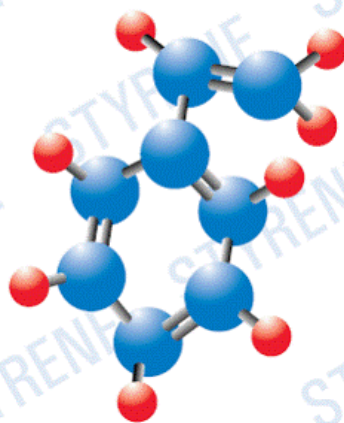


# Safe Handling and Storage of **Styrene Monomer**





## **Environmental, Health & Safety Policy**

Americas Styrenics is committed to safety excellence. We strive to make optimal use of the resources that we consume and to minimize emissions and waste.

We challenge ourselves to be a safer, more environmentally-conscious organization. We are committed to manufacturing, handling, transporting and disposing of chemical products safely. Americas Styrenics cares about the communities where we live and work by creating a culture that puts safety above all and enacts responsible environmental practices.

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## **PRODUCT STEWARDSHIP POLICY**

Americas Styrenics LLC is committed to good stewardship of our products. We manage product stewardship issues by providing customers, distributors, and traders with information regarding potential hazards and appropriate safe use and handling of our products. We will continuously review health, safety, environmental, and regulatory issues as they relate to Americas Styrenics' customers and markets.

We will meet our product stewardship commitments through the effective implementation of our Operating Discipline Management System (ODMS). Successful implementation of this management system will ensure that health, safety, and environmental protection are an integral part of designing, manufacturing, marketing, distributing, using, recycling, and disposing of our products.

**The information contained in this technical bulletin is not intended to, nor does it, amend or replace the Safety Data Sheet (SDS) for Styrene Monomer. The most current Safety Data Sheet can be obtained from Americas Styrenics by calling +1-844-512-1212 or from the Americas Styrenics web site ([www.AmSty.com](http://www.AmSty.com)) and should be carefully reviewed prior to working with this product.**

## **INTRODUCTION**

Americas Styrenics LLC is the third largest producer of styrene monomer in North America and one of the largest producers of polystyrene.

Styrene was first developed in 1928, and is now one of the most important monomers produced by the chemical industry. It serves as a 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 to produce a wide variety of polymers and copolymers. Styrene is readily polymerized and copolymerized by both batch and continuous processes (mass, emulsion, suspension and solution polymerization).

Americas Styrenics manufactures Styrene Monomer at its plant in St. James, Louisiana. The St James plant was originally owned by Gulf Oil Chemical Company and has been in operation since 1971. The plant has been ISO 9001 certified since 1994. St. James has been an OSHA VPP Star site since 2000.

**NOTE:**

**THIS GUIDE DOES NOT AMEND OR REPLACE OFFICIAL PUBLICATIONS, CURRENT SAFETY REGULATIONS, SAFETY DATA SHEETS, OR COMMERCIAL TERMS OF SALE. AMERICAS STYRENICS LLC MAKES NO GUARANTEE OF THE ACCURACY OF THE CONTENT OF THIS GUIDE 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 GUIDE.**

## 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>2,10</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 <sub>c</sub> ) <sup>3</sup>	39.5 atm (580 psia)		
Critical Temperature (t <sub>c</sub> ) <sup>3</sup>	374.4 °C (706 °F)		
Critical Volume (V <sub>c</sub> ) <sup>3</sup>	0.369 L/mole		
Cubical Coefficient of Expansion (per °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		
Decomposition Temperature	No data available		
Density of Liquid, (in air) <sup>5</sup>	<u>Temp. (°C)</u>	<u>g/cc</u>	<u>lb/US Gal.</u>
	0	0.9230	7.7031
	10	0.9138	7.6263
	20	0.9046	7.5496
	30	0.8954	7.4728
	40	0.8862	7.3960
	50	0.8770	7.3192
Dielectric Constant of Liquid <sup>6</sup>	<u>Temp. (°C)</u>	<u>ε</u>	
	20	2.4257	
	40	2.3884	
	60	2.3510	
Electrical Conductivity at 25 °C	2.8 x 10 <sup>-14</sup> mhos/cm		
Entropy of Gas at 25 °C (S°) <sup>2</sup>	82.48 kcal/(g-mole)-dy.		

Property	Value																				
Evaporation Rate (Butyl Acetate = 1)	0.49																				
Flammability (Solid, Gas)	Not Applicable																				
Flammability Limit – Upper	6.1 % (V)																				
– Lower	1.1 % (V)																				
Flash Point: <sup>7</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/(g-mole)																				
Freezing Point <sup>2</sup>	-30.628 °C (-23.13 °F)																				
Heat of Combustion Gas at Constant Pressure, 25 °C, to form gaseous products ( $\Delta H_o$ ) <sup>2</sup>	-1018.83 kcal/(g-mole)																				
Heat of Formation: <sup>2</sup> gas at 25 °C ( $\Delta H_f^\circ$ )	35.22 kcal/(g-mole)																				
liquid at 25 °C ( $\Delta H_f^\circ$ )	24.83 kcal/(g-mole)																				
Heat of Polymerization at 90 °C ( $\Delta H$ ) <sup>8</sup>	-17.8 kcal/(g-mole)																				
Heat of Vaporization at 145.1 °C <sup>10</sup>	8.82 kcal/(g-mole)																				
Henry's Law Constant (H) at 25 °C <sup>11</sup>	0.00275 atm m <sup>3</sup> /(g-mole)																				
Kinematic Viscosity at 25 °C	0.8 mm <sup>2</sup> /s																				
Molecular Weight	104.14 g/(g-mole)																				
Odor	Aromatic																				
Odor Threshold	0.1 ppm																				
Partition Coefficient: n-Octanol / Water at 25 °C	2.95 log P(o/w)																				
pH	Not Applicable																				
Physical State at Room Temperature	Liquid																				
Refractive Index: <sup>4</sup>	<table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">Temp. (°C)</th> <th style="text-align: center;"><math>N_D</math></th> </tr> </thead> <tbody> <tr><td style="text-align: center;">0</td><td style="text-align: center;">1.5579</td></tr> <tr><td style="text-align: center;">10</td><td style="text-align: center;">1.5523</td></tr> <tr><td style="text-align: center;">15</td><td style="text-align: center;">1.5495</td></tr> <tr><td style="text-align: center;">20</td><td style="text-align: center;">1.5467</td></tr> <tr><td style="text-align: center;">25</td><td style="text-align: center;">1.5439</td></tr> <tr><td style="text-align: center;">30</td><td style="text-align: center;">1.5410</td></tr> <tr><td style="text-align: center;">40</td><td style="text-align: center;">1.5354</td></tr> <tr><td style="text-align: center;">50</td><td style="text-align: center;">1.5298</td></tr> <tr><td style="text-align: center;">60</td><td style="text-align: center;">1.5242</td></tr> </tbody> </table>	Temp. (°C)	$N_D$	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
Temp. (°C)	$N_D$																				
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																				



Property	Value	
Relative Density <sup>2</sup>	<u>(°C)</u>	<u>g/cc</u>
	0	0.9250
	10	0.9158
	20	0.9066
	30	0.8974
	40	0.8882
	50	0.8790
	60	0.8698
	70	0.8605
	80	0.8513
	90	0.8421
100	0.8329	
Relative Vapor Density (Air = 1) at 20 °C	3.6	
Solubility of Oxygen (from air) in Styrene	<u>Temp. (°C)</u>	<u>ppm</u>
	15	53
	25	50
	35	45
Solubility: Styrene in Water <sup>9</sup>	<u>Temp. (°C)</u>	<u>(g/100 g H<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>9</sup>	<u>Temp. (°C)</u>	<u>(g/100 g styrene)</u>
	0	0.020
	20	0.060
	40	0.100
	60	0.140
	80	0.180
Solubility in: <sup>10</sup>	Acetone	∞
	CS <sub>2</sub>	∞
	Benzene	∞
	Ether	∞
	n-Heptane	∞
	Ethanol	∞
Specific Heat <sup>8</sup>	<u>(°C)</u>	<u>(cal/g-°C)</u>
	0	0.4004
	20	0.4131
	40	0.4269
	60	0.4421
	80	0.4590
	100	0.4774

Property	Value	
Specific Heat (vapor) <sup>2</sup>	<u>Temp. (°C)</u>	<u>C<sub>p</sub> (cal/g-°C)</u>
	0	0.256
	25.0	0.280
Surface Tension <sup>8</sup>	<u>(°C)</u>	<u>dynes/cm</u>
	0	34.5
	20	32.3
	40	30.0
	60	27.8
	80	25.6
Thermal Conductivity	<u>Temp. °C (°F)</u>	<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
Vapor Pressure <sup>2</sup>	<u>Temp. (°C)</u>	<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	
Viscosity <sup>4</sup>	<u>Temp. (°C)</u>	<u>(Centipoise)</u>
	0	1.040
	20	0.763
	40	0.586
	60	0.470
	80	0.385
	100	0.326
	120	0.278
Volumetric Shrinkage upon Polymerization (typical)	17%	

## 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. Calculated using ASTM D1555-09 tables.
6. J. Petro and C. P. Smyth, J. Amer. Chem. Soc., 80, 73 (1958).
7. Manufacturing Chemists Association Chemical Safety Data Sheet SD-37 (Rev. 1971), p. 5.
8. R. H. Boundy and R. F. Boyer (Eds.), "Styrene: Its Polymers, Copolymers, and Derivatives", Reinhold, New York, 1952, Ch. 3.
9. W. H. Lane, Ind. Eng. Chem. (Anal. Ed.), 18, 295, (1946).
10. R. R. Dreisbach, "Physical Properties of Chemical Compounds", Vol. 1, Am. Chem. Soc., 1955, p. 159.
11. K. Bocek, Experimetia, Suppl 23: 231-40 (1976).

## Analytical Methods

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

1. D1209 Color of Clear Liquids (Platinum-Cobalt Scale)
2. D1364 Water in Volatile Solvents (Karl Fischer Reagent Titration Method)
3. D2119 Aldehydes in Styrene Monomer
4. D2121 Polymer Content of Styrene Monomer
5. D2340 Peroxides in Styrene Monomer
6. D4052 Density and Relative Density of Liquids by Digital Density Meter
7. D4176 Free Water and Particulate Contamination in Distillate Fuels (Visual Inspection Procedures)
8. D4590 Colorimetric Determination of p-tert-Butylcatechol in Styrene Monomer by Spectrophotometry <sup>(a)</sup>
9. D5135 Analysis of Styrene by Capillary Gas Chromatography
10. D5386 Color of Liquids using Tristimulus Colorimetry
11. D6229 Standard Test Method for Trace Benzene in Hydrocarbon Solvents by Capillary Gas Chromatography
12. D7375 Trace Quantities of Water in Aromatic Hydrocarbons and Their Mixtures by Coulometric Karl Fisher Titration
13. D7504 Standard Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography and Effective Carbon Number
14. D7704 Standard Test Method for Total Aldehydes in Styrene Monomer by Potentiometric Titration
15. D8005 Standard Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)
16. E1064 Standard Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration

(a) AmSty routinely provides TBC Test Comparison Cards to customers (upon request) for estimating inhibitor levels. Please contact your Account Management Specialist or Sales representative for information.

## 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 guide.

#### 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, detergent, 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

### **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 and 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. Make sure the tank car's internal pressure has been relieved before removing the manhole or outlet valve cap.
3. Visually inspect hoses and fittings prior to use.
4. 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.
5. Purging all lines with nitrogen prior to transfer of product reduces risk of flash fires.
6. Unload the car through the dome connection or through the bottom outlet. Check carefully for leaks.
7. Use of air pressure to unload tank cars is not recommended. If pressure must be used, the operator should demonstrate caution and only use an inert gas such as nitrogen.
8. Use an approved pump to unload the tank car. If the car does not have an eductor (discharge) pipe, insert a pipe through the open dome and pump its contents out through the pipe.
9. Carefully vent the car through a flame arrester during unloading.
10. If unloading is interrupted, disconnect all unloading connections, close all valves tightly and securely apply all other closures.
11. Tank cars should be cleaned and prepared for shipment in accordance with DOT regulations prior to releasing.

## 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 the primary 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 all important factors in maintaining a long shelf life.

**Contact AmSty (+1-844-512-1212) with questions regarding Styrene Monomer inhibition and inhibitor testing.**

#### **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/g-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 149 °F (65 °C) 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. 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.

#### **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 (1.6 °C) 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, but AmSty may be contacted for guidance at +1-844-512-1212. 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.

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 in a pond or confined area.

### TBC Inhibitor Test Comparison Card

The AmSty TBC Inhibitor Test Comparison Card can be used to estimate inhibitor levels under laboratory and field conditions. This Test Comparison Card may be obtained by contacting your Sales representative or by mailing a request to:

Americas Styrenics LLC  
24 Waterway Avenue  
Suite 1200  
The Woodlands, TX 77380

**Note:** TBC Specification analysis must be performed using ASTM Method D4590.

### 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, and (2) they can act

as an antioxidant and prevent polymerization by reacting with oxidation products in the monomer. **Note:** 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 drop below 10 ppm to maintain adequate inhibition. Normal levels are 10-15 ppm, but some customers may require up to 100 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 the 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 lb (186 kg). 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.

**Table 1**

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

Monomer Temperature	12 ppm TBC		50 ppm TBC
	Saturated with Air	Less than 3 ppm O <sub>2</sub>	Saturated with Air
60 °F (15.6 °C)	6 months	10 to 15 days	1 year
85 °F (29.4 °C)	3 months	4 to 5 days	6 months
110 °F (43.3 °C)	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	
80 °F (26.7 °C) or Higher	Twice a week	Polymer	ASTM D2121
		Inhibitor	ASTM D4590
70 – 79 °F (21.1 – 26.1 °C)	Weekly	Color	ASTM D5386
		Aldehydes	ASTM D2119
Below 70 °F (21.1 °C)	Bi-weekly	Peroxides	ASTM D2340
		Appearance	ASTM D4176

**Table 2C**

**Suggested Inspection Schedule for  
Styrene Bulk Storage**

<b>Inspection</b>	<b>Frequency</b>
Air Vents	Quarterly
Vacuum Pressure Relief	
Flame Arrester	
Foam Reservoir should be inspected for polymer	
Tank Interior	Every three (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 of approximately 1-2 ft<sup>3</sup>/hr/million lb (0.06-0.12 m<sup>3</sup>/hr/million kg) 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 g TBC/liter Styrene)**

<b>Gallons Styrene</b>	<b>0</b>	<b>100</b>	<b>200</b>	<b>300</b>	<b>400</b>	<b>500</b>	<b>600</b>	<b>700</b>	<b>800</b>	<b>900</b>
	<b>cc of Concentrate Required</b>									
<b>0</b>	—	20.4	40.7	61.1	81.4	101.8	122.1	142.5	162.8	183.2
<b>1000</b>	204	224	244	265	285	305	326	346	366	387
<b>2000</b>	407	427	448	468	488	509	529	549	570	590
<b>3000</b>	611	631	651	672	692	712	733	753	773	794
<b>4000</b>	814	834	855	875	895	916	936	957	977	997
<b>5000</b>	1018	1038	1058	1079	1099	1119	1140	1160	1180	1201
<b>6000</b>	1221	1241	1262	1282	1303	1323	1343	1364	1384	1404
<b>7000</b>	1425	1445	1465	1486	1506	1526	1547	1567	1587	1608
<b>8000</b>	1628	1648	1669	1689	1710	1730	1750	1771	1791	1811
<b>9000</b>	1832	1852	1872	1893	1913	1933	1954	1974	1994	2015
<b>10000</b>	2035	2056	2076	2096	2117	2137	2157	2178	2198	2218

\* Calculated using styrene density in air at 20 °C

**TABLE 3B**

**cc of Concentrate Required to Increase TBC in Styrene by 1 ppm\*  
(85 % TBC and 15 % Methanol)**

Gallons Styrene	cc of TBC Required									
	0	100	200	300	400	500	600	700	800	900
0	—	0.4	0.8	1.1	1.5	1.9	2.3	2.6	3.0	3.4
1000	3.8	4.2	4.5	4.9	5.3	5.7	6.1	6.4	6.8	7.2
2000	7.6	7.9	8.3	8.7	9.1	9.5	9.8	10.2	10.6	11.0
3000	11.4	11.7	12.1	12.5	12.9	13.2	13.6	14.0	14.4	14.8
4000	15.1	15.5	15.9	16.3	16.7	17.0	17.4	17.8	18.2	18.5
5000	18.9	19.3	19.7	20.1	20.4	20.8	21.2	21.6	22.0	22.3
6000	22.7	23.1	23.5	23.8	24.2	24.6	25.0	25.4	25.7	26.1
7000	26.5	26.9	27.3	27.6	28.0	28.4	28.8	29.1	29.5	29.9
8000	30.3	30.7	31.0	31.4	31.8	32.2	32.6	32.9	33.3	33.7
9000	34.1	34.4	34.8	35.2	35.6	36.0	36.3	36.7	37.1	37.5
10000	37.9	38.2	38.6	39.0	39.4	39.7	40.1	40.5	40.9	41.3

\* Calculated using styrene density in air at 20 °C

Example: Current TBC level = 8 ppm; desired TBC level = 15; Difference = 7 ppm; Volume = 5900 gallons of styrene

22.3 (from table) X 7 = 156 cc of TBC required

## 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 when handling TBC. See information on toxicological properties and safe handling of TBC as well as the manufacturer's SDS.

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 Table 3A.

## Polymer Formation During Storage

The polymer formed 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 formed in tanks also creates 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 15 by ASTM D5386 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 into or dissolving from the walls and roof of the storage tank.
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 occur 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. Figures 1 and 2 show two different types of storage installations.

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 is recommended for environments where temperatures exceed 75 °F (23.9 °C) for long periods of time.

Most consuming locations insulate storage tanks to dampen the effect of high daytime 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. To facilitate mixing where external refrigeration is employed, it is recommended that either the outlet line or the

inlet line operate through a floating swing-pipe, adjusted so that the monomer is always either withdrawn or discharged a few inches below the surface. Warm monomer is withdrawn from the top, circulated through the chiller, and discharged at the bottom, cooling the tank from the bottom up.

This type of system will also perform satisfactorily where the outlet and inlet lines are reversed and the pump withdraws monomer from the bottom, circulates it through the chiller and discharges through the swing-pipe near the surface. Eddy currents induced by temperature differences between the chilled monomer and the stored monomer lead to relatively uniform mixing.

Tank linings have proven quite successful in controlling or reducing polymer and stalactite formation. A tight, non-porous, 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 (15 – 20 cm) 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.

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

#### **TABLE 4**

##### **Types of Coatings and Suppliers**

###### Inorganic Zinc Silicate Primer

1. Dimetcote 6      PPG Industries Europe

###### Baked Phenolic

1. Heresite P403L      Heresite Protective Coatings
2. Phenguard 930, 935, and 940      PPG Protective & Marine Coatings

###### Modified Phenolic Epoxy

1. Amercoat 346      PPG Coatings Europe

###### Epoxy Novolac

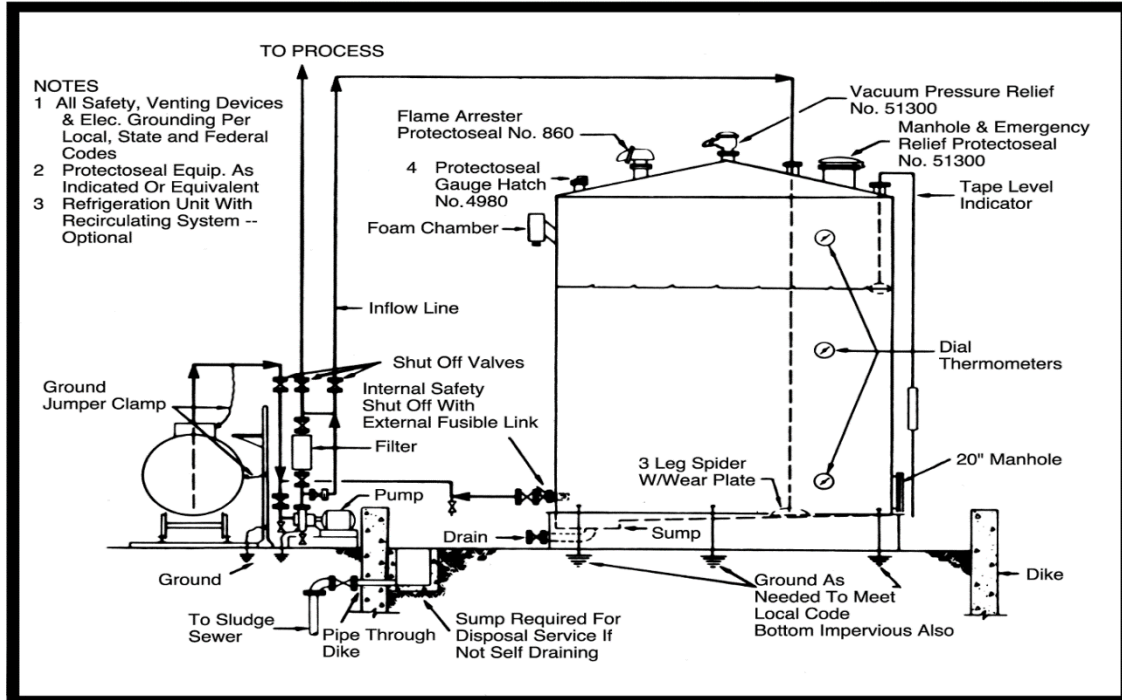
1. Devchem 253      Akzo Nobel

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.

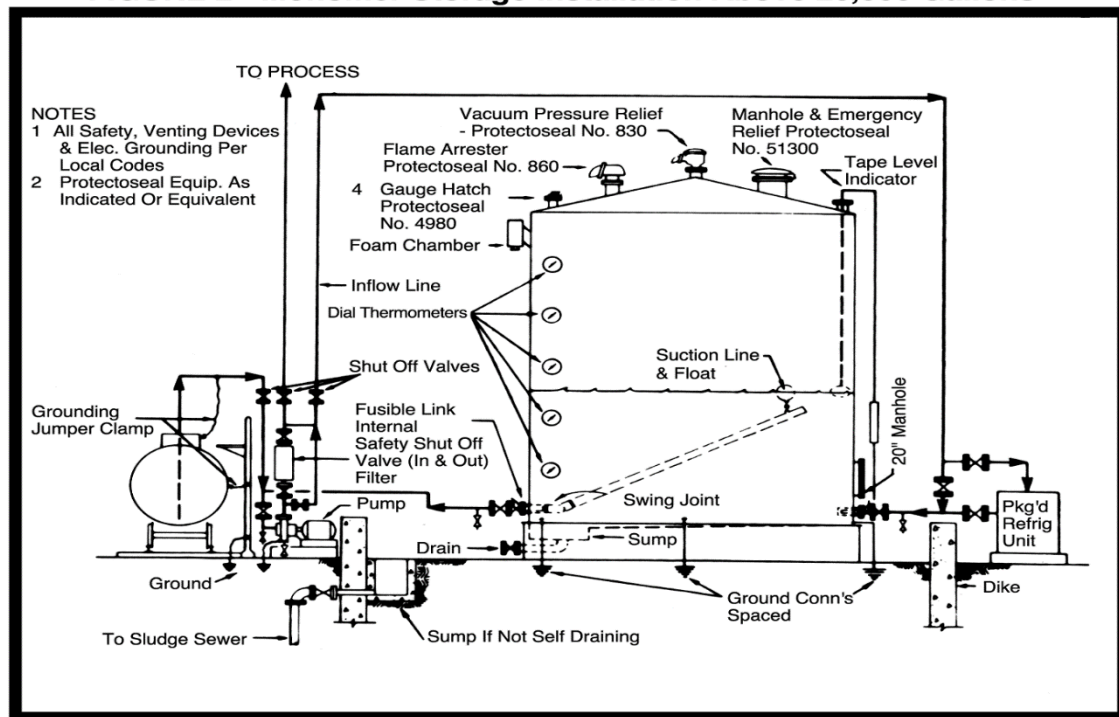
Requirements of diking, tank spacing, and other features pertaining to safety are detailed in guidelines set by the National Fire Protection Association (see NFPA 30). These, as well as local building codes and governmental regulations, should be consulted since some requirements vary with the size and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



**FIGURE 1 - Monomer Storage Installation up to 20,000 Gallons**



**FIGURE 2 - Monomer Storage Installation Above 20,000 Gallons**



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 coating, Teflon<sup>®</sup>, 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 1-inch (2.5 cm) 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. Bellow valves are recommended for 2-inch (5 cm) 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 manufacturer 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 enclosed 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 Viton® seats 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® GRAPH-LOCK®, Garlock® Gylon® 3500 Series, Teflon®, Viton® B, Durlon® 9000N, Grafoil® GHE, or their equivalents are satisfactory for flanged connections at ambient conditions. Reinforced graphite composite gaskets are also recommended. Gaskets made of rubber or other styrene-soluble materials should be avoided.

## Filters

Since small amounts of foreign matter may enter storage tanks from various sources, a filter in the transfer piping between the tank(s) 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 replaced 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® tube, or the equivalent. Multi-layered polypropylene and Teflon® 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 each use. Ethylbenzene or toluene may be used to clean these 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® GF-S, Viton® B, Teflon®, 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-in (3.2 mm). 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 Metal Blast” zone. Otherwise, re-blasting 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).

**Warning** - 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 lining-

application work since the solvents are also flammable. 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 Monomer until the requirements of 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 USA

### **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; Non-refrigerated 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 Monomer 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.

Safety Data Sheets for styrene are available from AmSty 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 AmSty at +1-844-512-1212 to request the SDS for Styrene Monomer, or download it from [www.AmSty.com](http://www.AmSty.com). **NOTE: This guide is not a substitute for the SDS.**

The following briefly summarizes the toxicological information. The precautions recommended are 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 +1.703.741.5970.**

CHEMTREC will provide the caller preliminary emergency assistance in the form of Safety Data Sheet (SDS) information. In all cases, once CHEMTREC determines the incident involves an AmSty material, CHEMTREC will immediately contact the Americas Styrenics' Emergency Response representative, who will

then be responsible for coordinating an appropriate response to the transportation incident.

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 lb (453.6 kg). 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.

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 AmSty 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 a 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 fires 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

Autoignition Temp.: 490 °C (914 °F)

Flammable Limits in Air: 0.9 - 6.8 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 the 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 indicated 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.

Styrene 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 ensure 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.

Personnel conducting the cleanup 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®, Polyethylene-Ethylene Vinyl Alcohol laminated film, 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, CFR, 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

### STYRENE:

**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 at 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 SDS for styrene for a more complete discussion of the toxicity of styrene.

#### **4-TERT-BUTYLCATECHOL (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 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 a 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 SDS 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

##### **LABELING:**

Containers should be labeled in accordance with applicable OSHA and DOT requirements.

Identification numbers are required on each side and each end if the 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. Markings for non-bulk packaging (119 gallons or less) include the proper shipping name, identification number preceded by UN or NA, the technical name if applicable, and the consignee or consignor's name and address.

Labels are required on non-bulk packages and must be located on the same surface and near the marking.

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

Requirements concerning marking, labeling, placarding, and the preparation of shipping papers vary somewhat 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 show sample labels and placards. Labels and placards applicable to flammable liquids are required for styrene monomer. Bulk containers should remain placarded when emptied unless the special requirements of Subpart F are met.

##### **CHEMICAL DESIGNATIONS:**

U. S. Coast Guard 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**

<b>Code of Federal Regulations Category</b>	<b>Flammable Liquid NAS Hazard Rating for Bulk Water Transportation</b>
<u>Fire</u>	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:**

<b>Category</b>	<b>Rating</b>
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>
723.50	(Low Volume Exemption)	<b>NO</b>
720.36	(R&D Exemption)	<b>NO</b>
720.38	(Test Marketing Exemption)	<b>NO</b>
723.25	(Polymer Exemption)	<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?

INDIRECT **YES** (21 CFR 177.1640)

Limited to 1.0 WT% as residual styrene monomer in General Purpose Polystyrene (GPPS) or 0.5 WT% in High Impact Polystyrene (HIPS).

- 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 AmSty SDS for Styrene Monomer, Section 15 for additional regulatory information.

## Revision Statements

July 2011

1. Updated EH&S Policy, inside cover
2. Updated page 8 with Sales Specification values
3. Updated list of Analytical ASTM test methods, page 9
4. Updated Flammability Limits, page 28
5. Various editorial corrections

November 2016

1. Updated AmSty logo, phone numbers and overall format
2. Updated EH&S Policy
3. Removed Sales Specification
4. Updated Product Stewardship Policy
5. Updated Introduction
6. Updated Physical Properties list
7. Updated References list
8. Updated Analytical Methods list
9. Updated Tables 1, 2B, 3A and 3B
10. Updated lists of approved materials for Gaskets and O-rings

**PART 6**

**APPENDIX**

**Glossary of Terms, Abbreviations and Organizations**

ACGIH	American Conference of Governmental Industrial Hygienists
ANSI	American National Standards Institute
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
Bonding	The connection of two or more conductive objects by means of a conductor (most commonly a wire or metal plate)
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CG	Coast Guard
CHEMTREC	Chemical Transportation Emergency Center
DOT	Department of Transportation
EPA	Environmental Protection Agency
FDA	Food & Drug Administration
IMO	International Maritime Organization
ISGOTT	International Safety Guide for Oil Tanker and Terminals
ISO	International Organization of Standardization
MSHA	Mine Safety and Health Administration
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
ppm	Parts per million
RQ	Reportable Quantity
SDS	Safety Data Sheet
SIRC	Styrene Information and Research Center

SQC	Statistical Quality Control
TWA	Time-Weighted Average
UN	United Nations
USCG	United States Coast Guard
WT%	Weight percent