.

This publication addresses the need for an easy to use source of information describing the physical properties, toxicity and first aid measures, safety, disposal, labeling and styrene storage information for this relatively safe but perishable chemical. Styrene's reactivity is such that it must be handled within a range of specially prescribed conditions. This is necessary not only to avoid certain safety hazards but also to prevent deterioration in the quality of the styrene. However, it has been well-demonstrated that styrene can be used, handled, and stored without difficulty when its physical and chemical properties are understood and the precautions associated with these properties are applied.

**NOTE:**

**THIS BROCHURE DOES NOT AMEND OR REPLACE OFFICIAL PUBLICATIONS, SAFETY REGULATIONS NOW IN USE, MATERIAL SAFETY DATA SHEETS OR COMMERCIAL TERMS OF SALE. CHEVRON PHILLIPS CHEMICAL COMPANY LP MAKES NO GUARANTEE OF THE ACCURACY OF THE CONTENTS OF THIS BROCHURE OR ANY WARRANTY OF ANY KIND, EITHER EXPRESSED OR IMPLIED, WITH RESPECT TO THE USE OF THIS INFORMATION OR ITS APPLICABILITY. THE USER ASSUMES ALL RISK AND LIABILITY ASSOCIATED WITH THE INFORMATION IN THIS BROCHURE.**

## PART 1

### PROPERTIES OF STYRENE MONOMER

#### PHYSICAL PROPERTIES OF STYRENE MONOMER

The data contained in this section have been obtained experimentally or derived from the chemical literature referenced at the end of the section.

Property	Value		
Autoignition temperature (in air) <sup>1</sup>	490°C (914°F)		
Boiling point: <sup>2,9</sup>	760 mm Hg	145.14°C (293.25°F)	
	100 mm Hg	82.4°C	
	30 mm Hg	54.7°C	
	10 mm Hg	33.6°C	
	1 mm Hg	-1.6°C	
Color	Colorless		
Corrosivity	Noncorrosive to metals except to copper and alloys of copper.		
Critical pressure ( $p_c$ ) <sup>3</sup>	39.5 atm. (580 psia)		
Critical temperature ( $t_c$ ) <sup>3</sup>	374.4°C (706°F)		
Critical volume ( $V_c$ ) <sup>3</sup>	0.369 L/mole		
Cubical coefficient of expansion (per deg. C) <sup>4</sup>	9.710 x 10 <sup>-4</sup> at 20°C		
	9.805 x 10 <sup>-4</sup> at 30°C		
	9.902 x 10 <sup>-4</sup> at 40°C		
Density, (in air)	<u>Temp. (°C)</u>	<u>g/cc</u>	<u>lb/US Gal.</u>
	0	0.9223	7.701
	10	0.9137	7.627
	20	0.9050	7.553
	30	0.8964	7.479
	40	0.8877	7.405
	50	0.8791	7.329
Dielectric constant of liquid <sup>5</sup>	<u>Temp. (°C)</u>	<u>ε</u>	
	20	2.4257	
	40	2.3884	
	60	2.3510	

Property	Value	
Entropy of gas at 25°C ( $S^\circ$ ) <sup>2</sup>	82.48 kcal/(gm-mole)-dy.	
Electrical Conductivity at 25°C	2.8 x 10 <sup>-14</sup> mhos/cm	
Evaporation Rate (Relative to Butyl Acetate)	1.92	
Flash point: <sup>6</sup> (Tag. closed cup)	31°C (88°F)	
(Tag. open cup)	37°C (98°F)	
Free energy of formation of gas at 25°C ( $\Delta G_f^\circ$ ) <sup>2</sup>	51.10 kcal/gm-mole	
Freezing point <sup>2</sup>	-30.628°C (-23.13°F)	
Heat of combustion gas at const. press., 25°C, to form gaseous products ( $\Delta H_o$ ) <sup>2</sup>	-1018.83 kcal/(gm-mole)	
Heat of formation: <sup>2</sup> gas at 25°C( $\Delta H_f^\circ$ )	35.22 kcal/(gm-mole)	
liquid at 25°C( $\Delta H_f^\circ$ )	24.83 kcal/(gm-mole)	
Heat of polymerization at 90°C ( $\Delta H$ ) <sup>7</sup>	-17.8 kcal/gm-mole	
Heat of vaporization at 145.1°C <sup>9</sup>	8.82 kcal/(gm-mole)	
Molecular weight	104.14 gms/(gm-mole)	
Odor	Characteristic, aromatic	
Physical state at room temperature	Liquid	
Refractive index: <sup>4</sup>	<u>Temp. (°C)</u>	<u>N<sub>D</sub></u>
	0	1.5579
	10	1.5523
	15	1.5495
	20	1.5467
	25	1.5439
	30	1.5410
	40	1.5354
	50	1.5298
60	1.5242	
Solubility of Oxygen (from air) in Styrene	<u>Temp. (°C)</u>	<u>PPM</u>
	15	53
	25	50
	35	45

Property	Value	
Solubility: Styrene in water <sup>8</sup>	<u>Temp. (°C)</u>	<u>(gms/100gmsH<sub>2</sub>O)</u>
	0	0.018
	20	0.029
	40	0.040
	60	0.051
	80	0.062
Solubility: Water in styrene <sup>8</sup>	<u>Temp. (°C)</u>	<u>(gms/100gms styrene)</u>
	0	0.020
	20	0.060
	40	0.100
	60	0.140
	80	0.180
Solubility in: <sup>9</sup>	Acetone	∞
	CCl <sub>4</sub>	∞
	Benzene	∞
	Ether	∞
	n-Heptane	∞
	Ethanol	∞
Relative Density/(Specific Gravity) <sup>2</sup>	<u>(°C)</u>	<u>gm/cc</u>
	0	0.9238
	10	0.9151
	20	0.9075
	30	0.9009
	40	0.8949
	50	0.8897
	60	0.8850
	70	0.8809
	80	0.8771
	90	0.8738
100	0.8707	
Specific Heat <sup>7</sup>	<u>(°C)</u>	<u>(cal/gm-°C)</u>
	0	0.4004
	20	0.4131
	40	0.4269
	60	0.4421
	80	0.4590
	100	0.4774
Specific Heat (vapor) <sup>2</sup>	<u>Temp. (°C)</u>	<u>C<sub>p</sub> (cal/gm-°C)</u>
	0	0.256
	25.0	0.280

Property	Value	
Surface Tension <sup>1</sup>	(°C)	<u>dynes/cm</u>
	0	34.5
	20	32.3
	40	30.0
	60	27.8
	80	25.6
	100	23.5
Viscosity <sup>4</sup>	Temp. (°C)	Viscosity (Centipoise)
	0	1.040
	20	0.763
	40	0.586
	60	0.470
	80	0.385
	100	0.326
Vapor Pressure <sup>2</sup>	Temp. (°C)	Vapor Pressure <u>mm/Hg</u>
	0	1.15
	10	2.34
	20	4.50
	30	8.21
	40	14.30
	50	23.87
	60	38.41
	70	59.78
	80	90.31
	90	132.82
	100	190.63
	110	267.62
	120	368.22
	130	497.39
	140	660.64
	150	864.00
160	1113.97	
Volumetric Shrinkage upon polymerization (typical)	17%	
Thermal Conductivity	Temp. °C(°F)	<u>BTU/(hr.ft<sup>2</sup>.°F)</u>
	0 (32)	0.080
	25 (77)	0.079
	50 (122)	0.076
	75 (167)	0.0735
	100 (212)	0.0708
	150 (302)	0.063
	200 (392)	0.0598

## REFERENCES

1. G. W. Jones, G. S. Scott, and W. E. Miller, Bureau of Mines Report of Investigations 3630.
2. American Petroleum Institute Research Project 44, "Selected Values of Properties of Hydrocarbons and Related Compounds."
3. "Physical Constants of Hydrocarbons C<sub>1</sub> to C<sub>10</sub>," ASTM Special Technical Publication No. 109A (1963).
4. "Kirk-Othmer Encyclopedia of Chemical Technology," (2nd Ed.), Vol. 19, Interscience, New York, 1968, p. 56-57.
5. J. Petro and C. P. Smyth, J. Amer. Chem. Soc., 80, 73 (1958).
6. Manufacturing Chemists Association Chemical Safety Data Sheet SD-37 (Rev. 1971), p. 5.
7. R. H. Boundy and R. F. Boyer (Eds.), "Styrene: Its Polymers, Copolymers, and Derivatives," Reinhold, New York, 1952, Ch. 3.
8. W. H. Lane, Ind. Eng. Chem. (Anal. Ed.), 18, 295, (1946).
9. R. R. Dreisbach, "Physical Properties of Chemical Compounds," Vol. 1, Am. Chem. Soc., 1955, p. 159.
10. Styrene Monomer: Environmental, Health, Safety, Transport and Storage Guidelines, Styrene Producers Association, CEFIC Sector Group, Brussels, Belgium, 3 March 2008

**TYPICAL ANALYSIS OF CHEVRON PHILLIPS CHEMICAL COMPANY LP STYRENE<sup>1</sup>**

<u>Component</u>		
Styrene.....	%	99.93
Benzene.....	ppm	<1
Toluene.....	ppm	<1
Ethylbenzene.....	ppm	50
α methylstyrene.....	ppm	175
m + p-xylene.....	ppm	120
o-Xylene.....	ppm	125
Cumene.....	ppm	100
n-Propylbenzene.....	ppm	60
m + p-Ethyltoluene.....	ppm	20
Vinyltoluene.....	ppm	10
Phenylacetylene.....	ppm	50
m + p-Divinylbenzene.....	ppm	<10
o-Divinylbenzene.....	ppm	<5
Polymer.....	ppm	1
TBC.....	ppm	12
Aldehydes as Benzaldehyde.....	ppm	15
Peroxides as Benzoylperoxides.....	ppm	5
Chlorides as Cl.....	ppm	<1
Sulfur as S.....	ppm	<1

<sup>1</sup>This typical analysis is for information only, and does not necessarily represent specification limits.

## **ANALYTICAL METHODS**

The following ASTM methods are recommended for the analysis of styrene monomer:

1. D1209 Color of Clear Liquids (Platinum-Cobalt Scale)
2. D2119 Aldehydes in Styrene Monomer
3. D2121 Polymer Content of Styrene Monomer
4. D2340 Peroxides in Styrene Monomer
5. D4045 Sulfur in Petroleum Products by Hydrogenolysis and Rateometric Colorimetry
6. D4052 Density and Relative Density of Liquids by Digital Density Meter
7. D4590 Inhibitor, Colorimetric Determination of p-tert-Butylcatechol in Styrene Monomer by Spectrophotometry
8. D5135 Analysis of Styrene by Capillary Gas Chromatography
9. D5386 Color of Liquids using Tristimulus Colorimetry
10. D5808 Determining Organic Chloride in Aromatic Hydrocarbons and Related Chemicals by Microcoulometry
11. D7375 Trace Quantities of Water in Aromatic Hydrocarbons and Their Mixtures by Coulometric Karl Fisher Titration

## **PART 2**

### **SAMPLING AND HANDLING**

#### **TRAINING**

In any workplace where styrene is handled, used, stored or transported, a training program must be implemented to ensure worker's awareness of styrene properties, toxicity, and safety procedures. The training program should include the following:

1. Properties and health hazards of styrene.
2. Styrene physical hazards including the potential for fire and explosion.
3. Styrene's primary routes for entry into body.
4. Safe work and good housekeeping practices.
5. The importance of protection from styrene contact; the proper clothing and cleaning requirements.
6. Signs and symptoms of styrene exposure and action to be taken and medical conditions aggravated by exposure to styrene.
7. The care that must be taken whenever and wherever styrene is used, handled, stored and transported.
8. Emergency procedures for leaks, spills, and fires, including protective clothing to be worn in such instances.
9. The availability of written styrene usage, health hazard and training program procedures.

It is recommended that this training program should be part of a worker's initial training and should be scheduled at least annually thereafter.

Additional accidental release, fire and health information is presented in a subsequent section of this brochure.

#### **RECOMMENDED PRACTICE FOR SAMPLING STYRENE**

This information is provided for use in establishing sampling and handling procedures. This information should only be utilized in conjunction with an existing health and safety program and cannot be used as a substitute for expert safety and medical advice.

Take extreme care to prevent spills. In case material is spilled, wash contaminated areas thoroughly with large quantities of water and collect the liquid in the plant chemical waste system.

#### **SAMPLING:**

Samples may be taken through the manway opening by means of a clean, dry 1-qt. (1-L) glass bottle held in a clean, dry sheath of nickel or stainless steel attached to a long rod or lightweight chain of the same material. Fit the bottle with a stopper to which is attached a light metal chain. Lower the bottle to near the bottom of the tank and pull out the stopper with a sharp jerk of the chain. Raise it at such a rate that it is about three fourths full when it emerges from the liquid. Stopper the bottle before attempting to rinse the material from the outside. Label the sample bottle according to OSHA Regulations. Note - Fresh air and other personal protective gear may be required depending on predetermined exposure limits.

Emphasis should be placed on cleanliness and dryness. Both the sample bottle and its holder must be CLEAN AND DRY. Transfer the sample to a dry, dark brown bottle for storage. A suitable bottle for storing the sample is known as a "Boston Round". The closure should be a screw cap with a Teflon®

or aluminum foil liner. If new bottles are used, first rinse them thoroughly with acetone or methanol and then dry in a hot-air oven. Hold in a desiccator while cooling to ambient temperature. Protect them from dirt or moisture by enclosure in a polyethylene bag. Rinse used bottles very thoroughly with water, detergents, and solvents and then treat as new bottles.

The sampling system should be bonded to the tank manway (e.g. by resting the chain on the lip of the manway) prior to sampling.

#### **REFERENCE DOCUMENTS:**

ASTM D3437: Practice for Sampling and Handling Cyclic Compounds

ASTM E300: Practice for Sampling Industrial Chemicals

ANSI Z 288.1: Flammable and Combustible Liquids Code

API RP 500A: Classification of Locations for Electrical Installations in Petroleum Refineries

OSHA Regulations, 29 CFR, Paragraphs 1910.1000 and 190.2000

U.S. DOT Regulations, 49 CFR, Transportation Subchapters B and C, Parts 171-179

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#### **SAMPLING DEVICES**

Quality control within the process industry is of prime importance. This demands stringent checks, not only of the finished product, but also throughout the various stages of production, distribution and use.

The need for representative samples plays a critical role in ensuring product quality. Yet sampling directly often includes the risks of exposure to the operator as well as contamination and pollution to the environment. Use of a system such as the DOPAK<sup>®</sup> sampling method for process samples and HERMetric<sup>®</sup> Sampler for tank samples significantly reduces such risks. Texas Sampling Inc. also markets closed loop sampling systems.

#### **STATIC ELECTRICITY AND GROUNDING**

Static electricity can cause difficulties such as fires and explosions unless certain precautions are observed. Styrene monomer, has a high volume resistivity, and can pick up and hold a static charge during transfer operations. Key operations which have the potential of generating a flammable atmosphere and/or static charge include tank and container filling, splash filling, tank cleaning, sampling, gauging, switch loading, filtering, mixing/agitation, and vacuum truck operations. To minimize the hazard of static electricity during these operations, bonding and grounding may be necessary but may not by themselves be sufficient. For more information, refer to OSHA Standard 29 CFR 1910.106, "Flammable and Combustible Liquids", National Fire Protection Association (NFPA) 77, "Recommended Practice on Static Electricity" and/or the American Petroleum Institute (API) Recommended Practice 2003, "Protection Against Ignitions Arising Out of Static, Lightning, and Stray Currents.

The use of insulating flanges or non-insulating hoses are recommended for marine vessel/shore connections.

Submerged filling is recommended for all flammable liquids. The inlet line should discharge at, or near, the bottom and make electrical contact with the tank to eliminate uncontrolled electrical discharge.

Operators wearing rubber-soled shoes, particularly on certain composition floors made of good insulating materials, may pick up considerable static electricity.

#### **PRODUCT LOADING/UNLOADING REQUIREMENTS**

When loading or unloading a vessel or barge:  
Refer to current ISGOTT and USCG rules.

When loading or unloading tank cars:

1. Use only clean, oil- and dirt-free, spark-resistant tools and implements.

2. Do not stand within the gauge of the track until the hand brake of the tank car is known to be secured and the brake shoes are tight against the treads of the wheels.
3. Carefully place wheel chocks tight against either side of the wheels and keep fingers away from pinch points.
4. Place blue caution sign with white lettering warning: "Stop: Crew at Work" or "Stop: Tank Car". Place on track or on tank car facing either end of entrance to track.
5. Make sure the tank car's internal pressure has been relieved before removing the manhole or outlet valve cap or plug..
6. Visually inspect hoses and fittings prior to use and replace worn, corroded, or damaged parts.
7. Ground the tank car before connecting any part of it to the unloading lines or equipment. Loading and unloading lines should be continuously bonded during loading/unloading.
8. Purging all lines with nitrogen prior to transfer of product reduces risk of flash fires.
9. Unload the car through the dome connection or through the bottom outlet. Check carefully for leaks. Never place face or torso over any opening in a tank, especially as you remove closure caps or plugs, gauge the tank car, or examine the safety relief valve or safety vent.. Before removing bottom outlet valve end cap, or plug, operate the valve several times to ensure that it is not stuck in the open position and that it can be closed quickly and effectively if necessary.
10. Use of air pressure to unload tank cars is not recommended. If pressure must be used, the operator should demonstrate caution.
11. Use an approved pump to unload the tank car. If the car does not have an eductor pipe, insert a pipe through the open dome and pump its contents out that way.
12. Carefully vent the car through a flame arrester during unloading.
13. If unloading is interrupted, disconnect all unloading connections, close all valves tightly and securely apply all other closures to a tool tight condition, except the thermometer well which should be applied hand tight.
14. The exteriors of tank cars should be cleaned of any spilled material before unloading them and before returning them to transportation. Before using any of the safety appliances inspect them to ensure that they are safe to use and not contaminated with spilled material. . Before offering the residue tank car back into transportation determine that applicable tank car openings are closed too tight. Inspect the stencils to determine that the tank and safety relief valve are within their proper re-test periods. The safety appliances such as ladders, manway operating platforms, safety railings, and walkways must not be severely corroded, bent, loose or broken. The placards and markings must be legible and the shipment is prepared in accordance with all applicable DOT regulations.

### **SAFETY REFERENCES**

The following publications are excellent references for styrene monomer handling information:

**Manual Sheet TC-4,**  
**Chemical Manufacturer's Association**  
Recommended Practice for Unloading  
Flammable Liquids from Tank Cars

**NFPA 30 -**  
Flammable and Combustible Liquids Code

**NFPA 70 -**  
National Electrical Code®

**NFPA 77 -**  
Recommended Practice on Static Electricity

**API RP 2003**  
Protection Against Ignitions Arising Out of  
Static, Lightning, and Stray Currents

## **PART 3**

### **STYRENE MONOMER STORAGE**

The prevention of polymer build-up is generally of greatest concern in the storage of styrene monomer. Prevention of color formation is also important, but this is normally caused by contamination such as rust. Low temperatures, maintaining proper inhibitor and dissolved oxygen levels, correct construction materials, and good housekeeping are factors important in maintaining a long shelf life.

#### **POLYMERIZATION IN STORAGE**

Styrene polymerizes slowly at normal ambient temperatures but very rapidly at elevated temperatures. Styrene polymerization is initiated by heat, lack of inhibitor and dissolved oxygen, and contact with peroxides and other free-radical initiators, ionic initiators, and redox initiators. Polymerization can take place in storage as well as under more controlled conditions. The polymerization process is exothermic, evolving 288 btu/lb (17.8 kcal/gm-mole). If this evolved heat cannot be dissipated rapidly enough, the temperature of the monomer will rise, increasing the rate of polymerization and, with it, the rate of evolution of heat. The temperature may rise to the point where the reaction becomes very rapid and self-sustaining (a runaway polymerization). Normally temperatures above 65°C (149°F) are needed to initiate runaway polymerizations.

During a runaway polymerization, the temperature will reach and exceed the boiling point of styrene. The vapor may erupt violently from the tank vents or, if the vents are plugged or too small, it can create enough pressure to rupture the tank. As the liquid polymerizes and becomes more viscous, vapor bubbles may become trapped, expanding the liquid and causing spills or rupture of the tank.

The important point is that polymerization may occur spontaneously in storage tanks.

Depending on the quantity of material being stored, serious consequences may result.

#### **PREVENTION OF POLYMERIZATION**

Polymerization during storage may be prevented by close attention to monomer temperature, inhibitor level, polymer content and oxygen content. Determinations of inhibitor content, oxygen level in the vapor space, polymer content, and monomer temperature should be made on a routine basis (details are provided in Part 4). Styrene-containing vessels should be protected from external sources of heat. Running pumps against closed valves (dead-heading) should be avoided. Care should be taken that vents, valves, pressure-relief devices, gauges, and controls do not become plugged with polymer. (Requirements for the preceding are discussed in detail in the Styrene Monomer Storage Section of this publication).

#### **HANDLING RUNAWAY POLYMERIZATIONS**

The action to take will depend on how far the runaway has proceeded. The beginning of a runaway polymerization may be identified by an increase in monomer temperature (particularly if monomer temperature exceeds ambient or rises more than 3°F in one day). The higher the temperature the further the runaway has progressed and the more difficult to stop. Decisions concerning what actions to take must be made on-site. The following suggestions are listed approximately in the order recommended for halting a runaway polymerization and dealing with an advanced runaway:

1. Add up to 0.5% TBC and aerate. Aeration can be accomplished by bubbling in air, or stirring the product while exposed to air. Facilities storing and handling styrene monomer should have TBC inhibitor on hand in case of emergency. Solutions of

TBC may be obtained by contacting your Chevron Phillips Chemical Company LP representative or through your purchasing agent.

2. Reduce temperature of tank with water spray. If the tank is insulated, the insulation should be removed as quickly as possible and prior to spraying with water. Use ice, if feasible, but not in the product directly, as it will tend to remove the TBC. If placed in the product, ice should be in a sealed metal container.
3. Keep vessel vented.
4. Dilute with ethylbenzene or toluene if tank is not venting and product temperature is below 231°F (110°C) to retard polymerization and reduce viscosity.
5. If possible remove product from tank before it solidifies, to save the tank. Use drums, diked area, or float on water.

## **INHIBITION**

TBC (4-tert-butylcatechol) is customarily added to styrene to prevent polymer formation and oxidative degradation during shipment and subsequent storage.

Inhibitors prevent polymerization in two ways. (1) They can react with and deactivate the free radical in a growing chain. (2) They can act as an antioxidant and prevent polymerization by reacting with oxidation products in the monomer. It should be noted that sufficient oxygen must be present for inhibition. In the absence of oxygen polymerization will proceed as if no inhibitor were present.

The TBC level should be checked at regular intervals. (See Table 2B of this section) Additional inhibitor should be added to maintain a safe level.

The time required for TBC concentrations to fall to a dangerously low level varies greatly because of different storage and handling conditions. The depletion rates in actual storage may be appreciably faster or slower depending on the set of environmental conditions. Factors which affect depletion of

TBC are heat, water and air, with heat being the most important.

If the inhibitor has been depleted and polymerization has begun, inhibitor should be added immediately. If unstable monomer is not treated promptly, it may become unsalvageable.

Additional inhibitor should be added when inhibitor levels drops below 10 ppm to maintain adequate inhibition. Normal levels are 10-15 ppm, but some customers require up to 60 ppm because of unique storage conditions or process requirements. After addition, the storage tank should be recirculated until inhibitor is uniformly mixed and testing shows that target levels have been achieved. The tank should also be aerated to provide the proper amount of dissolved oxygen. Refer to Table 3A or 3B to determine proper amount of inhibitor to add.

The relatively small quantities of TBC required to raise the inhibitor level in stored monomer can most easily be added by using an 85% TBC/15% Methanol blend or a concentrated stock solution in the monomer or other solvent. Concentrated stock solution has an indefinite storage life when stored in the dark at normal ambient temperatures.

A TBC concentrate for use in increasing the inhibitor level in styrene monomer can be prepared by dissolving 704 grams of pure TBC in 1 gal of styrene monomer (186 gram/liter). At this concentration, 1 cc of the concentrate will raise the level of inhibitor 1 ppm in a drum of styrene having a net weight of 410 pounds. Table 3A lists the amount of concentrate required to increase the inhibitor level of bulk quantities by 10 ppm.

Styrene vapors in storage tanks are not inhibited and can polymerize on roofs of storage tanks and around vents. Vapor space inhibitors are available but are not viewed as being adequately effective.

**SPECIAL NOTE - USE OF SOLID TBC**

TBC is also available in a solid or crystal form. When packaged in a polystyrene bag of various sizes, the TBC can be added to the styrene by simply adding the prescribed amount (see Table 3C) to the tank (trailer, tank container, rail car, or vessel). The styrene monomer will dissolve the polystyrene bag

containing the crystal. TBC Crystal will dissolve with mixing in 20 to 60 minutes.

**Caution:** Personal Protective Equipment is required for handling solid TBC. In Addition, solid TBC inventory must be monitored in storage. The recommended shelf life of a polystyrene bag containing TBC is no more than 12 months (365 days), at which time the solid TBC may be recycled and re-packaged.

**Table 1**

**Effect of Inhibitor and Oxygen on the Shelf Life of Styrene at Various Temperatures**

Temp.	12 ppm TBC		50 ppm TBC Saturated with Air
	Saturated with Air	Less than 3ppm O <sub>2</sub>	
15.6°C (60°F)	6 mo.	10 to 15 days	1 year
29.4°C (85°F)	3 mo.	4 to 5 days	6 months
43.3°C (110°F)	8 to 12 days	Less than 24 hours	Less than 30 days

**Table 2A**

**Suggested Monitoring Schedule for Styrene Bulk Storage**

Monomer Temperature	Daily
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**Table 2B**

**Suggested Testing Schedule for Styrene Bulk Storage**

Monomer Temperature	Frequency	Key Properties
26.7°C (80°F) or higher	Weekly	Polymer Inhibitor ASTM D2121 ASTM D4590
21.1 - 26.1°C (70 - 79°F)	Bi-weekly	Color Appearance ASTM D5386 or D1209 Visual
Below 21.1°C (70°F)	Monthly	Aldehydes Peroxides ASTM D2119 ASTM D2340

**Table 2C**

**Suggested Inspection Schedule for Styrene Bulk Storage**

Inspection	Frequency
Air Vents Vacuum pressure relief Flame arrester Foam reservoir should be inspected for polymer	Quarterly
Tank interior	Every 3 years, if coated Annually, if uncoated

**OXYGEN REQUIREMENTS**

The problem presented by air is complex. TBC is not an effective inhibitor for styrene monomer in the complete absence of dissolved oxygen. Excessive amounts of oxygen in the storage tank, on the other hand, may lead to other serious storage and handling problems.

Monomer vapors above the liquid level in the tank are uninhibited. These uninhibited vapors and condensed monomer droplets are readily oxidized on contact with air. These droplets containing oxidation products will polymerize quite rapidly and adhere to the rusted, porous surfaces of unlined steel tanks. They form stalactites on the roof and coat the sidewalls above the liquid level.

Complete elimination of oxygen from the vapor space will lead to depletion of dissolved oxygen from the liquid monomer. If this dissolved oxygen is greatly reduced, the TBC inhibitor becomes ineffective and rapid polymerization of the stored monomer will take place. 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 approximately 1-2 ft<sup>3</sup> /hr/million pounds of styrene monomer. (Orbisphere Laboratories Oxygen Analyzer is suitable for measuring dissolved oxygen content.)

**TABLE 3A**

**CC of Concentrate (TBC In Styrene) Required for 10 ppm TBC in Styrene\*  
(186 gm. TBC/liter styrene)**

<b>Gallons</b>	<b>→</b>	<b><u>100</u></b>	<b><u>200</u></b>	<b><u>300</u></b>	<b><u>400</u></b>	<b><u>500</u></b>	<b><u>600</u></b>	<b><u>700</u></b>	<b><u>800</u></b>	<b><u>900</u></b>
	<b>↓</b>	<b>18.2cc</b>	<b>36.8</b>	<b>55.2</b>	<b>73.6</b>	<b>92.0</b>	<b>110.4</b>	<b>128.8</b>	<b>147.2</b>	<b>165.6</b>
<b>1,000</b>	<b>184</b>	<b>202</b>	<b>221</b>	<b>239</b>	<b>258</b>	<b>276</b>	<b>294</b>	<b>313</b>	<b>331</b>	<b>350</b>
<b>2,000</b>	<b>368</b>	<b>386</b>	<b>405</b>	<b>423</b>	<b>442</b>	<b>460</b>	<b>478</b>	<b>497</b>	<b>515</b>	<b>534</b>
<b>3,000</b>	<b>552</b>	<b>570</b>	<b>589</b>	<b>607</b>	<b>626</b>	<b>644</b>	<b>662</b>	<b>681</b>	<b>699</b>	<b>718</b>
<b>4,000</b>	<b>736</b>	<b>754</b>	<b>773</b>	<b>791</b>	<b>810</b>	<b>828</b>	<b>846</b>	<b>865</b>	<b>883</b>	<b>902</b>
<b>5,000</b>	<b>920</b>	<b>938</b>	<b>957</b>	<b>975</b>	<b>994</b>	<b>1012</b>	<b>1030</b>	<b>1048</b>	<b>1067</b>	<b>1086</b>
<b>6,000</b>	<b>1104</b>	<b>1122</b>	<b>1141</b>	<b>1159</b>	<b>1178</b>	<b>1196</b>	<b>1214</b>	<b>1233</b>	<b>1251</b>	<b>1270</b>
<b>7,000</b>	<b>1288</b>	<b>1306</b>	<b>1325</b>	<b>1343</b>	<b>1362</b>	<b>1380</b>	<b>1398</b>	<b>1417</b>	<b>1435</b>	<b>1454</b>
<b>8,000</b>	<b>1472</b>	<b>1490</b>	<b>1509</b>	<b>1527</b>	<b>1546</b>	<b>1564</b>	<b>1582</b>	<b>1601</b>	<b>1619</b>	<b>1638</b>
<b>9,000</b>	<b>1656</b>	<b>1674</b>	<b>1693</b>	<b>1711</b>	<b>1730</b>	<b>1748</b>	<b>1766</b>	<b>1785</b>	<b>1803</b>	<b>1822</b>
<b>10,000</b>	<b>1840</b>	<b>1858</b>	<b>1877</b>	<b>1895</b>	<b>1914</b>	<b>1932</b>	<b>1950</b>	<b>1969</b>	<b>1987</b>	<b>2006</b>

\* Calculated using styrene density at 20°C

**TABLE 3B**

**- CC OF CONCENTRATE REQUIRED TO INCREASE TBC IN STYRENE BY 1 PPM  
(85% TBC and 15% METHANOL)**

Gallons Styrene	0	100	200	300	400	500	600	700	800	900
	CC of TBC Required									
0	---	0.39	0.78	1.17	1.56	1.96	2.35	2.74	3.13	3.52
1000	3.91	4.30	4.69	5.09	5.48	5.87	6.26	6.65	7.04	7.43
2000	7.82	8.22	8.61	9.00	9.39	9.78	10.17	10.56	10.95	11.34
3000	11.74	12.13	12.52	12.91	13.30	13.69	14.08	14.47	14.87	15.26
4000	15.65	16.04	16.43	16.82	17.21	17.60	18.00	18.39	18.78	19.17
5000	19.56	19.95	20.34	20.73	21.13	21.52	21.91	22.30	22.69	23.08
6000	23.47	23.86	24.25	24.65	25.04	25.43	25.82	26.21	26.60	26.99
7000	27.38	27.78	28.17	28.56	28.95	29.34	29.73	30.12	30.51	30.91
8000	31.30	31.69	32.08	32.47	32.86	33.25	33.64	34.03	34.43	34.82
9000	35.21	35.60	35.99	36.38	36.77	37.16	37.56	37.95	38.34	38.73
10000	39.12	39.51	39.90	40.29	40.69	41.08	41.47	41.86	42.25	42.64
11000	43.03	43.42	43.81	44.21	44.60	44.99	45.38	45.77	46.16	46.55
12000	46.94	47.34	47.73	48.21	48.51	48.90	49.29	49.68	50.07	50.47
13000	50.86	51.25	51.64	52.03	52.42	52.81	53.20	53.60	53.99	54.38
14000	54.77	55.16	55.55	55.94	56.33	56.72	57.12	57.51	57.90	58.29
15000	58.68	59.07	59.46	59.85	60.25	60.64	61.03	61.42	61.81	62.20
16000	62.59	62.98	63.38	63.77	64.16	64.55	64.94	65.33	65.72	66.11
17000	66.50	66.90	67.29	67.68	68.07	68.46	68.85	69.24	69.63	70.03
18000	70.42	70.81	71.20	71.59	71.98	72.37	72.76	73.16	73.55	73.94
19000	74.33	74.72	75.11	75.50	75.89	76.28	76.68	77.07	77.46	77.85
20000	78.24	78.63	79.02	79.41	79.81	80.20	80.59	80.98	81.37	81.76
21000	82.15	82.54	82.94	83.33	83.72	84.11	84.50	84.89	85.28	85.67
22000	86.07	86.46	86.85	87.24	87.63	88.02	88.41	88.80	89.19	89.59
23000	89.98	90.37	90.76	91.15	91.54	91.93	92.32	92.72	93.11	93.50
24000	93.89	94.28	94.67	95.06	95.45	95.85	96.24	96.63	97.02	97.41
25000	97.80	98.19	98.58	98.97	99.37	99.76	100.15	100.54	100.93	101.32

Example: Current TBC level = 8 ppm; desired TBC level = 15; Difference = 7 ppm; Volume = 5,900 gallons of styrene

23.08 (from table) X, 7 = 162 cc of TBC required

**TABLE 3B**

**SOLID TBC ADDITION CALCULATION TABLE**

Truck											
Volume											
184,000	lbs	Amount of Solid TBC to be added, in Ounces									
<b>Initial</b>		<b>Target TBC Level in truck or vessel</b>									
<b>TBC level</b>		<b>15</b>	<b>20</b>	<b>25</b>	<b>30</b>	<b>35</b>	<b>40</b>	<b>45</b>	<b>50</b>	<b>55</b>	<b>60</b>
<b>10.0</b>		14	30	44	58	74	88	104	118	132	148
<b>10.5</b>		14	28	42	58	72	86	102	116	132	146
<b>11.0</b>		12	26	42	56	70	86	100	114	130	144
<b>11.5</b>		10	26	40	54	70	84	98	114	128	142
<b>12.0</b>		8	24	38	52	68	82	98	112	126	142
<b>12.5</b>		8	22	36	52	66	80	96	110	126	140
<b>13.0</b>		6	20	36	50	64	80	94	108	124	138
<b>13.5</b>		4	20	34	48	64	78	92	108	122	136
<b>14.0</b>		2	18	32	48	62	76	92	106	120	136
<b>14.5</b>		2	16	30	46	60	76	90	104	120	134
<b>15.0</b>		0	14	30	44	58	74	88	104	118	132
<b>Initial</b>		<b>Target TBC Level in truck or vessel</b>									
<b>TBC level</b>		<b>15</b>	<b>20</b>	<b>25</b>	<b>30</b>	<b>35</b>	<b>40</b>	<b>45</b>	<b>50</b>	<b>55</b>	<b>60</b>
<b>10.0</b>		15	20	25	30	35	40	45	50	55	60
<b>10.5</b>		15	20	25	30	35	40	45	50	55	60
<b>11.0</b>		15	20	25	30	35	40	45	50	55	60
<b>11.5</b>		15	20	25	30	35	40	45	50	55	60
<b>12.0</b>		15	20	25	30	35	40	45	50	55	60
<b>12.5</b>		15	20	25	30	35	40	45	50	55	60
<b>13.0</b>		15	20	25	30	35	40	45	50	55	60
<b>13.5</b>		15	20	25	30	35	40	45	50	55	60
<b>14.0</b>		15	20	25	30	35	40	45	50	55	60
<b>14.5</b>		15	20	25	30	35	40	45	50	55	60
<b>15.0</b>		15	20	25	30	35	40	45	50	55	60
		2	6	8	12	16	18	22	26	30	32
<b>Initial</b>		<b>Target TBC Level in truck or vessel</b>									
<b>TBC level</b>		<b>15</b>	<b>20</b>	<b>25</b>	<b>30</b>	<b>35</b>	<b>40</b>	<b>45</b>	<b>50</b>	<b>55</b>	<b>60</b>
<b>10.0</b>		11	12	13	14	15	16	17	19	20	21
<b>10.5</b>		11	13	13	15	16	17	18	19	21	21
<b>11.0</b>		12	13	14	15	16	17	18	20	21	22
<b>11.5</b>		12	14	14	16	17	18	19	20	22	22
<b>12.0</b>		13	14	15	16	17	18	19	21	22	23
<b>12.5</b>		13	15	15	17	18	19	20	21	23	23
<b>13.0</b>		14	15	16	17	18	19	20	22	23	24
<b>13.5</b>		14	16	16	18	19	20	21	22	24	24
<b>14.0</b>		15	16	17	18	19	20	21	23	24	25
<b>14.5</b>		15	17	17	19	20	21	22	23	25	25
<b>15.0</b>		16	17	18	19	20	21	22	24	25	26
TBC Conc.		100%									

**Packages of Solid TBC to be added**

15			20			25			30			35			40			45			50			55			60		
1 lb	8oz	2oz	1 lb	8oz	2oz	1 lb	8oz	2oz	1 lb	8oz	2oz	1 lb	8oz	2oz	1 lb	8oz	2oz	1 lb	8oz	2oz	1 lb	8oz	2oz	1 lb	8oz	2oz	1 lb	8oz	2oz
0	1	3	1	1	3	2	1	2	3	1	1	4	1	1	5	1	0	6	1	0	7	0	3	8	0	2	9	0	2
0	1	3	1	1	2	2	1	1	3	1	1	4	1	0	5	0	3	6	0	3	7	0	2	8	0	2	9	0	1
0	1	2	1	1	1	2	1	1	3	1	0	4	0	3	5	0	3	6	0	2	7	0	1	8	0	1	9	0	0
0	1	1	1	1	1	2	1	0	3	0	3	4	0	3	5	0	2	6	0	1	7	0	1	8	0	0	8	1	3
0	1	0	1	1	0	2	0	3	3	0	2	4	0	2	5	0	1	6	0	1	7	0	0	7	1	3	8	1	3
0	1	0	1	0	3	2	0	2	3	0	2	4	0	1	5	0	0	6	0	0	6	1	3	7	1	3	8	1	2
0	0	3	1	0	2	2	0	2	3	0	1	4	0	0	5	0	0	5	1	3	6	1	2	7	1	2	8	1	1
0	0	2	1	0	2	2	0	1	3	0	0	4	0	0	4	1	3	5	1	2	6	1	2	7	1	1	8	1	0
0	0	1	1	0	1	2	0	0	3	0	0	3	1	3	4	1	2	5	1	2	6	1	1	7	1	0	8	1	0
0	0	1	1	0	0	1	1	3	2	1	3	3	1	2	4	1	2	5	1	1	6	1	0	7	1	0	8	0	3
0	0	0	0	1	3	1	1	3	2	1	2	3	1	1	4	1	1	5	1	0	6	1	0	7	0	3	8	0	2

**This table shows resulting TBC if required amount is added to the nearest 2 oz of the exact amount**

**Summary - For a Truck Weight and Target TBC**  
**Required Solid TBC Addition - single best value**  
**For any starting level of TBC**

Wt.	15	20	25	30	35	40	45	50	55	60	<==Target TBC
41K	2	4	8	12	14	18	22	24	28	32	
43K	2	6	8	12	16	18	22	26	30	32	
45K	2	6	10	12	16	20	24	28	30	34	
47K	2	6	10	14	16	20	24	28	32	36	

**This table shows resulting TBC if one amount is added to the nearest 2 oz of the exact amount for all starting TBC levels**

## **ADDITION OF TBC TO STORED MONOMER**

Styrene monomer in storage should be checked periodically for TBC content and additional inhibitor added as required (see previous section on Inhibition). A good policy is to add additional inhibitor when the level drops to the minimum specification level. The TBC content of styrene monomer in storage should never be allowed to be depleted or remain below the 10 ppm level. The storage tank (or drum) should always be recirculated or mixed after inhibitor is added. This ensures uniform blending of the TBC and supplies an adequate amount of dissolved oxygen in the monomer for effective inhibition. Caution must be exercised in handling TBC. See information on toxicological properties and safe handling of TBC as well as manufacturer's MSDS.

TBC concentrates (85% TBC in 15% methanol) can also be obtained from Chevron Phillips Chemical Company on an emergency basis. Table 3B lists the amount of concentrate required to increase the bulk quantity by 1 ppm. The amount of inhibitor required to achieve the assured inhibition level can also be calculated using the following formula:

cc's of TBC concentrate =

$$\text{lbs. of styrene} \times \frac{\text{PPM TBC} - \text{PPM TBC required in product} \times 503}{1,000,000}$$

## **POLYMER BUILDING IN STORAGE**

The polymer deposited under storage conditions will be discolored, cross-linked, and high in peroxides, aldehydes, and other oxidation products. Deposits of contaminated polymer could eventually produce serious color and polymer problems in monomer stored under air in unlined steel tanks. Internal reflux, (the vaporization and condensation due to normal temperature differentials) will dissolve small amounts of this polymer and carry it back into the tank, thereby increasing both the polymer content and the color of the stored monomer.

Polymer deposits in tanks also create difficult removal and cleaning problems. If stalactites

are allowed to grow, their weight may damage the roof or roof-supporting structure of large vertical storage tanks.

## **COLOR PROBLEMS**

Styrene in storage occasionally develops color which can be carried into the polymerization product. For this reason, a maximum color specification of APHA 10 has been set for many styrene end uses.

Color may develop in several ways:

1. Copper or copper-containing alloys can form soluble copper salts when contacted by styrene. These will impart a green or blue-green color to the monomer and may also inhibit its polymerization.
2. Highly-colored styrene oxidation products may form in the liquid monomer or be introduced by polymer falling or dissolving from the walls and roof.
3. TBC may oxidize to form highly-colored reaction products.
4. Iron, usually originating from rust in tanks or in piping, may react or complex with TBC at the ppm level to give styrene a yellow or yellow-green color.
5. Styrene lying stagnant in a line may develop color and, if flushed into a tank, may make the entire tank off color.

Color problems in storage can be minimized by:

1. Avoiding use of copper or copper alloyed material in contact with styrene monomer.
2. Paying careful attention to the oxygen level in the styrene and in the vapor space above the styrene.
3. Employing proper tank design and maintenance to avoid rust and polymer build-up on tank walls and roof.
4. Applying good transfer practices.

Color in styrene monomer can be reduced to acceptable limits by:

1. Distilling the colored monomer.
2. Blending with non-colored styrene. Caution should be used, however, since color does not always blend proportionately. Small trial blends should be made to determine the feasibility of this approach.
3. Passing the styrene over silica gel or alumina. This method has the disadvantage of removing the TBC inhibitor, which must be replaced. Acidic or highly-activated alumina may cause the styrene to polymerize. Verify the applicability of the material selected by using a small bench scale test.

### **PARTICULATE MATTER**

Styrene should be free of particulate matter when it is polymerized. Although some particulate matter in styrene originates from outside contamination via the receiving-transfer system, it is also formed by the reaction of concentrated TBC solutions with iron. This may happen in lines which have contained styrene but have been blown dry.

Particulate matter in styrene may be avoided by:

1. Paying careful attention to cleanliness.
2. Properly coating the inside of tanks and transfer lines which may contain high concentrations of TBC or which may be blown dry after carrying TBC-inhibited styrene. Stainless steel vessels and lines are also recommended.
3. Filtering styrene to remove particulate matter before storage, shipment, or use.

### **DRUMS**

Drums of styrene monomer should not be permitted to stand in the sun for more than a short period of time. As soon as possible after being received, drums should be moved to a cool, shaded area. In hot weather drums can be cooled with a water spray. It is also

advisable that inventories be kept to a minimum during summer months and that monomer is stored no longer than necessary. Adding additional TBC during hot weather is also recommended. Styrene should be stored in white drums that reflect sunlight as a means to control temperature.

### **TANKS**

In designing bulk storage facilities, certain basic factors must be considered. Styrene monomer can be stored for relatively long periods of time if simple, but carefully prescribed conditions are met. In addition to the usual precautions taken with flammable liquids against fire and explosion hazards, precautions must be taken against conditions that will promote the formation of polymer and oxidation products. To accomplish this, the design and construction of a satisfactory bulk storage system for styrene requires careful consideration to eliminate excessive temperatures and to prevent contamination with polymer from infrequently used lines and other equipment. Figure 1 illustrates a typical tank design.

A self-supporting-type dome roof is recommended for vertical storage tanks. This type of construction simplifies the installation of linings and permits rapid drainage of uninhibited condensed vapors back into the liquid monomer, thus reducing the polymer and stalactite problem. Roof and sidewall openings above the normal liquid levels in the tank should be of large diameter and the number kept to a minimum.

Large diameter openings are easily lined and can also be used for dual-service purposes where feasible.

Insulation and refrigeration of storage tanks are recommended for environments where temperatures exceed 75°F for long periods of time.

Most consuming locations insulate storage tanks to dampen the effect of high day time temperatures but do not install refrigeration due to cost.

Lined carbon steel tanks are generally used for the bulk storage of styrene monomer.

Vertical storage tanks are commonly used for large volume storage. Horizontal tanks are equally satisfactory for bulk storage, but are generally used for smaller installations. The inlet and outlet lines for these tanks are normally located near the bottom.

Tank linings have proven successful in controlling or reducing polymer and stalactite formation. A tight, nonporous, non-wettable, smooth surface prevents retention and attachment of the condensed uninhibited monomer droplets, and they rapidly drain back into the inhibited liquid monomer before polymerization takes place. Baked phenolic, modified epoxy and inorganic zinc silicates have proven satisfactory for this purpose. Baked phenolic and modified epoxy coatings are nonconductive, however, and it is recommended that the bottom and lower 6 to 8 inches of vertical storage tanks be coated with inorganic zinc silicate linings to provide electrical grounding.

Table 4 lists some suppliers and specific products for the various types of coatings as of this printing. List is subject to change and Chevron Phillips does warrant or certify any product or supplier.

Various Phenguard coatings applied with TBC have reportedly been effective in controlling polymer growth inside storage tank (including vapor space) and reducing maintenance. The specific Phenguard coating and the supplier (who will supply specific directions for preparing and applying these coatings) are listed in Table 4.

**Table 4  
Type of Coatings and Suppliers**

Inorganic Zinc Silicate

- |                    |  |
|--------------------|--|
| 1. Interzinc 98    | Matcote Co.  |
| 2. Interzinc 88    | P.O. Box 920762<br>Houston, TX 77292                       |
| 3. Dimetcote No. 4 | Ameron Protective  |
| 4. Dimetcote No. 6 | Coatings Division<br>201 North Berry St.<br>Brea, CA 92621 |

Baked Phenolic

- |                  |   |
|------------------|---|
| 1. Heresite P403 | Heresite Chemical Co.<br>822 South 14th Street<br>Manitowac, WI 54220 |
|------------------|---|

- |                                  |   |
|----------------------------------|---|
| 2. Lithcote Phenolic LC-24       | Lithcote Corporation<br>111 West Jackson Blvd.<br>Chicago, IL 60604 |
| 3. Phenguard 7409, 7435 and 7436 | Sigma Coatings<br>P.O. Box 816<br>Harvey, LA. 70058                 |

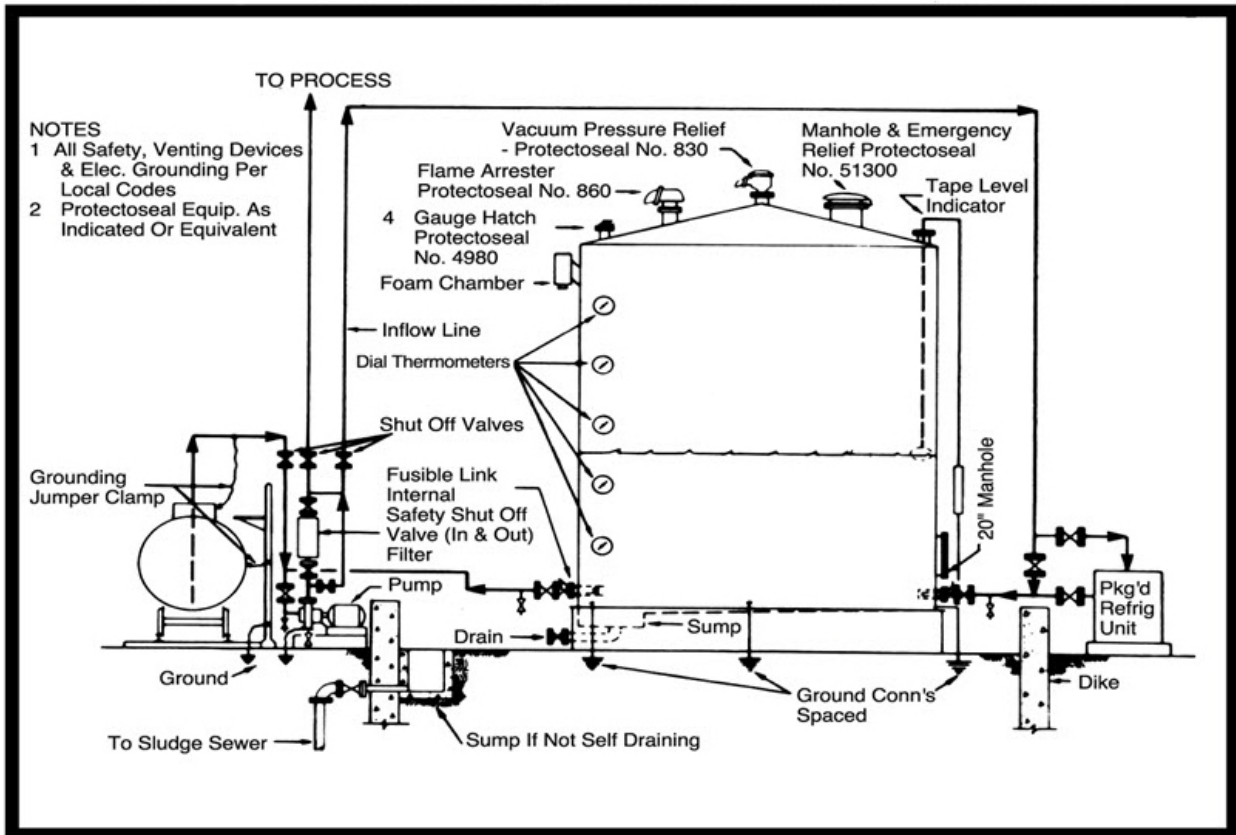
Modified Epoxy

- |                  |  |
|------------------|--|
| 1. Lithcote LC34 | Lithcote Corporation<br>111 West Jackson Blvd.<br>Chicago, IL 60604          |
| 2. Amercoat 346  | Ameron Protective Coatings Division<br>201 North Berry St.<br>Brea, CA 92621 |

Other equivalent or comparable coatings are undoubtedly available and may be equally satisfactory, but it would be advisable to check their resistance characteristics and obtain information on their performance for this application from the manufacturer before use. Rubber-based linings should not be used.

Requirements of diking, tank spacing, and other features pertaining to safety are detailed in guidelines set by the National Fire Protection Association (see NFPA 30). These, as well as local building codes and governmental regulations, should be consulted since some requirements vary with the size and configuration of an installation.

**FIGURE 1 – STYRENE MONOMER STORAGE TANK**



All electrical equipment associated with the tank should conform to the National Electrical Code (NFPA 70).

### **PIPING**

Piping is normally of carbon steel, although stainless steel and aluminum may also be used. **Copper and copper-containing alloys in contact with styrene must be avoided.** Stainless steel pipe is recommended for concentrated TBC solutions but steel pipe lined with baked phenolic, Teflon®, or the equivalent can also be used to reduce formation of particulate matter.

All piping should be sloped and have no pockets where styrene can become stagnant. All low points should be provided with drains or some other means of removing the monomer. Above-ground piping should be insulated and properly grounded. Provision should be made either for circulating styrene through all lines or for blowing them empty

with nitrogen. Do not leave styrene in blocked lines because thermal expansion could damage valves and seals and the monomer is more likely to become oxygen and inhibitor depleted.

Flanged or welded connections are suggested. For larger piping, butt welded fittings are preferred. Socket weld fittings are preferred for small connections.

All storage tanks and loading points should be fitted with sampling points. Never use brass, bronze, or any line material containing copper.

The following are recommended practices in engineering pipelines for styrene:

1. Lines smaller than one inch should not be used.
2. A minimum of flanged connections should be used on styrene pipelines. Flanges should be avoided due to leak potential.

3. Styrene lines should not be buried because of the difficulty of checking for leakage.
4. All lines should be sloped so that they can be completely drained for maintenance.
5. All newly installed styrene pipelines should be pressure tested by an approved method before insulation is applied.
6. Bellows valves are recommended for 2-inch and smaller lines to eliminate emissions from packing.

### **PUMPS**

Centrifugal pumps are preferred for styrene service. They should be fitted with closed impellers and mechanical seals.

The pump manufacturers can recommend the proper pump if the following parameters are known: 1) flow rate, 2) size and length of suction and discharge lines, 3) suction and discharge pressures and, 4) the styrene monomer temperature. A drain valve should be installed at the lowest point in the system so that the pump and all piping can be completely drained before any maintenance work is done. Totally closed fan cooled motors are recommended; however local fire and insurance codes should be consulted to determine if an explosion proof motor must be used.

All pump motors should meet National Electrical Code standards (NFPA 70).

The following practices are recommended to minimize the possibility of pump leakage.

1. Mechanical seals in conformance with API RP 682. Tandem seals with barrier fluid are recommended.
2. Pumps in conformance with API Standard 610.
3. The pump should be designed so that the pump bearings will be able to carry thrust at no flow. Consider selecting non-metallic (PEEK) wear rings to minimize damage if the pumps run dry.

4. The pump shaft should be highly polished.
5. Pumps should not be subjected to forces beyond specified pump tolerances.
6. Vibration monitoring with automatic pump shutdown may be applicable in certain situations.

### **VALVES**

Ball valves with seats of Viton<sup>®</sup> are satisfactory for styrene service under ambient storage conditions. Gate valves are less satisfactory but they are usually less expensive and may be used.

### **GASKETS**

Garlock<sup>®</sup> No. 7021, Viton<sup>®</sup>, Teflon<sup>®</sup>, Durable Nitrile<sup>®</sup>, Grafoil<sup>®</sup> GHE, or its equivalent is satisfactory for flanged connections at ambient conditions. Reinforced graphite composite gaskets are also recommended. Gaskets made of rubber or other styrene-soluble materials should not be used.

### **FILTERS**

Since small amounts of foreign matter may enter storage tanks from various sources, a filter in the transfer piping between the tank and processing equipment is recommended. Cartridge type filters with a fine or medium replaceable cartridge or bag filters are suggested. Polyester, Nomex, Rayon and Nylon fiber filters are compatible with styrene.

Filter cartridges should be inspected and renewed periodically.

### **HOSES**

If hoses are needed for loading or unloading operations, they should be flexible and chemical-resistant. A satisfactory type is Goodyear, rough-bore, style WH-7 with Viton<sup>®</sup> tube, or the equivalent. Multi-layered polypropylene and Teflon<sup>®</sup> are also recommended.

Flexible metal hoses are widely used and recommended but require special care to prevent damage during use.

Styrene monomer should not be allowed to remain in any hose after use because the monomer will polymerize and form undesirable reaction products. Promptly drain and clean these lines after usage. Toluene or ethylbenzene may be used to clean lines.

All lines must be adequately grounded to discharge static electricity.

All hoses should have suitable pressure and temperature ratings and be grounded to discharge static electricity.

### **O-RINGS**

Viton<sup>®</sup>, Teflon<sup>®</sup>, Fluou<sup>®</sup>, or their equivalents are recommended.

### **PROCEDURE FOR COATING TANKS**

All internal surfaces should be coated (except for the floor and bottom of the vertical walls below the normal liquid level) to prevent accumulation of static electricity. This includes, in addition to the tank, all internal surfaces of nozzles, manholes, manhole covers, internal fittings and all surfaces that may contact the liquid contents of the tank or be exposed to vapors from the liquid. If any internal fittings are of non-ferrous metal, they should be removed and replaced when the lining is completed.

All sharp edges and high points should be ground smooth and rounded to a minimum radius of 1/8". Welded seams need not be ground flush; however, welds should be free from undercuts or pinholes. If either exists, they should be ground out, filled with weld metal or epoxy putty, and ground smooth. Weld spatter beads should be removed by grinding or by the sand blasting which follows.

All internal surfaces to be lined should be sandblasted to the degree defined as "White Metal Blast" by Steel structures Painting Council Specification SP-5-63. Anchor pattern depth should conform to a minimum of 1.5 mils and a maximum of 2 mils. Loose material such as sand, grit, dust, or any foreign matter should be removed from the tank, preferably by use of an industrial vacuum cleaner.

The first coating should be applied within eight hours after sandblasting is completed. It must be applied before any rust appears or "turning" occurs in the "White Blast." Otherwise, reblasting to the "White" condition will be necessary.

1. A brushed prime coat should be applied to all welds, rounded edges and other irregular surfaces, working the paint well into the metal.
2. Apply a full sprayed coat of primer over brushed surfaces. Allow to dry overnight. Dry film thickness should be 1.5-2.5 mils.
3. Apply one sprayed coat of intermediate primer to all surfaces. Allow to dry overnight. The total dry film thickness of this and the preceding coat should be 3-4 mils. (Note: some colored primers may dissolve in styrene and discolor it unless the primer is completely covered by subsequent coats of paint.)
4. Apply one sprayed coat of finish paint to all surfaces. Allow to dry overnight. The total dry film thickness following this step should be 4.5-6 mils

Recommendations of the paint manufacturer regarding mixing, thinning, etc. should be followed. Curing and drying times, should be in accordance with the paint manufacturer's recommendations.

The completed lining should be free of pinholes, abrasions or other breaks in film continuity, runs, sags and overspray. Each coat should be inspected after it has dried and before the following coat is applied).

Caution - The solvents used in these paints can be toxic if breathed or absorbed in large quantities. They may also cause dermatitis in some individuals. Consequently, it is recommended that personnel wear supplied-air respirators and protective clothing while working. Forced-air ventilation should be provided during blast-cleaning and linings-application work since the solvents are also flammable. The ventilation should be maintained at all times while personnel are in enclosed areas and for thirty minutes to an hour after lining work has been completed for

the day. An adequate number of air changes must be provided to keep solvent vapors below lower explosive limits. After lining work has been completed, forced-air ventilation should be maintained until all solvent fumes have been removed.

**Personnel should never be permitted to enter an empty tank which has been used for Styrene until the requirements of the OSHA confined space standard (29 CFR 1910.146) have been met and the safe entry recommendations of API Standard 2015 have been met including, but not limited to, required concentrations for oxygen and limitations on concentrations of Styrene.**

**Specific bulk storage designs must conform to insurance underwriter's codes and local fire and building regulations. Critical design, placement, installation and maintenance requirements are usually addressed in these codes and regulations and must be followed.**

### **API DESIGN REFERENCES**

API Petroleum Institute  
1220 L Street, NW  
Washington, DC 20005

Part I - Design

API RP 520: Sizing, Selection and Installation of Pressure-relieving Devices in Refineries

Part II - Installation

API Standard 601: Metallic Gaskets for Raised-Face Pipe Flanges and Flanged Connections (Double-Jacketed Corrugated and Spiral-Wound)

API Standard 620: Design and Construction of Large, Welded, Low-Pressure Storage Tanks

API Standard 650: Welded Steel Tanks for Oil Storage

API Standard 2000: Venting Atmospheric and Low-Pressure Storage Tanks; Nonrefrigerated and Refrigerated

API RP 2003: Protection Against Ignitions Arising Out of Static, Lightning, and Stray Currents

API RP 2028: Flame Arresters in Piping Systems

API RP 2210: Flame Arresters for Vents of Tanks Storing Petroleum Products

API RP 2350: Overfill Protection for Storage Tanks in Petroleum Facilities

API Standard 2015: Requirements for Safe Entry and Cleaning of Petroleum Storage Tanks

API Standard 653: Tank Inspection, Repair, Alteration, and Reconstruction

## PART 4

### ACCIDENTAL RELEASE, FIRE AND HEALTH

Although the handling of styrene is considered to present a low degree of health risk, exposure to this product should always be minimized. Extensive experience has shown that this monomer can be handled safely if its toxicological properties are clearly understood and proper precautions are practiced.

Material Safety Data Sheets for styrene are available from Chevron Phillips Chemical Company LP to help customers further satisfy their own safe handling and disposal needs and OSHA Hazard Communication Rule requirements. Such information should be requested and studied prior to working with this product. Please call Chevron Phillips Chemical Company LP at (800) 231-1212 to request the MSDS for styrene. NOTE: This booklet does not substitute for the MSDS.

The following briefly summarizes the toxicological information. The precautions recommended are, of necessity, general in nature, because specific recommendations can be made only when the conditions of handling are known.

#### ACCIDENTAL RELEASE MEASURES

If a transportation incident involving styrene does occur, the Chemical Transportation Emergency Center (CHEMTREC) should be contacted for immediate assistance. CHEMTREC is a public service organization established by the American Chemistry Council to provide assistance in hazardous material incidents. **FOR A CHEMICAL EMERGENCY CALL CHEMTREC AT (800) 424-9300 toll free in the United States, Canada, Puerto Rico, and the Virgin Islands. For emergency calls outside the United States call + (703) 527-3887. Collect calls are accepted.**

CHEMTREC will provide the caller preliminary emergency assistance in the form of Material Safety Data Sheet (MSDS) information. In all cases once CHEMTREC determines the

incident involves a Chevron Phillips Chemical material, CHEMTREC will immediately contact the on-call Chevron Phillips Chemical Company LP Crisis Management Team (CMT) member at 1-866-4HAZMAT (442-9628). The contacted Chevron Phillips Chemical CMT member will then be responsible for coordinating an appropriate response to the transportation incident. In addition, if the CMT member determines that the incident involves exposure or potential health effects, the on-call Chevron Phillips Chemical toxicologist will also be contacted.

Eliminate all sources of ignition in the vicinity of the spill or released vapor. Stop the source of the leak or release. Clean up releases as soon as possible, observing personal protection precautions (see below). Contain liquid to prevent further contamination of soil, surface water or groundwater. Styrene is expected to be toxic to aquatic organisms. Avoid contaminating soil or releasing this material into sewage or drainage systems and bodies of water. Clean up small spills using appropriate techniques such as sorbent materials or pumping. Where feasible and appropriate, remove contaminated soil. Follow prescribed procedures for reporting and responding to larger releases. The Reportable Quantity (RQ) under CERCLA Section 302.4 is 1000 lbs. USA regulations require reporting spills of this material that could reach any surface waters. The toll free number for the U.S. Coast Guard National Response Center is (800) 424-8802.

#### SPILLS

If styrene has been spilled, it can be removed safely for disposal. Before attempting to clean up the spill be sure that the flow of liquid has been stopped and that all sources of ignition are eliminated. Small spills (non-marine) can be removed by covering the spill with sand or a suitable absorbent. Some absorbing agents, such as untreated clays and micas, will cause an exothermic reaction which might ignite the

monomer. For this reason, absorbing agents should be tested for their effect on polymerization of the monomer before they are used on large spills. Claymax<sup>®</sup>, a loose “vermiculite-like” material has proved to be an effective absorbent. Claymax<sup>®</sup> may be purchased from:

Road Fabric, Inc.  
Environmental Division  
27 West 045 St. Charles Road  
Carol Stream, IL 60188  
Phone: (630) 293-3111

Contact local environmental or health authorities for approved disposal of the absorbing agent. 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.

Larger spills should be contained within a dike, and water 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 recovery.

Styrene is toxic to aquatic organisms and should be kept out of sewage and drainage systems and all bodies of water.

## **DISPOSAL**

All disposal procedures are to be carried out in strict conformance to federal, state and local regulations. Styrene monomer and absorbent-containing styrene must be incinerated in an approved designated furnace. Please contact Chevron Phillips Chemical Company Aromatics Technical Service Group at (877) 771-7176 if additional assistance is required.

## **FIRE HAZARDS**

This product presents a fire hazard. The liquid evaporates, and forms vapor (fumes) which can catch fire and burn with explosive violence. Invisible vapor spreads easily and can be set on fire by many sources such as pilot lights, welding equipment, and electrical motors and switches.

For fires involving this material, do not enter any enclosed or confined fire space without proper protective equipment. This may

include self-contained breathing apparatus to protect against the hazardous effects of normal products of combustion or oxygen deficiency. Normal combustion forms carbon dioxide and water vapor; incomplete combustion can produce carbon monoxide. Extinguish with foam, dry chemical or carbon dioxide. Use water in flooding quantities as fog; solid streams of water may be ineffective. Cool exposed containers with water.

Flash Point: 31°C (88°F) Closed Cup

Ignition Temp.: 490°C (914°F)

Flammable Limits in Air: 1.1 - 6.1 Vol%

Electrical Hazards: Class 1, Group D

Behavior in Fire: Vapor is heavier than air and may travel a considerable distance to a source of ignition and flash back. At elevated temperatures, such as in fire conditions, polymerization may take place, which may lead to container explosion.

Burning Rate: 5.2 mm/min.

NFPA Fire Hazard Rating: 3

## **FLAMMABILITY**

Styrene monomer is classified by both OSHA 29 CFR 1910.26 and National Fire Protection Association (NFPA) Code 30 as a Class IC flammable liquid. The National Electric Code (NFPA 70) refers to styrene as a Class I, Group D material.

Styrene will burn and requires the same precautions against fire and explosion hazards that commonly apply to other combustible and flammable liquids. The flammability properties of styrene are given in the Physical Properties section (Part 1, Pages 3-6).

## EXPLOSIVE MIXTURES

Styrene vapor is heavier than air and could travel considerable distances to an ignition source and flash back to the source.

It is important to prevent the formation of explosive or combustible mixtures, and to take precautions to avoid ignition of any such mixtures.

Monomer handling areas should be well ventilated and motors must be explosion-proof. **ALL TANK CARS, TANK TRUCKS, HOSE CONNECTIONS AND OTHER EQUIPMENT MUST BE GROUNDED FOR THE SAFE DISCHARGE OF STATIC ELECTRICITY.** Storage tanks and other containers that have been emptied of monomer must be flushed out with steam, nitrogen, or water to remove monomer vapor. The tank atmosphere should be tested before the tank is entered or worked on with welding equipment.

The dangers of fire and explosion are real because styrene can form explosive mixtures in air at room temperatures. Precautions should be taken to assure that no ignition of vapors can occur, especially where elevated temperatures are involved.

Precautions include:

1. Regular equipment inspections
2. Immediate repair of leaks
3. Good ventilation
4. Proper facilities to contain spills quickly
5. Use of special alloy, non-sparking tools
6. Periodic tests of pressure equipment
7. Elimination of all possible ignition sources

It is also important, at all times, to prevent the formation of explosive or combustible mixtures at other than normal pressures and temperatures. While the actual operating conditions may be outside the explosive limits,

the vapor system may pass through the explosive range in reaching the desired operating conditions. Thus, a vacuum impregnation at 50°C and 100 mm Hg pressure involves a non-explosive mixture of styrene vapor and air. However, during the evacuation step from atmospheric pressure to 100 mm pressure, the system goes through the explosive range. If the evacuation is performed at 20°C and the system is then heated to 50°C, the explosive range will be avoided completely.

If the system is properly flushed with nitrogen or other inert gases (helium, carbon dioxide) prior to evacuation, or if such gases are used for pressurizing, all such dangers are reduced.

## FIRES

Locations that depend on local fire companies should provide them with information concerning the properties of styrene, their operations and details (including diagrams) of storage vessels, quantities stored and other pertinent details.

Fires involving styrene monomer can be safely extinguished with foam, dry chemical, or carbon dioxide. Water fog can also be used, however, a water stream is not an effective extinguishing agent for styrene. If electrical equipment such as motors, open hot plates, or open electrical switches are involved, foam should be used with caution. When burning, styrene gives off toxic by-products, such as carbon monoxide gas. For this reason, breathing of fumes, smoke, and gas from a styrene fire should be avoided. Do not enter any enclosed or confined fire space without full protective equipment, which include a self-contained breathing apparatus.

People conducting the clean up should be trained to satisfy OSHA Hazardous Operations and Emergency Response Standard 29 CFR 1910.120 requirements.

After the fire has been put out, any residual monomer should be secured in proper storage or cleaned up to prevent loss to the environment. If significant product is lost contact your local environmental agency.

## **PERSONAL PROTECTIVE EQUIPMENT AND OCCUPATIONAL EXPOSURE LIMITS**

Wear safety glasses with side shields as a good safety practice when working with styrene. Wear impervious protective clothing to prevent skin contact. Selection of protective clothing may include gloves, apron, boots and complete facial protection and will depend on operations conducted. Users should determine acceptable performance characteristics of protective clothing. Consider physical requirements and other substances present when selecting protective clothing. Suggested materials for protective gloves include Viton®, 4H (Polyethylene-Ethylene Vinyl Alcohol laminate), and Polyvinyl Alcohol (PVA) (avoid contact with water; PVA deteriorates in water). Determine if airborne concentrations are below the recommended exposure limits. If not, select a NIOSH/MSHA-approved organic vapor respirator that provides adequate protection from measured concentrations of this material. Use a positive-pressure, air-supplying respirator if there is potential for uncontrolled release, if exposure levels are not known, or if other circumstances exist where air-purifying respirators may not provide adequate protection.

The OSHA Permissible Exposure Limit (time-weighted average) is 100 ppm. The styrene industry, represented by SIRC, CFA, CI, ICPA and NMMA has agreed to establish a voluntary program with OSHA to comply with an 8-hour (time-weighted average) occupational exposure limit of 50 ppm and a 15 minute limit of 100 ppm. The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a Threshold Limit Value (TLV) of 20 ppm (8 hour time-weighted average) and a Short Term Exposure Limit (15 min) of 40 ppm.

OSHA Permissible Exposure Limit:  
Time Weighted Average (TWA) = 100 ppm

ACGIH Threshold Limit Value:  
Time Weighted Average (TWA) = 20 ppm

## **HEALTH HAZARDS AND FIRST AID**

**EYE CONTACT:** Styrene is not expected to cause prolonged or significant eye irritation.

**First Aid:** If styrene gets into the eyes, no specific first aid measures are required. As a precaution, remove contact lenses, if worn, and flush eyes with water.

**SKIN CONTACT:** Contact with the skin causes irritation which may include pain, reddening, swelling, and blistering. Skin contact may cause drying or defatting of the skin. Styrene is not expected to cause an allergic skin response. **First Aid:** If skin contact should occur, wash skin immediately with soap and water and remove contaminated clothing and shoes. Get medical attention if irritation persists. Discard contaminated clothing and shoes or thoroughly clean before reuse.

**INGESTION:** Harmful or fatal if swallowed. Because of its low viscosity, styrene can directly enter the lungs if swallowed or if subsequently vomited. Once in the lungs it is very difficult to remove and can cause severe injury or death. **First Aid:** If swallowed, do not induce vomiting. Give the person a glass of water or milk to drink and get immediate medical attention. Never give anything by mouth to an unconscious person.

Note to Physician: Ingestion of this product or subsequent vomiting may result in aspiration of light hydrocarbon liquid, which may cause pneumonitis.

**INHALATION:** Most humans can detect the odor of styrene vapor around 2-5 ppm and, at around 100 ppm, begin to feel discomfort due to eye and nose irritation. The vapor or fumes from this material may cause respiratory irritation, including coughing or difficulty breathing. Breathing this material at concentrations above the recommended exposure limit may cause central nervous system effects, including drowsiness, dizziness, headache, nausea, vomiting, weakness, loss of coordination, blurred vision, confusion, or disorientation. At extreme exposure, central nervous system effects may include respiratory depression, tremor or convulsions, loss of consciousness, coma or death. Several epidemiology studies involving over 90,000 workers in the styrene, polystyrene and reinforced plastics industries together show no increased cancer risk from occupational exposure to styrene. Styrene may cause cancer in laboratory animals (mice

only), but the available information is inadequate to determine if this material can cause cancer in humans. Repeated inhalation of this material at concentrations above the recommended exposure limit may cause damage to the liver based on animal data. Although damage to the olfactory cells in the nose has been found in mice and rats, reinforced plastics workers exposed to an average of 26 ppm of styrene showed no evidence of impairment in the ability to detect or identify odors. Information from human experience and the results of animal studies suggest no significant risk of birth defects or reproductive toxicity of styrene in humans. **First Aid:** If a person should accidentally be overcome or experience any ill effects caused by breathing styrene, move the exposed person to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention if symptoms continue.

See the MSDS for styrene for a more complete discussion of the toxicity of styrene.

#### **4-TERT-BUTYL CATECHOL (TBC):**

TBC is typically added to styrene monomer to inhibit polymer formation and oxidative degradation during storage and shipment. Typically, product is inhibited when TBC levels are between 10-15 ppm, but if long storage times or high temperatures are anticipated, product is inhibited up to 100 ppm. Many customers store limited quantities of TBC concentrate or solid TBC for emergency use.

TBC is severely injurious (extremely corrosive) to the skin and eyes, and may be absorbed through the skin in toxic amounts. TBC is a known skin sensitizer and may cause depigmentation of the skin. Once an individual has become sensitive, even exposure to very small amounts can cause a response. Concentrated solutions in styrene can be expected to cause greater irritation than would be expected from just the monomer. Slight damage to the liver has been reported in a rat feeding study.

Personnel should wear goggles and/or full face shield and protective clothing including gloves and apron made of Viton® while working with TBC or its concentrated

solutions. It should not be pipetted by mouth. In case an accidental contact with TBC or its strong solutions should occur, it should be removed immediately from the skin by washing with soap and plenty of water; for eyes, flush them with plenty of water; for at least 30 minutes and get medical attention immediately.

**PLEASE CONSULT THE MSDS FOR TBC PRIOR TO HANDLING THIS CHEMICAL.**

#### **ENVIRONMENTAL HAZARDS**

Styrene is expected to be toxic to aquatic organisms. Styrene is expected to be readily biodegradable.

## **PART 5**

### **TRANSPORTATION INFORMATION AND REGULATORY PROFILE**

#### **TRANSPORTATION INFORMATION**

##### **STYRENE MONOMER HANDLING CLAUSE**

###### **PRIOR CARGO'S AND CONTENTS**

The Owner is to notify the Charterer of vessel's stowage and last 3 cargoes at least 7 days prior to loading. Owner's failure to provide last cargo information within the timeframe stipulated above may result in a mandatory wall wash requirement. Charterers will provide Owners a copy of instructions sent to their load port surveyor for any wall wash requirements for ship's cargo tank (s) inspection at the load port. These instructions will be based on the last cargoes which Owners provide. Last 3 cargoes in ships tanks, pumps and lines (including sampling system) are to be clean and unleaded.

###### **STOWAGE, WALL WASHES AND SAFE CARRIAGE**

Ship's cargo tanks are to be properly cleaned for the safe carriage of Styrene Monomer by the Master/Owner. Styrene Monomer cargoes should be stowed as per relevant international and IMO regulations with respect to compatibility, heat adjacency and other requirements. Ship's cargo tanks utilized for the carriage of Styrene monomer shall have separate cargo pumps, cargo lines, vent lines, and sample lines constructed of suitable stainless steel material. Cargo tanks may be of either stainless steel or suitably coated with coatings in excellent condition. The tank coating shall be fully compatible with the carriage of styrene monomer. Piping systems should not pass through other cargo tanks containing incompatible cargoes. Heating coils in cargo tanks carrying Styrene monomer shall be of constructed of suitable material compatible with styrene monomer and shall be blown free of any moisture, disconnected and blanked closed.

Charterer may at the Charterer's discretion request a visual inspection of the cargo tanks, especially those tanks with coatings, where the tanks will be observed for cracking,

peeling, and blistering of the coating which lines the base material of the tank. Fully exposed areas, particularly at the bottom of the cargo tanks will be noted and reported to the Charterer.

Charterer may order additional testing such as wall washes to determine if any prior cargoes are detectable for any and all types of cargo tanks. Sampling and subsequent analysis by the Charterer's representative is not consider approval of the Master's/Owner's cleaning method or the condition of the ship's tanks, piping, pumps, and associated equipment. (See API MPMS 17.12)

###### **MONITORING AND REPORTING**

During the voyage, the product temperature (in °C) in the tank, and the oxygen content in the tank vapor phase must be checked and documented at least once a day. The monitoring results of the tests should be sent to Charterer twice a week via email.

The results must be recorded also in a temperature and oxygen log on board. When instructed by Charterers, such records are to be surrendered to the charterer's representative (or charterer appointed surveyor) prior to discharge. Charterer's representative (or charterer appointed surveyor) would be made known to the vessel owner prior vessel arrival at discharge port.

An alert must be send to the Charterer on a daily basis via email when:

- The temperature exceeds the 30°C (85°F)
- The temperature increased more than 2°C in one day

###### **ON BOARD INHIBITOR AND HANDLING**

The storage of TBC is not recommended on vessels.

**LABELING:**

Bulk or non-bulk packages must be marked, labeled and/or placarded in accordance with applicable International safety, health or transport regulations, OSHA, and/or DOT requirements.

Identification number markings are required on each side and each end if a packaging capacity is 1000 gallons or more; on two opposing sides if the packaging capacity is greater than 119 gallons but less than 1000 gallons. Each bulk packaging must also be marked with the proper shipping name. Markings for non-bulk packaging (119 gallons or less) must include the identification number preceded by UN or NA followed by the proper shipping name. The "RQ" marking is required on non-bulk packages that contain a reportable quantity of Styrene, which is a Hazardous Substance.

When labels are required on non-bulk packages and they must be located on the same surface and near the markings.

Placards are required on each side and each end of bulk packaging.

Requirements concerning marking, labeling, placarding, and the preparation of shipping papers vary depending on the transport mode, packaging configuration, and quantity of hazardous material being transported.

Marking, labeling, and placarding requirements are explained in detail in 49 CFR 172 Subparts D, E, and F respectively. Subparts E and F display sample labels and placards. Labels and placards applicable to flammable liquids are required for styrene. Bulk packaging should remain placarded when emptied unless the special requirements of Subpart F are met.

**CHEMICAL DESIGNATIONS:**

CG Compatibility Class:	Aromatic Hydrocarbon
Formula:	$C_6H_5CH=CH_2$
UNI/UN Designation:	3.0/2055
DOT ID No.:	2055
CAS Registry No.:	100-42-5

**INTERNATIONAL MARITIME ORGANIZATION (IMO):**

Proper Shipping Name:	Styrene Monomer, stabilized
Class	3
UN Number	UN 2055
Symbol	Flammable Liquid
Pollution Category	C
European Behavior Classification	F, E, R (Floater, Evaporator, Reactide)

**SHIPPING INFORMATION:**

Grades of Purity:	99.9%
Storage Temperature:	Ambient
Inert Atmosphere:	No requirement
Venting:	Open (flame arrester)

## **Hazard Classifications**

Code of Federal Regulations: Flammable liquid NAS Hazard Rating for Bulk Water Transportation:

<u>Category</u>	<u>Rating</u>
Fire	3
<u>Health</u>	
Vapor Irritant	2
Liquid or Solid Irritant	2
Poisons	2
<u>Water Pollution</u>	
Human Toxicity	1
Aquatic Toxicity	3
Aesthetic Effect	2
<u>Reactivity</u>	
Other Chemicals	2
Water	0
Self Reaction	3

### *NFPA HAZARD CLASSIFICATION:*

<u>Category</u>	<u>Rating</u>
Health Hazard (Blue)	2
Flammability (Red)	3
Reactivity (Yellow)	2

### *WATER POLLUTION:*

Harmful to aquatic life in very low concentrations  
 Fouling of shoreline  
 May be dangerous if it enters water intakes  
 Notify local health and wildlife officials  
 Notify operators of nearby water intakes

## **DRUMS**

The UN Standard 1A1 steel, non-removable head drum should be used to transport styrene monomer. The performance-oriented standards for the 1A1 are described in 49 CFR 178 Subpart M. For styrene monomer the following level three tests must be performed: hydrostatic pressure, leak proof, drop, stacking, and vibration.

When the drums used to ship styrene monomer are emptied, they should be immediately triple rinsed with a suitable solvent. The drums should not be cut or punctured prior to complete cleaning.

If over packing is used, the inner drum must be isolated from the outer drum as described in 49 CFR 173 Subpart E and must be segregated on the vehicle as described by 49 CFR 177 Subpart C.

## REGULATORY PROFILE

### Styrene

- 1) **ODCs:** Contains Class 1 or Class 2 Ozone Depleting Chemicals( ODCs)? **NO**
- 2) **TSCA:** Is this product or its components subject to any of the following TSCA requirements of 40 CFR, Part:
- |     |  |           |
|-----|--|-----------|
| 707 | (Export Notifications) (12b)                     | <b>NO</b> |
| 712 | (Chemical Information Reporting) (8a)            | <b>NO</b> |
| 716 | (Health & Safety Data Reporting) (8d)            | <b>NO</b> |
| 721 | (Significant New Use) (5e)                       | <b>NO</b> |
| 790 | (Health and/or Environmental Effects Testing(4e) | <b>NO</b> |
- Is this material distribution under limitations of a 5(e) or 5(f) Consent Order? **NO**
- Have there been any Section 8(e) submissions for this material? **YES**
- 3) **International Registration:** Are all components of this material listed on the following international inventories?:
- |        |                 |            |                             |
|--------|-----------------|------------|-----------------------------|
| TSCA   | (United States) | <b>YES</b> |                             |
| DSL    | (Canada)        | <b>YES</b> |                             |
| EINECS | (Europe)        | <b>YES</b> | (EINECS reg. no. 202-851-5) |
| METI   | (Japan)         | <b>YES</b> |                             |
| AICS   | (Australia)     | <b>YES</b> |                             |
| PICCS  | (Philippines)   | <b>YES</b> |                             |
| KMOE   | (Korean)        | <b>YES</b> | (KMOE reg. no. 3-1289)      |
- 4) **FDA:** Do FDA regulations permit use of this material as a direct or indirect food additive?
- |          |            |                    |
|----------|------------|--------------------|
| DIRECT   | <b>YES</b> | (21 CFR 172.515)   |
| INDIRECT | <b>YES</b> | (21 CFR 177.1640): |
- limited to 1.0 wt% as residue in polystyrene basic polymer or 0.5 wt% in rubber-modified polystyrene basic polymer.
- 5) **HAZARDOUS METALS:** Does the sum of the concentration levels of lead, cadmium, mercury and hexavalent chromium present in this material exceed 100 ppm by weight? **NO**
- 6) **ADDITIONAL REGULATORY INFORMATION:** See Chevron Phillips Chemical Company LP MSDS CPC00089, Section 15 for additional regulatory information.

## **PART 6**

### **APPENDIX**

#### **GLOSSARY OF TERMS, ABBREVIATIONS AND ORGANIZATIONS**

ACGIH	American Conference of Governmental Industrial Hygienists
AIAG	Automotive Industry Action Group
AIHA	American Industrial Hygiene Association
AALA	American Association for Laboratory Accreditation
ACC	American Chemistry Council
ANSI	American National Standards Institute
API	American Petroleum Institute
ASME	American Society of Mechanical Engineers
ASQ	American Society for Quality
ASTM	American Society for Testing and Materials
BABT	British Approvals Board of Communication
Bonding	The connection of two or more conductive objects by means of a conductor (most commonly a wire or metal plate)
BSI	British Standards Institute
CAA	Clean Air Act
CAAA	Clean Air Act Amendments
CAD	Computer-Aided Design
CANUTEC	Canadian Transport Emergency Centre
CE mark	Conformity European Union Mark
CEFIC	European Chemical Industry Council
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CG	Coast Guard

CHEMTREC	Chemical Transportation Emergency Center
Confined Space	An area that by design has limited openings for entry and exit. A confined space has unfavorable natural ventilation and is not intended for continuous worker occupancy.
CPC	Chemical protective clothing
DOT	Department of Transportation
ECHA	European Chemical Agency (Helsinki)
EPA	Environmental Protection Agency
ESD	Electro static discharge
EU	European Union
FDA	Food & Drug Administration
Flashpoint	The minimum temperature at which a liquid gives off vapor in sufficient concentrations to form an ignitable mixture with air near the surface of a liquid.
FMEA	Failure Mode Effect Analysis
GLP	Good Laboratory Practices
Grounding	The connection of one or more conductive objects to the ground: a specific form of bonding. Grounding is also referred to as earthing.
HAP	Hazardous Air Pollutant
HAZWOPER	Hazardous Waste Operations and Emergency Response
HON	Hazardous Organic NESHAP
IATA	International Air Transport Association
ICAO	International Civil Aviation Organization
IDLH	Immediately dangerous to life and health, the airborne concentration of a toxic material from which one could escape within 30 minutes without any escape-impairing symptoms or irreversible health effects.
IEEE	Institute of Electrical and Electronics Engineers
IMDG	International Maritime Dangerous Goods
IMO	International Maritime Organization
IQA	Institute of Quality Assurance

ISGOTT	International Safety Guide for Oil Tanker and Terminals
ISO	International Organization of Standardization
LFL	Lower Flammability Limit
MACT	Maximum Achievable Control Technology
MIL	Military
MPMS	Manual of Petroleum Measurement Standards (API)
MSDS	Material Safety Data Sheet
MSHA	Mine Safety and Health Administration
NACCB	National Accreditation Council for Certification Board
NDE	Nondestructive Evaluation
NDT	Nondestructive Testing
NEC	National Electrical Code
NESHAP	National Emission Standard for Hazardous Air Pollutants
NFPA	National Fire Protection Association
NIST	National Institutes of Standards and Technology
NIOSH	National Institute for Occupational Safety and Health
NPDES	National Pollutant Discharge Elimination System
OEM	Original Equipment Manufacture
OSHA	Occupational Safety and Health Administration
PM	Preventative Maintenance
PPE	Personal protective equipment
ppm	Parts per million.
QA	Quality Assurance
QC	Quality Control
RAB	Registrar Accreditation Board
RCRA	Resource Conservation and Recovery Act
REACH	European Community (EU) regulations - Registration, Evaluation, Authorization, and Restriction of Chemical Substances

RQ	Reportable Quantity
SARA	Superfund Amendment and Reauthorization Act
SCC	Standards Council of Canada
SIRC	Styrene Information and Research Center
SPC	Statistical Process Control
SQC	Statistical Quality Control
STEL	Short Term Exposure Limit
TOC	Total Organic Carbon
TPQ	Threshold planning quantity - under the Superfund Amendments Reauthorization Act (SARA Title III) Section 302, 304, 4311/312, a chemical specific quantity, in pounds, that triggers certain reporting requirements
TQC	Total Quality Control
TQM	Total Quality Management
TWA	Time-Weighted Average
UL	Underwriters Laboratory
Ullage	Amount by which a packaging falls short of being liquid full
UN	United Nations
USCG	United States Coast Guard
Vapor Pressure	The pressure exerted by a volatile liquid while under defined equilibrium conditions. Vapor pressure is usually measured in millimeters of mercury (mm Hg).
VOC	Volatile Organic Compound