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Executive Summary

The Toxics Use Reduction Act (TURA) was passed in 1989 with the goal of reducing toxic waste generated in Massachusetts by 50% by 1997 using toxics use reduction as the means of meeting this goal. TURA data from the 1990 reporting year, the most recent data currently available, showed that styrene was the chemical used in the highest quantity in Massachusetts. Total styrene use in the state for 1990 was reported as approximately 395 million pounds.

The large quantity of styrene in use in Massachusetts raises questions regarding the safety of this chemical. Of primary concern is the health and safety of workers using styrene, public exposure to styrene emissions and the potential for an accidental release of the chemical during transportation or during use in the industrial facility.

Styrene is commonly used in the production of plastics and resins. Exposure to this chemical is most likely to occur in the industrial setting where inhalation of styrene vapors and skin contact with liquid styrene are possible. Styrene has multiple toxic properties. At concentrations less than 100 ppm, styrene can cause irritation of the eyes, respiratory tract and mucous membranes. For long-term occupational exposure, there is evidence of nervous system and respiratory disorders. Styrene is also considered to be a mutagen, a developmental toxin and is classified by the Environmental Protection Agency (EPA) as a Group C carcinogen; this category is for chemicals with limited evidence of carcinogenicity in animals in the absence of human data. Styrene is highly volatile and flammable. Polymerization inhibitor levels must be properly maintained in order to prevent rapid polymerization which is exothermic and may result in explosive conditions.

The primary use of styrene in Massachusetts and nationwide is in the production of polystyrene. The polystyrene production industry in this state consumed 99% of the styrene used in Massachusetts in 1990 according to the TURA data. Polystyrene typically is manufactured in large facilities where high volumes of the plastic are produced. Worker exposure to styrene in these facilities is usually well monitored and maintained within OSHA permissible exposure limits. However, with the large quantity of styrene used in polystyrene production, handling accidents potentially could be a significant source of worker and public exposure. Over the past six years, since the Department of Environmental Protection (DEP) began recording accidental releases, 28 accidental releases of styrene have been reported. Almost all of these releases have occurred on-site at the industrial facility. The extent of worker exposure due to these releases is unknown. Very few releases have occurred during styrene transportation; therefore styrene exposure to the public from accidental releases has not been significant.

All facilities reporting styrene use in 1990 under TURA reported air emissions of styrene. Most air emissions associated with production of styrene-based products arise from loading
operations, styrene storage, handling operations, equipment leaks, process vents and secondary sources such as waste treatment and disposal facilities.

The remaining one percent of reported styrene use in Massachusetts was for styrene-based resin blending, polymer latex production and polyester resin use. Based on in-process emissions data and current occupational health research, manufacturing processes that use styrene-based unsaturated polyester resins clearly present the greatest potential for routine worker exposures to styrene. Typically, unsaturated polyester resin operations involve manual operations that require the worker to be in close proximity to the styrene vapors throughout the process. Additionally, the industries using unsaturated polyester resins are often small shops where lack of capital funds may delay the incorporation of control measures.

Several states have initiated programs to reduce industrial styrene emissions and exposures. These programs have focused on industries using styrene based polyester resins, particularly fiberglass reinforced plastics manufacturers. States’ projects have evaluated the efficacy of replacing traditional resins with low styrene resins. Other programs have investigated production-based options to reduce emissions, including process changes and equipment modifications. Although these programs have concentrated on unsaturated polyester resin use, all facilities using styrene should consider improvements to reduce styrene emissions in light of the uncertainty of the health effects of long-term exposures.
Introduction

The Toxics Use Reduction Act (TURA) was passed in 1989 with the goal of reducing toxic waste generated in Massachusetts by 50% by 1997 using toxics use reduction as the means of meeting this goal. Companies who use over a threshold amount of any reportable chemical are required to list the quantities of chemicals used, quantity of byproduct generated, and other information on chemical use and emissions in their facility. TURA data from the 1990 reporting year, the most recent data currently available, showed that styrene was the chemical used in the highest quantity in Massachusetts. Total styrene use in the state for 1990 was reported as approximately 395 million pounds.

With such large quantities of styrene in use in Massachusetts, there are questions regarding the safety of this chemical. The extent and effects of exposure to workers in facilities using styrene and to the general public are of primary concern when such large quantities of any chemical are in use. This document examines the effects of styrene on human health and the environment and the potential for occupational exposures and accidental releases. By reviewing the health and safety hazards of styrene, the manufacturing processes using styrene, the process emissions and the history of accidental releases, the areas of greatest concern in styrene use are identified.

Styrene in the Environment

Styrene is a colorless to yellowish, oily liquid at room temperature. It is manufactured from the petroleum hydrocarbons benzene and ethylene and is used in the production of plastics and resins (see Figure 1). Exposure to styrene is most likely to occur in the industrial setting where inhalation of styrene vapors and skin contact with liquid styrene are possible. In addition to industrial emissions, styrene is released into the environment in automobile exhaust, stack emissions from waste incineration, cigarette smoke and from burning styrene-based products. Styrene has been detected in small quantities in foods which are packaged in polystyrene containers. Low levels of styrene exposure also occur through consumers' use of products containing styrene such as floor waxes, paints, adhesives, putty, metal cleaners, fiberglass boats and varnishes. Styrene is also an FDA approved flavoring agent used in ice cream and candy.¹

Chemical and Physical Properties

The chemical and physical properties of styrene summarized here are listed in the Appendix. Styrene has a vapor pressure of 6.6 mm Hg and exists as a liquid at room temperature. It is slightly soluble in water (310 mg/L at 77°F or 25°C) and will volatilize rapidly from water. Styrene is not likely to bioconcentrate in biological organisms because of its solubility in water and its volatility. At temperatures greater than 90°F (32°C), styrene will readily
Figure 1. Polystyrene Production
polymerize if chemical inhibitors are not added. The polymerization of styrene releases heat and may become explosive. Styrene is highly flammable and must be properly stored to avoid hazardous conditions.

**Health Hazards**

The health risks associated with styrene exposure have been the subject of considerable attention over the last twenty years. Studies have been conducted using laboratory animals and human volunteers, and epidemiological studies have been done which examine groups of workers who have experienced long-term styrene exposures. The results of such studies on styrene are often inconclusive.

Styrene has been shown to cause irritation of the mucous membranes, the eyes and the respiratory tract at exposure levels over 100 parts per million (ppm). For durations of a few minutes and exposures exceeding 200 ppm, human volunteers have experienced drowsiness, nausea and disturbed balance. Workers who have had long-term occupational exposure to styrene have experienced neurological damage and respiratory disorders. Laboratory studies have shown styrene oxide, a major metabolite of styrene, to be mutagenic in experimental systems. Although the evidence is not strong, styrene is also considered a developmental toxin. No data were found that implicated styrene as a reproductive toxin.

There is some evidence for an association between industrial styrene exposures and increased risk of lymphatic and hematopoietic tumors. However, this evidence is insufficient to designate styrene as carcinogenic due to limitations in these studies such as multiple chemical exposures and small cohort sizes. The International Agency for Research on Cancer (IARC) classifies styrene as a Group 2B Carcinogen, which is defined as "Possibly carcinogenic in humans based on sufficient evidence in animals but inadequate evidence in humans." Styrene is currently classified by the US EPA as a Group C carcinogen; this category is for chemicals with limited evidence of carcinogenicity in animals in the absence of human data.

The National Toxicology Program (NTP) in its "Management Status Report" lists a 1979 study of styrene with equivocal evidence of carcinogenicity for male mice, and negative evidence for female mice and both male and female rats. Equivocal evidence is demonstrated by studies that show a marginal increase of neoplasms that may be chemically related. Styrene is also currently under study by NTP; in July 1993 its status is given as "prechronic studies completed: chemical in review for further evaluation."

In 1989, the Occupational Safety and Health Administration (OSHA) lowered the time weighted average (TWA) permissible exposure limit (PEL) for styrene vapor exposure from 100 ppm to 50 ppm (Table 1), effective on December 31, 1993. Until these regulations go into effect, an approved respirator program must be used to meet the reduced exposure limit. Once in effect, industry must meet the exposure limit requirements by purchasing and
installing better engineering control equipment, or by making process changes which eliminate or reduce emissions to acceptable levels.

At exposure levels below the OSHA PEL of 50 ppm, different studies have reached contradictory conclusions. One 1989 study of workers handling polyester resin materials concluded that "occupational exposure to styrene concentrations in air up to 100 ppm causes no adverse acute or chronic effects on the central nervous system."\(^6\) Another study of workers handling polyester resins, conducted in 1992, found "minor but significant organic mental disorders in the subjects exposed to a mean dose of 30 ppm."\(^7\) The question as to whether neurotoxic effects are incurred by low level styrene exposures remains unanswered while further research continues.

The PEL was reduced based on several studies demonstrating possible nervous system toxicity, irritation and potential carcinogenic effects. OSHA reduced the PEL to "one-tenth the lowest concentration possibly causing lymphoid or hematopoietic tumors in female rats".\(^8\) The short-term exposure limit (STEL) was reduced based on eye and respiratory tract irritation. The National Institute of Occupational Safety and Health (NIOSH) also recommended the reduction of the TWA exposure limit to 50 ppm. Their recommendation was based on nervous system effects.

Table 1: OSHA Exposure Limits\(^9\)
(NIOSH, Pocket Guide to Chemical Hazards, 1990)

<table>
<thead>
<tr>
<th>Type of Exposure Limit</th>
<th>Exposure Limit</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PEL</strong> (Permissible Exposure Limit)</td>
<td>50 ppm</td>
<td>The Time Weighted Average (TWA) concentration; average exposure over a 10 hour workday, over a 40 hour workweek is not to exceed this level.</td>
</tr>
<tr>
<td><strong>STEL</strong> (Short Term Exposure Limit)</td>
<td>100 ppm</td>
<td>Exposure is not to exceed this level for any 15 minute period.</td>
</tr>
<tr>
<td><strong>IDLH</strong> (Immediately Dangerous to Life or Health)</td>
<td>5000 ppm</td>
<td>The maximum concentration from which one could escape within 30 minutes without a respirator without experiencing any escape-impairing or irreversible effects.</td>
</tr>
</tbody>
</table>

**Safety Hazards**

Styrene is highly volatile, flammable and, if inhibitor levels are not properly maintained, is subject to hazardous polymerization. Without the addition of a chemical inhibitor, styrene
polymerizes slowly (approximately 0.2% per hour) at room temperature. The rate of polymerization increases rapidly with increasing temperatures. For example, the polymerization rate increases to 25% per hour at 284°F (140°C). Since this is an exothermic reaction, the polymerization becomes self accelerating once initiated, resulting in runaway polymerization. As the temperature increases, the unreacted styrene vaporizes inside the vessel and can cause potentially explosive conditions. Such hazardous conditions can be avoided by controlling the level of polymerization inhibitor.

The potential for formation of an explosive mixture is a function of the explosive limits, temperature and pressure. Temperatures greater than 90°F (32°C) can raise the vapor concentrations to potentially explosive levels. The flash point (the temperature at which the liquid styrene gives off a vapor sufficient to form an ignitable mixture) is 88°F (31°C) and the fire point (the temperature at which the liquid styrene forms vapors fast enough to sustain combustion) is 93°F (34°C). With the potential for such dangerous conditions at relatively low temperatures, it is very important to store styrene in clean, properly ventilated storage containers in a cool area with adequate polymerization inhibitor.

**Method of Manufacture**

Production of styrene is dependent on natural gas and petroleum. The majority of styrene produced in the United States is carried out by the conversion of benzene and ethylene to ethylbenzene, followed by the dehydrogenation of ethylbenzene. Dehydrogenation is shown by the reaction:

\[
\text{Ethylbenzene} \xrightarrow{650^\circ C} \text{Styrene} + \text{Hydrogen}
\]

These processes, as well as polymerization processes used to produce plastics, were developed in the 1920’s and 1930’s in Germany and the U.S. Large scale production began in the U.S. in 1935. With a dramatic increase in the demand for synthetic rubber during World War II, the demand for styrene (a feedstock chemical in the production of synthetic rubber) also escalated. Since that time, the trend in styrene demand has continued to rise. However, recently the rate of growth of styrene demand has decreased. From 1982 - 1991, the demand for styrene increased by 4.7%/year in the U.S. Currently, growth in demand is not expected to average more than 2.5%/year through 1996. The reduced growth is due to declining export opportunities and mounting environmental pressures on the production of polystyrene. In 1992, consumption of polystyrene, by far the largest styrene derivative, dropped 3.4%.
Table 2. U.S. Styrene Producers
*(Chemical Marketing Reporter, January 1, 1993)*

<table>
<thead>
<tr>
<th>PRODUCER</th>
<th>CAPACITY (lbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amoco, Texas City, TX</td>
<td>800,000,000</td>
</tr>
<tr>
<td>Arco, Channelview, TX</td>
<td>1,400,000,000</td>
</tr>
<tr>
<td>Arco, Channelview, TX</td>
<td>1,125,000,000</td>
</tr>
<tr>
<td>Chevron, St. James, LA</td>
<td>1,500,000,000</td>
</tr>
<tr>
<td>Cos-Mar, Carville, LA</td>
<td>1,900,000,000</td>
</tr>
<tr>
<td>Dow, Freeport, TX</td>
<td>1,400,000,000</td>
</tr>
<tr>
<td>Huntsman, Bayport, TX</td>
<td>1,250,000,000</td>
</tr>
<tr>
<td>Rexene, Odessa, TX</td>
<td>320,000,000</td>
</tr>
<tr>
<td>Sterling, Texas City, TX</td>
<td>1,600,000,000</td>
</tr>
<tr>
<td>Westlake, Lake Charles, LA</td>
<td>350,000,000</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>11,645,000,000</strong></td>
</tr>
</tbody>
</table>

Ten facilities in the U.S. have the capacity to produce an annual total of 11 billion pounds of styrene. These facilities are all located in Texas and Louisiana; there are no styrene production facilities in Massachusetts (see Table 2).

**Styrene Use in Massachusetts**

Total styrene use in Massachusetts, as reported under the requirements of the Toxics Use Reduction Act (TURA), in 1990 was over 395 million pounds. Figure 2 shows the locations of companies in Massachusetts using styrene. Companies which manufacture or process less than 25,000 lbs. of a chemical annually and companies which "otherwise use" less than 10,000 lbs. of a chemical annually are not included in this estimate.

Much of the information on the quantities and specific uses of styrene in Massachusetts is derived from the TURA data (1990) and EPA’s Toxics Release Inventory (TRI) data (1990 and 1991), which are reported by industry. Both TURA and TRI require industry to report emissions for any chemical used over a threshold quantity. Additionally, TURA requires facilities to report chemical use over a threshold quantity.
Styrene use in Massachusetts, as reported in the 1990 TURA database, is summarized in Table 3. Inconsistencies exist both within the TURA database and between the TURA and TRI databases. 1990 is the first year for which companies were required to file TURA reports; therefore, the quality of the data is not expected to be high. In the TURA database, for example, it appears that at least one company assumed that styrene was "Shipped In or As Product" in polystyrene, whereas other filers did not consider that their products contained styrene since it had been processed and converted to polystyrene or other products. In addition, there are cases where the by-product is less than total emissions. At a minimum, byproduct should equal emissions, because emissions are a subset of byproducts. Inconsistencies between the TURA and TRI databases include two companies which filed for styrene under TRI for 1990, but which did not list styrene use in the 1990 TURA database. It should be noted that the information presented here is drawn from the databases as they existed at the time of publication of this report. Both the TRI and TURA databases are continually being updated as facilities file for past years, revise their past reports, and as data entry errors are discovered.

The primary use of styrene nationwide, and in Massachusetts, is in the production of polystyrene. Styrene is also used to produce other polymer products such as styrene-acrylonitrile (SAN), acrylonitrile-butadiene-styrene (ABS), unsaturated polyester resins and styrene butadiene rubber (SBR). In Massachusetts, styrene uses include:

- polystyrene production (Mobil Chemical, American Polymers, Polysar Inc.)
- use as a resin in the production of fiberglass boats (Boston Whaler)
- use in manufacturing a polyester resin for molding bowling balls (E. Parrela Co.)
- polymerization of styrene to manufacture solid resins and resin solutions (ICI Resins US)

Polystyrene production accounts for approximately 99% of styrene used in Massachusetts among companies reporting styrene use under TURA in 1990. Nationwide, polystyrene production consumes 66% of the styrene produced in the U.S. in 1992. Table 4 shows the uses of styrene nationwide. Each of these manufacturing processes are described below.

- **Polystyrene**

  Polystyrene is a transparent, solid, very light weight plastic produced by the polymerization of styrene monomer. The polymer is produced in a wide range of formulations including crystal, high impact and expandable. As a "homopolymer", polystyrene is brittle and therefore, additives are used to increase its impact resistance. Polystyrene has excellent electrical and insulation properties. The major end uses for polystyrene are in packaging, such as egg cartons, fast-food packages, cups and containers for food, juices and dairy products. Polystyrene is also commonly used in manufacturing insulation board, small appliances, tape cassettes, toys and housewares.
Table 3: Styrene Use in Massachusetts  
(Based on 1990 TURA data)

<table>
<thead>
<tr>
<th>Facility Name (Location)</th>
<th>Styrene Use</th>
<th>Processed Amount (lbs)</th>
<th>% of Mass. Styrene Use</th>
<th>Generated As By-Product Amount (lbs)</th>
<th>Shipped In or As Product Amount (lbs)</th>
<th>Fugitive Air Emissions (lbs)</th>
<th>Point Air Emissions (lbs)</th>
<th>Discharge to POTW (lbs)</th>
<th>Other Off-Site Discharge (lbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>American Polymers</td>
<td>Polystyrene production</td>
<td>43,518,066</td>
<td>11.01%</td>
<td>2,999</td>
<td>43,515,606</td>
<td>750</td>
<td>2,000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ashworth Bros Inc.</td>
<td>Resin blending, mixing</td>
<td>82,847</td>
<td>0.02%</td>
<td>7,455</td>
<td>75,392</td>
<td>2,609</td>
<td>4,845</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Boston Whaler, Inc.</td>
<td>Polyester resin use</td>
<td>36,512</td>
<td>0.01%</td>
<td>36,512</td>
<td>0</td>
<td>0</td>
<td>36,512</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>E. Parrella Co, Inc.</td>
<td>Polyester resin use</td>
<td>104,100</td>
<td>0.03%</td>
<td>873</td>
<td>0</td>
<td>244</td>
<td>750</td>
<td>0</td>
<td>244</td>
</tr>
<tr>
<td>ICI Resins US</td>
<td>Resin manufacture</td>
<td>1,002,530</td>
<td>0.25%</td>
<td>1,073</td>
<td>0</td>
<td>149</td>
<td>44</td>
<td>43</td>
<td>0</td>
</tr>
<tr>
<td>Interpolymer Corp.</td>
<td>Polymer latex production</td>
<td>1,015,640</td>
<td>0.26%</td>
<td>39</td>
<td>0</td>
<td>5</td>
<td>255</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Marson Corporation</td>
<td>Resin blending, mixing</td>
<td>888,300</td>
<td>0.22%</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>255</td>
<td>0</td>
<td>70</td>
</tr>
<tr>
<td>Mobil Chemical</td>
<td>Polystyrene production</td>
<td>75,000,000</td>
<td>18.97%</td>
<td>44,000</td>
<td>27,000</td>
<td>15,000</td>
<td>3,500</td>
<td>5</td>
<td>10,060</td>
</tr>
<tr>
<td>Monsanto Chemical Co.</td>
<td>Not specified</td>
<td>79,000</td>
<td>0.02%</td>
<td>16,000</td>
<td>0</td>
<td>290</td>
<td>110</td>
<td>150</td>
<td>15,310</td>
</tr>
<tr>
<td>Monson Chemicals</td>
<td>Fills tanks, drums, small containers</td>
<td>22,978</td>
<td>0.01%</td>
<td>1</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>New England Plastic Coated Products Inc.</td>
<td>Polyester resin use</td>
<td>35,364</td>
<td>0.01%</td>
<td>4,597</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Novacor Chemical, Inc.</td>
<td>Polystyrene production</td>
<td>109,007,402</td>
<td>27.58%</td>
<td>527,989</td>
<td>0</td>
<td>5,484</td>
<td>10,917</td>
<td>0</td>
<td>470,395</td>
</tr>
<tr>
<td>Polysar Incorporated</td>
<td>Polystyrene production</td>
<td>164,444,107</td>
<td>41.61%</td>
<td>2,728,657</td>
<td>0</td>
<td>6,400</td>
<td>10,367</td>
<td>5</td>
<td>8,028</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td>395,236,846</td>
<td>100.0%</td>
<td>3,370,295</td>
<td>47,544,336</td>
<td>30,936</td>
<td>69,555</td>
<td>203</td>
<td>504,037</td>
</tr>
</tbody>
</table>
Table 4: Styrene Uses in U.S.
(*Chemical Marketing Reporter, January 1, 1993*)

<table>
<thead>
<tr>
<th>Use</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>66</td>
</tr>
<tr>
<td>Acrylonitrile-butadiene-styrene (ABS) resins and styrene-acrylonitrile (SAN)</td>
<td>10</td>
</tr>
<tr>
<td>Styrene Butadiene Latex (SB Latex)</td>
<td>6</td>
</tr>
<tr>
<td>Styrene Butadiene Rubber (SBR)</td>
<td>7</td>
</tr>
<tr>
<td>Unsaturated polyester resins, miscellaneous and export</td>
<td>11</td>
</tr>
</tbody>
</table>

- **Styrene-acrylonitrile (SAN) polymer resins and Acrylonitrile-butadiene-styrene (ABS) resins**
  SAN is typically produced by emulsion polymerization using styrene and acrylonitrile monomers. The styrene content of SAN ranges from 65 - 85%. SAN copolymers are characterized by good hardness, rigidity, and dimensional stability, high heat deflection and chemical resistance. Some end uses of SAN include the production of drinking tumblers, instrument panel lenses and dishes. The majority of SAN produced is used to manufacture ABS. ABS possesses the same useful properties of SAN while a rubber additive increases impact resistance. ABS is used in the manufacture of piping conduit, automotive components, refrigerator door liners, telephones and luggage.

- **Styrene Butadiene Latex (SB Latex)**
  SB Latex is composed of monomer units of styrene and butadiene that contain > 45% styrene and has plastic-like qualities. It is characterized by excellent resistance to water and very good electrical insulation properties. SB Latex is used in the production of carpet and upholstery back coatings, binder for felt base of vinyl floor tile and as a component of latex paints.

- **Styrene Butadiene Rubber (SBR)**
  SBR is composed of monomer units of styrene and butadiene that contain < 45% styrene and has rubber-like characteristics. SBR is the most widely used type of synthetic rubber in the U.S. It is used to manufacture tires, automotive parts such as hoses, gaskets and seals, and for non-automotive uses such as conveyor belts, shoe soles, adhesives and sporting goods.
• Unsaturated polyester resins
Styrene is used as a cross-linking agent with liquid unsaturated polyester to produce thermosetting, insoluble and infusible unsaturated polyester resins. These resins are combined with reinforcing material, often fiberglass, to produce a product with an excellent strength-to-weight ratio. End products using unsaturated polyester resins include fiberglass boats, tub and shower units, truck camper tops, recreational vehicles, wall panels, cultured marble products, electrical components and automotive parts.

Styrene Emissions

• Releases to the Air: All facilities emitting reportable quantities of styrene in Massachusetts, report fugitive and/or point source air emissions of styrene. Most air emissions associated with styrene production arise from loading operations, styrene storage, handling operations, equipment leaks, process vents and secondary sources, such as waste treatment and disposal facilities. Accidental or emergency releases may also contribute to styrene emissions to the air. The quantity of styrene emitted during the manufacturing process is highly dependent on what product is being made and which manufacturing method is used. The EPA has calculated emission factors for most processes where styrene is used. An emission factor relates the quantity of a pollutant released to the atmosphere with a source activity and is used to estimate air toxics emissions when emissions measurements are not available. Emission factors for these processes are expressed by pounds of styrene emitted per ton of product. They are presented in Table 5 to provide a comparison of the quantity of styrene released to the air by the various manufacturing processes using styrene.

Based on these emission factors and on current occupational health research, manufacturing processes that use unsaturated polyester resins clearly present the greatest potential for worker exposure to styrene. Although the polystyrene industry uses 99% of the reported styrene in Massachusetts, losses of styrene during normal production are quite low (however, the potential for accidental releases is high because of the quantities in use, as discussed later). In contrast, styrene emissions during processes using unsaturated polyester resins are much higher and occur routinely. The quantity of styrene used in facilities using unsaturated polyester resins is unknown. Although these uses account for less than 1% of reportable styrene use, many facilities who use these resins are small and would use less than the reporting threshold quantities. Worker exposure to the styrene emissions in the fabrication of products involving polyester resins is heavily dependent on the type of processing used, the ventilation system and on the specific conditions of operation. These resins are most often used in producing fiberglass reinforced plastic products where a mold-based process is used. The mold is wetted with a resin (containing approximately 45% styrene), the reinforcement is manually fitted to the mold, after which it is saturated with more resin. This saturation step can be done manually ("hand layup") or using a mechanical sprayer ("spray layup"). Both layup methods require the worker to be in close proximity to the styrene vapors throughout the process.
Another reason elevated exposure levels may be found in the reinforced plastics industry is that the industry generally consists of small shops where lack of capital funds may delay the incorporation of control measures. One study of the fiberglass boatbuilding industry in New England found worker exposures greater than 50 ppm (8 hour TWA) in 31% of the companies studied. The researchers noted that the management of these companies volunteered to participate in the study, most likely because they did not believe that they had exposure problems. Therefore, styrene exposures in the participating companies were probably slightly lower on average than in the industry as a whole.

Non-occupational exposures to styrene emissions in the air may occur from inhalation of styrene from consumer products such as paints, varnishes and adhesives or from plastics manufacturing facilities releases. According to 1991 TRI data, Massachusetts facilities reporting styrene emissions emitted approximately 137,000 pounds of styrene to the air. This represented a 15% increase (over 18,000 pounds) over 1990 TRI reported air emissions.
These emissions were not correlated with production quantities; therefore, the change in emissions per unit of product is unknown.

If released to the atmosphere, styrene will react rapidly with hydroxyl radicals and ozone. The combined half-life is estimated to be 2.5 hours, indicating that styrene does not persist in the atmosphere.23 Styrene is a very active generator of photochemical smog (also known as ground level ozone) due to indirect photochemical reactions.23

- **Releases to the Water:** If released to water, styrene is expected to volatilize relatively rapidly and it is rarely found in significant concentrations in ground water or surface water. Only two facilities in Massachusetts reported any discharge to a Publicly Owned Treatment Works (POTW), and these quantities were very small.24 Facilities that manufacture styrene (there are none in Massachusetts), generally discharge some styrene in their wastewater. Contamination of water is also possible from accidental or emergency releases. Styrene is not likely to bioconcentrate in biological organisms due to its solubility in water and its volatility.

- **Releases to Land:** None of the Massachusetts facilities reporting styrene emissions under TRI reported direct land disposal of styrene. However, accidental or emergency releases potentially could contaminate soil. If released to soil, styrene will biodegrade and leach with a low to moderate soil mobility. An insignificant quantity of styrene was disposed of in landfills by Massachusetts companies in 1991.

- **Generated as By-product:** Industrial processes that use styrene as a feedstock generate a significant quantity of styrene as by-product (see Table 2). Styrene generated as by-product that is not accounted for as emissions typically is recovered and recycled back into the process. For example, in polystyrene manufacturing processes, polystyrene beads are passed through a devolatilization extruder for recovery of unreacted styrene monomer. The recovered monomer is recycled into the polymerization reactor.25

- **Off-site Disposal Methods:** Several Massachusetts facilities dispose of styrene off-site.26 In 1991 TRI data, a total of over 250,000 lbs. of styrene were reported as "Other Off-site Discharges", which includes off-site treatment, disposal, recycling and energy recovery. Incineration and energy recovery accounted for 95% of the off-site discharges from Massachusetts companies in 1991. Out-of-state hazardous waste handlers received 98% of these off-site transfers. Off-site styrene disposal methods are summarized in Table 6.
Accidental Releases in Massachusetts

There have been 28 accidental releases of styrene reported in Massachusetts over a seven year period since the Department of Environmental Protection (DEP) began keeping such records in 1987. The causes of accidental releases in the state include equipment failures in the manufacturing facilities, transportation equipment malfunctions and human errors. Twenty-four of the 28 releases occurred on-site at a production facility using styrene. Most accidental releases were related to equipment malfunctions or human errors. Equipment malfunctions included valve failures, pump failures, pipe leaks and tanker truck valve leaks. Accidental releases caused by human error included tank overfill and valves accidentally left open after maintenance operations. The largest recorded release occurred in 1988 when 2,500 gallons of styrene were spilled from two highway tank trucks. The cause of the spill was reported as "vandals apparently opened valves on the trucks overnight." All other releases have been under 300 gallons and approximately half of these releases were less than 50 gallons.

Handling, Storage and Transportation

To date, environmental releases of styrene during transportation, storage and processing in Massachusetts have been small. This is evident when the quantities of styrene accidentally released over the past six years are compared to the large quantities of styrene used and
transported by industries in Massachusetts. However, with these enormous quantities in use in the state, it is critical that proper handling practices are strictly followed.

Typically, styrene is transported via tank truck, rail car or barge. Styrene transfer and handling operations during loading to storage tanks can contribute significantly to air emissions at a facility storing styrene. In addition, the transfer of styrene to tanks from tank trucks or rail cars is a potential fire hazard. All ignition sources such as fire, sparks, static electricity and smoking materials must be prohibited in areas where styrene is transferred, used or stored. Additionally, fire hazards can be reduced by isolating formulating operations in a well-ventilated area equipped with an automatic sprinkler system. The use of fluoroelastomer hoses instead of a rubber-type flexible hose to unload styrene is recommended, since the rubber hose may not be resistant to styrene. Styrene fires can be safely extinguished with the proper use of foam, dry powder or carbon dioxide.

Drums containing styrene must be inspected and handled carefully to prevent leaks, explosions and hazardous polymerization. Storage containers must be clean and properly ventilated. If the material is stored for more than 30 days, the polymerization inhibitor level should be checked twice weekly. Improper inhibitor levels could result in runaway polymerization.

Containers that have held styrene must be thoroughly cleaned with steam, drained and dried before reuse. Even small amounts of styrene left in the drum after improper cleaning present a fire hazard. Styrene used in small quantities in the production area, such as in the reinforced plastics industry, should not be stored in a drum; instead, safety cans should be used to prevent high local concentrations.

**Pollution Prevention Programs**

Several states have initiated programs to reduce industrial styrene emissions and exposure. These programs have focused on industries using styrene-based polyester resins, including boatbuilding, sports equipment, tub and shower components and aerospace and aircraft components. Several projects have evaluated the efficacy of incorporating low styrene emissions (LSE) resins (<35% styrene as opposed to the industry standard of 45%) into existing operations. These LSE resins were developed in California to conform to new, stricter air emissions standards.

Minnesota Technical Assistance Program (MnTAP) also studied the low styrene resins for fiberglass reinforced plastics operations. In one type of resin used in the MnTAP study, the styrene content was reduced to 33% from the conventional 45% styrene. To obtain comparable resin properties, the polyester component of the resin was modified by incorporating some dicyclopentadiene (DCPD) character into the polyester chain. Another resin type studied used a benzoyl peroxide (BIO) catalyzed resin system to reduce styrene emissions. These resins give lower styrene emissions than a conventional methyl ethyl ketone.
peroxide (MEKP) catalyzed resin due to a faster reaction rate. MnTAP found both types of LSE resins could save money by eliminating the need to install additional ventilation equipment in order to meet the revised OSHA workplace exposure standards.

In North Carolina, the Pollution Prevention Pays Program sponsored a project on pollution reduction in the fiberglass boatbuilding and open mold plastics industries. This study examined production-based options to reduce emissions such as closed mold systems, modification to spray gun systems and changes in resin storage as well as use of the low emission resins. In addition to state efforts, the EPA published a guide to pollution prevention for the fiberglass reinforced and composite plastics industry in 1991. These programs have focused primarily on the industries using polyester resins, but there are opportunities for pollution prevention in the polystyrene industry. The greatest potential exists in the prevention of accidental releases. Although the accidental releases to date have been minimal, the potential for significant releases does exist with the enormous quantity of styrene transported and used in Massachusetts. Through regular inspections, maintenance and training of operators and maintenance personnel, most accidental releases could be avoided. Other programs implemented to reduce styrene emissions will reduce occupational exposures while improving the efficiency of the manufacturing process.

Conclusions

With such large quantities of styrene in use in Massachusetts, there are questions regarding the safety of this chemical. Of primary concern are the health and safety of workers using styrene and the potential for an accidental release of the chemical, during transportation or during use in the industrial facility. In this state, the industries of greatest concern are polystyrene production and industries using polyester resins.

Industries using polyester resins, especially in manufacturing fiberglass reinforced plastic products, are of concern because of the high exposure levels associated with these applications. Many of these facilities are small shops, where the quantity of styrene used is below the reporting threshold, making it difficult to identify the extent of exposure. Additionally, the capital may not be available in these shops to purchase and install the proper ventilation and pollution control equipment. Such facilities could benefit from implementation of some of the styrene use and emissions reduction programs that have been initiated in other states. These programs have successfully reduced styrene use and emissions through product substitutions, process changes and equipment modifications. Whenever product substitution is considered as an option, it is important to fully evaluate the toxicity and safety characteristics of the substitute materials.

Polystyrene production operations consume 99% of the reported styrene used in Massachusetts. Most facilities producing polystyrene in this state are large operations where emissions, and therefore worker exposure levels, typically are low. Steps taken to reduce these emissions, however, will improve the efficiency of the manufacturing process while
reducing occupational exposures. With the enormous quantity of styrene used in polystyrene production, accidental releases are a serious concern. To date, the accidental releases have been quite low, but the potential for significant release remains a threat. By improving handling, monitoring and maintenance practices, the polystyrene industry could reduce the risk of accidental releases.

All industries using styrene can benefit by reducing styrene use and emissions. The potential dangers of long-term exposures, including carcinogenic effects, are currently unknown. In order to protect workers' health, reducing styrene exposures should be considered whenever possible. Additionally, by December 31, 1993, all industries using styrene are required to meet the new, lower OSHA exposure limits. In order to meet these limits, industry can purchase more engineering control equipment or they can implement process changes that reduce or eliminate styrene exposures. Massachusetts industries can benefit from the information gathered in programs in California, Minnesota and North Carolina which have successfully helped industry reduce styrene use and emissions.
APPENDIX

Chemical and Physical Properties of Styrene

The chemical structure of styrene is:

![Chemical Structure of Styrene]

CAS #: 100-42-5

Synonyms: ethenylbenzene, cinnamene, cinnamol, phenethylene, phenylethene, phenylethylene, styrol, styrole, styrolene, vinylbenzene, vinylbenzol

Molecular Formula: C₈H₈

Molecular Weight: 104.14

Boiling Point: 293.4°F (145.2°C)

Freezing Point: -24°F (-31°C)

Density: 0.9060

Solubility: very slightly soluble in water (300 mg/l at 68°F (20°C)); soluble in alcohol and ether.

Vapor Pressure: 6.45 mm Hg at 77°F (25°C); 10.0 mm Hg at 95°F (35°C).

Stability: Flash-point 88°F (31°C); Fire-point 93°F (34°C). Polymerizes easily at room temperature in the presence of oxygen and oxidizes on exposure to light and air; is typically stored with added inhibitors (e.g., 0.001% tertiary butylcatechol).³
ENDNOTES


13. Ibid.

14. Ibid.

15. Ibid.


29. Davis, p. 87.
