6.6.3 Polystyrene

6.6.3.1 General

Styrene readily polymerizes to polystyrene by a relatively conventional free radical chain mechanism. Either heat or initiators will begin the polymerization. Initiators thermally decompose, thereby forming active free radicals that are effective in starting the polymerization process. Typically initiators used in the suspension process include benzoyl peroxide and di-tert-butyl per-benzoate. Potassium persulfate is a typical initiator used in emulsion polymerizations. In the presence of inert materials, styrene monomer will react with itself to form a homopolymer. Styrene monomer will react with a variety of other monomers to form a number of copolymers.

Polystyrene is an odorless, tasteless, rigid thermoplastic. Pure polystyrene has the following structure.

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{CH}_2 \\
\end{array}
\]

The homopolymers of styrene are also referred to as general purpose, or crystal, polystyrene. Because of the brittleness of crystal polystyrene, styrene is frequently polymerized in the presence of dissolved polybutadiene rubber to improve the strength of the polymer. Such modified polystyrene is called high-impact, or rubber-modified, polystyrene. The styrene content of high-impact polystyrene varies from about 88 to 97 percent. Where a blowing (or expanding) agent is added to the polystyrene, the product is referred to as an expandable polystyrene. The blowing agent may be added during the polymerization process (as in the production of expandable beads), or afterwards as part of the fabrication process (as in foamed polystyrene applications).

Polystyrene is the fourth largest thermoplastic by production volume. It is used in applications in the following major markets (listed in order of consumption): packaging, consumer/institutional goods, electrical/electronic goods, building/construction, furniture, industrial/machinery, and transportation.

Packaging applications using crystal polystyrene biaxial film include meat and vegetable trays, blister packs, and other packaging where transparency is required. Extruded polystyrene foam sheets are formed into egg carton containers, meat and poultry trays, and fast food containers requiring hot or cold insulation. Solid polystyrene sheets are formed into drinking cups and lids, and disposable packaging of edibles. Injection molded grades of polystyrene are used extensively in the manufacture of cosmetic and personal care containers, jewelry and photo equipment boxes, and photo film packages. Other formed polystyrene items include refrigerator door liners, audio and video cassettes, toys, flower pots, picture frames, kitchen utensils, television and radio cabinets, home smoke detectors, computer housings, and profile moldings in the construction/home-building industry.
6.6.3.2 General Purpose And High Impact Polystyrene\textsuperscript{1-2}

Homopolymers and copolymers can be produced by bulk (or mass), solution (a modified bulk), suspension, or emulsion polymerization techniques. In solution (or modified bulk) polymerization, the reaction takes place as the monomer is dissolved in a small amount of solvent, such as ethylbenzene. Suspension polymerization takes place with the monomer suspended in a water phase. The bulk and solution polymerization processes are homogenous (taking place in one phase), whereas the suspension and emulsion polymerization processes are heterogeneous (taking place in more than one phase). The bulk (mass) process is the most widely used process for polystyrene today. The suspension process is also common, especially in the production of expandable beads. Use of the emulsion process for producing styrene homopolymer has decreased significantly since the mid-1940s.

6.6.3.2.1 Process Descriptions\textsuperscript{1-3} -

Batch Process -

Various grades of polystyrene can be produced by a variety of batch processes. Batch processes generally have a high conversion efficiency, leaving only small amounts of unreacted styrene to be emitted should the reactor be purged or opened between batches. A typical plant will have multiple process trains, each usually capable of producing a variety of grades of polystyrene.

Figure 6.6.3-1 is a schematic representation of the polystyrene batch bulk polymerization process, and the following numbered steps refer to that figure. Pure styrene monomer (and comonomer, if a copolymer product is desired) is pumped from storage (1) to the feed dissolver (2). For the production of impact-grade polystyrene, chopped polybutadiene rubber is added to the feed dissolver, where it is dissolved in the hot styrene. The mixture is agitated for 4 to 8 hours to complete rubber dissolution. From the feed dissolver, the mixture usually is fed to an agitated tank (3), often a prepolymerization reactor, for mixing the reactants. Small amounts of mineral oil (as a lubricant and plasticizer), the dimer of alpha-methylstyrene (as a polymerization regulator), and an antioxidant are added. The blended or partially polymerized feed is then pumped into a batch reactor (4). During the reactor filling process, some styrene vaporizes and is vented through an overflow vent drum (5). When the reactor is charged, the vent and reactor are closed. The mixture in the reactor is heated to the reaction temperature to initiate (or continue) the polymerization. The reaction may also be begun by introducing a free radical initiator into the feed dissolver (2) along with other reactants. After polymerization is complete, the polymer melt (molten product) containing some unreacted styrene monomer, ethylbenzene (an impurity from the styrene feed), and low molecular weight polymers (dimers, trimers, and other oligomers), is pumped to a vacuum devolatilizer (6). Here, the residual styrene monomer, ethylbenzene, and the low molecular weight polymers are removed, condensed (7), passed through a devolatilizer condensate tank (9), and then sent to the byproduct recovery unit. Overhead vapors from the condenser are usually exhausted through a vacuum system (8). Molten polystyrene from the bottom of the devolatilizer, which may be heated to 250 to 280°C (482 to 536°F), is extruded (10) through a stranding die plate (a plate with numerous holes to form strands), and then immersed in a cold water bath. The cooled strands are pelletized (10) and sent to product storage (11).

Continuous Process -

As with the batch process, various continuous steps are used to make a variety of grades of polystyrene or copolymers of styrene. In continuous processes, the chemical reaction does not approach completion as efficiently as in batch processes. As a result, a lower percentage of styrene is converted to polystyrene, and larger amounts of unreacted styrene may be emitted from continuous
Figure 6.6.3-1. Simplified flow diagram of a batch polystyrene process.
A typical plant may contain more than one process line, producing either the same or different grades of polymer or copolymer.

A typical bulk (mass) continuous process is represented in Figure 6.6.3-2. Styrene, polybutadiene (if an impact-grade product is desired), mineral oil (lubricant and plasticizer), and small amounts of recycled polystyrene, antioxidants, and other additives are charged from storage (1) into the feed dissolver mixer (2) in proportions that vary according to the grade of resin to be produced. Blended feed is pumped continuously to the reactor system (3) where it is thermally polymerized to polystyrene. A process line usually employs more than one reactor in series. Some polymerization occurs in the initial reactor, often referred to as the prepolymerizer. Polymerization to successively higher levels occurs in subsequent reactors in the series, either stirred autoclaves or tower reactors. The polymer melt, which contains unreacted styrene monomer, ethylbenzene (an impurity from the styrene feed), and low molecular weight polymers, is pumped to a vacuum devolatilizer (4). Here, most of the monomer, ethylbenzene, and low molecular weight polymers are removed, condensed (5), and sent to the styrene recovery unit (8 and 9). Noncondensables (overhead vapors) from the condenser typically are exhausted through a vacuum pump (10). Molten polystyrene from the bottom of the devolatilizer is pumped by an extruder (6) through a stranding die plate into a cold water bath. The solidified strands are then pelletized (6) and sent to storage (7).

In the styrene recovery unit, the crude styrene monomer recovered from the condenser (5) is purified in a distillation column (8). The styrene overhead from the tower is condensed (9) and returned to the feed dissolver mixer. Noncondensables are vented through a vacuum system (11). Column bottoms containing low molecular weight polymers are used sometimes as a fuel supplement.

6.6.3.2.2 Emissions And Controls

As seen in Figure 6.6.3-1, six emission streams have been identified for batch processes: (1) the monomer storage and feed dissolver vent (Stream A); (2) the reactor vent drum vent (Stream B); (3) the devolatilizer condenser vent (Stream C); (4) the devolatilizer condensate tank (Stream D); (5) the extruder quench vent (Stream E); and (6) product storage emissions (Stream F). Table 6.6.3-1 summarizes the emission factors for these streams.

Table 6.6.3-1 (Metric Units). EMISSION FACTORS FOR BATCH PROCESS POLYSTYRENE

<table>
<thead>
<tr>
<th>Stream Identification</th>
<th>Emission Stream</th>
<th>Nonmethane VOC</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Monomer storage and feed dissolver tanks</td>
<td>0.09b</td>
<td>3</td>
</tr>
<tr>
<td>B</td>
<td>Reactor vent drum vent</td>
<td>0.12 - 1.35c</td>
<td>3 - 4</td>
</tr>
<tr>
<td>C</td>
<td>Devolatilizer condenser vent</td>
<td>0.25 - 0.75c</td>
<td>3 - 4</td>
</tr>
<tr>
<td>D</td>
<td>Devolatilizer condensate tank</td>
<td>0.002b</td>
<td>3</td>
</tr>
<tr>
<td>E</td>
<td>Extruder quench vent</td>
<td>0.15 - 0.3c</td>
<td>3 - 4</td>
</tr>
<tr>
<td>F</td>
<td>Product storage</td>
<td>negligible</td>
<td>3</td>
</tr>
<tr>
<td>Total Plant</td>
<td></td>
<td>0.6 - 2.5</td>
<td></td>
</tr>
</tbody>
</table>

* Stream identification refers to Figure 6.6.3-1. Units are grams VOC per kilogram of product.
* Based on fixed roof design.
* Reference 4. The higher factors are more likely during the manufacture of lower molecular weight products. Factor for any given process train will change with product grade.
Figure 6.6.3-2. Simplified flow diagram of a continuous polystyrene process.
The major vent is the devolatilizer condenser vent (Stream C). This continuous offgas vent emits 0.25 to 0.75 grams of VOC per kilogram (gVOC/kg) of product depending on the molecular weight of the polystyrene product being produced. The higher emission factor is more likely during the manufacture of lower molecular weight products. The emissions are unreacted styrene, which is flashed from the product polymer in the vacuum devolatilizer, and it is extremely diluted in air through leakage. The stream is exhausted through a vacuum system and then through an oil demister to the atmosphere. The oil demister is used primarily to separate out organic mist.

The second largest vent stream is likely to be the reactor vent drum vent, with an emission rate ranging from 0.12 to 1.35 gVOC/kg of product, this range also being associated with the molecular weight of the polystyrene product being produced. The higher emission factor is more likely during the manufacture of lower molecular weight products. These emissions, which are the only intermittent emissions from the process, occur only during reactor filling periods and they are vented to the atmosphere. The rate of 0.12 gVOC/kg of product is based on a facility having two batch reactors that are operated alternately on 24-hour cycles.

Stream E, the extruder quench vent, is the third largest emission stream, with an emission rate of 0.15 to 0.3 gVOC/kg of product. This stream, composed of styrene in water vapor, is formed when the hot, extruded polystyrene strands from the stranding die plate contact the cold water in the quenching bath. The resulting stream of steam with styrene is usually vented through a forced draft hood located over the water bath and then passed through a mist separator or electrostatic precipitator before venting to the atmosphere.

The other emission streams are relatively small continuous emissions. Streams A and D represent emissions from various types of tanks and dissolver tanks. Emissions from these streams are estimated, based on fixed roof tanks. Emissions from product storage, Stream F, have been reported to be negligible.

There are no VOC control devices typically used at polystyrene plants employing batch processes. The condenser (7) off the vacuum devolatilizer (6) typically is used for process reasons (recovery of unreacted styrene and other reactants). This condenser reduces VOC emissions, and its operating characteristics will affect the quantity of emissions associated with batch processes (Stream C in particular).

Total process uncontrolled emissions are estimated to range from 0.6 to 2.5 gVOC/kg of product. The higher emission rates are associated with the manufacture of lower molecular weight polystyrene. The emission factor for any given process line will change with changes in the grade of the polystyrene being produced.

Emission factors for the continuous polystyrene process are presented in Table 6.6.3-2, and the following numbered steps refer to Figure 6.6.3-2. Emissions from the continuous process are similar to those for the batch process, although the continuous process lacks a reactor vent drum. The emission streams, all of which are continuous, are: (1) various types of storage (Streams A and G); (2) the feed dissolver vent (Stream B); (3) the devolatilizer condenser vent (Stream C); (4) the styrene recovery unit condenser vent (Stream D); (5) the extruder quench vent (Stream E); and (6) product storage emissions (Stream F).

Industry’s experience with continuous polystyrene plants indicates a wide range of emission rates from plant to plant depending in part on the type of vacuum system used. Two types are now used in the industry, one relying on steam ejectors and the other on vacuum pumps. Where steam ejectors are used, the overheads from the devolatilizer condenser vent and the styrene recovery unit...
Table 6.6.3-2 (Metric Units). EMISSION FACTORS FOR CONTINUOUS PROCESS POLYSTYRENE

EMISSION FACTOR RATING: C

<table>
<thead>
<tr>
<th>Stream Identification</th>
<th>Emission Stream</th>
<th>Nonmethane VOC</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Uncontrolled</td>
<td>Controlled</td>
</tr>
<tr>
<td>A1</td>
<td>Styrene monomer storage</td>
<td>0.08</td>
<td>3, 5</td>
</tr>
<tr>
<td>A2</td>
<td>Additives</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>General purpose</td>
<td>0.002</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>High impact</td>
<td>0.001</td>
<td>5 - 6</td>
</tr>
<tr>
<td>A3</td>
<td>Ethylbenzene storage</td>
<td>0.001</td>
<td>5</td>
</tr>
<tr>
<td>B</td>
<td>Dissolvers</td>
<td>0.008</td>
<td>3, 5</td>
</tr>
<tr>
<td>C</td>
<td>Devolatilizer condenser vent b</td>
<td>0.05&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.04&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.96&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Styrene recovery unit condenser vent</td>
<td>0.05&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.13&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>C+D</td>
<td></td>
<td>0.024 - 0.3&lt;sup&gt;f&lt;/sup&gt;</td>
<td>0.004&lt;sup&gt;g&lt;/sup&gt;</td>
</tr>
<tr>
<td>E</td>
<td>Extruder quench vent</td>
<td>0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.15&lt;sup&gt;e,g,h&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Pellet storage</td>
<td>negligible</td>
<td></td>
</tr>
<tr>
<td>Other storage</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1</td>
<td>General purpose</td>
<td>0.008</td>
<td>3, 5</td>
</tr>
<tr>
<td>G2</td>
<td>High impact</td>
<td>0.007</td>
<td>3, 5</td>
</tr>
<tr>
<td>Total Plant</td>
<td></td>
<td>0.21&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.34&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Stream identification refers to Figure 6.6.3-2. Units are grams VOC per kilogram of product.
<sup>b</sup> Reference 9. Larger plants may route this stream to the styrene recovery section. Smaller plants may find this too expensive.
<sup>c</sup> For plants using vacuum pumps.
<sup>d</sup> Condenser is used downstream of primary process condensers; includes emissions from dissolvers. Plant uses vacuum pumps.
<sup>e</sup> For plants using steam jets.
<sup>f</sup> Lower value based on facility using refrigerated condensers as well as conventional cooling water exchangers; vacuum pumps in use. Higher value for facility using vacuum pumps.
<sup>g</sup> Plant uses an organic scrubber to reduce emissions. Nonsoluble organics are burned as fuel.
<sup>h</sup> This factor may vary significantly depending on overall process. Reference 6 indicates an emission factor of 0.0012 gVOC/kg product at a plant whose process design is "intended to minimize emissions".
condenser vent are composed mainly of steam. Some companies have recently replaced these steam ejectors with mechanical vacuum pumps. Emissions from vacuum pumps usually are lower than from steam ejectors.

It is estimated that the typical total VOC emission rate for plants using steam ejectors is about 3.34 gVOC/kg of product, with the largest emission stream being the devolatilizer condenser vent (2.96 gVOC/kg of product). Emissions from the styrene recovery unit condenser vent and the extruder quench vent are estimated to be 0.13 and 0.15 gVOC/kg of product, respectively, although the latter may vary significantly depending on overall plant design. One plant designed to minimize emissions reported an emission factor of 0.0012 gVOC/kg product for the extruder quench vent.

For plants using vacuum pumps, it is estimated that the total VOC emission rate is about 0.21 gVOC/kg of product. In these plants, emissions from the devolatilizer condenser vent and the styrene recovery unit condenser vent are each estimated to be 0.05 gVOC/kg of product. Styrene monomer and other storage emissions can be the largest emission sources at such plants, approximately 0.1 gVOC/kg of product. Some plants combine emissions from the dissolvers with those from the devolatilizer condenser vent. Other plants may combine the dissolver, devolatilizer condenser vent, and styrene recovery unit condenser vent emissions. One plant uses an organic scrubber to reduce these emissions to 0.004 gVOC/kg of product.

Condensers are a critical, integral part of all continuous polystyrene processes. The amount of unreacted styrene recovered for reuse in the process can vary greatly, as condenser operating parameters vary from one plant to another. Lowering the coolant operating temperature will lower VOC emissions, all other things being equal.

Other than the VOC reduction achieved by the process condensers, most plants do not use VOC control devices. A plant having controls, however, can significantly reduce the level of VOC emissions. One company, for example, uses an organic scrubber to reduce VOC air emissions. Another uses a condenser downstream from the primary process condensers to control VOCs.

6.6.3.3 Expandable Polystyrene1-2,10-11

The suspension process is a batch polymerization process that may be used to produce crystal, impact, or expandable polystyrene beads. An expandable polystyrene (EPS) bead typically consists of high molecular weight crystal grade polystyrene (to produce the proper structure when the beads are expanded) with 5 to 8 percent being a low-boiling-point aliphatic hydrocarbon blowing agent dissolved in the polymer bead. The blowing agent typically is pentane or isopentane although others, such as esters, alcohols, and aldehydes, can be used. When used to produce an EPS bead, the suspension process can be adapted in one of two ways for the impregnation of the bead with the blowing agent. One method is to add the blowing agent to a reactor after polymerization, and the other is to add the blowing agent to the monomer before polymerization. The former method, called the "post-impregnation" suspension process, is more common than the latter, referred to as the "in-situ" suspension process. Both processes are described below.

EPS beads generally are processed in one of three ways, (1) gravity- or air-fed into closed molds, then heated to expand up to 50 times their original volume; (2) pre-expanded by heating and then molding in a separate processing operation; and (3) extruded into sheets. EPS beads are used to produce a number of foamed polystyrene materials. Extruded foam sheets are formed into egg cartons, meat and poultry trays, and fast food containers. In the building/construction industry, EPS board is used extensively as a low-temperature insulator.
Post-impregnation Suspension Process -

This process is essentially a two-part process using two process lines in series. In the first process line, raw styrene monomer is polymerized and a finished polystyrene bead is produced. The second process line takes the finished bead from the first line, impregnates the bead with a blowing agent, and produces a finished EPS bead. Figure 6.6.3-3 is a schematic representation of this process.

In the first line, styrene monomer, water, initiator, and suspending agents form the basic charge to the suspension reactor (1). The styrene-to-water ratio varies with the type of polystyrene required. A typical ratio is about one-quarter to one-half monomer to water volume. Initiators are commonly used because the reaction temperature is usually too low for adequate thermal initiation of polymerization. Suspending agents are usually protective colloids and insoluble inorganic salts. Protective colloids are added to increase the viscosity of the continuous water phase, and insoluble inorganic salts such as magnesium carbonate (MgCO₃) are added to prevent coalescence of the drops upon collision.

In the reactor, the styrene is suspended, through use of mechanical agitation and suspending agents, in the form of droplets throughout the water phase. Droplet size may range from about 0.1 to 1.0 mm. The reactor is heated to start the polymerization, which takes place within the droplets. An inert gas, such as nitrogen, is frequently used as a blanketing agent in order to maintain a positive pressure at all times during the cycle to prevent air leaks. Once polymerization starts, temperature control is typically maintained through a water-cooled jacket around the reactor and is facilitated by the added heat capacity of the water in the reactor. The size of the product bead depends on both the strength of agitation and the nature of the monomer and suspending system. Between 20 and 70 percent conversion, agitation becomes extremely critical. If agitation weakens or stops between these limits, excessive agglomeration of the polymer particles may occur, followed by a runaway reaction. Polymerization typically occurs within several hours, the actual time varying largely with the temperature and with the amount and type of initiator(s) used. Residual styrene concentrations at the end of a run are frequently as low as 0.1 percent.

Once the reaction has been completed (essentially 100 percent conversion), the polystyrene-water slurry is normally pumped from the reactor to a hold tank (2), which has an agitator to maintain dispersion of the polymer particles. Hold tanks have at least three functions: (1) the polymer-water slurry is cooled to below the heat distortion temperature of the polymer (generally 50 to 60°C [122 to 140°F]); (2) chemicals are added to promote solubilization of the suspension agents; and (3) the tank serves as a storage tank until the slurry can be centrifuged. From the hold tanks, the polymer-water slurry is fed to a centrifuge (3) where the water and solids are separated. The solids are then washed with water, and the wash water is separated from the solids and is discarded. The polymer product beads, which may retain between 1 and 5 percent water, are sent to dryers (4). From the dryers, they may be sent to a classifier (5) to separate the beads according to size, and then to storage bins or tanks (6). Product beads do not always meet criteria for further processing into expandable beads, and "off-spec" beads may be processed and sold as crystal (or possibly impact) polystyrene.

In the second line, the product bead (from the storage bins of the first line), water, blowing agent (7), and any desired additives are added to an impregnation reactor (8). The beads are impregnated with the blowing agent through utilization of temperature and pressure. Upon
Figure 6.6.3-3. Simplified flow diagram of the expandable polystyrene post-impregnation suspension process.
completion of the impregnation process, the bead-water slurry is transferred to a hold tank (9) where acid may be added and part of the water is drained as waste water. From the hold tanks, the slurry is washed and dewatered in centrifuges (10) and then dried in low-temperature dryers (11). In some instances, additives (12) may be applied to the EPS bead to improve process characteristics. From the dryers, the EPS bead may undergo sizing, if not already done, before being transferred to storage silos (13) or directly to packaging (14) for shipment to the customer.

In-situ Suspension Process -

The in-situ suspension process is shown schematically in Figure 6.6.3-4. The major difference between this process and the post-impregnation suspension process is that polymerization and impregnation takes place at the same time in a single reactor. The reaction mixture from the mix tank (1), composed of styrene monomer, water, polymerization catalysts, and additives, are charged to a reactor (2) to which a blowing agent is added. The styrene monomer is polymerized at elevated temperatures and pressure in the presence of the blowing agent, so that 5 to 7 percent of the blowing agent is entrapped in the polymerized bead. After polymerization and impregnation have taken place, the EPS bead-water slurry follows essentially the same steps as in the post-impregnation suspension process. These steps are repeated in Figure 6.6.3-4.

6.6.3.3.2 Emissions And Controls10,12-16 -

Emission rates have been determined from information on three plants using the post-impregnation suspension process. VOC emissions from this type of facility are generally uncontrolled. Two of these plants gave fairly extensive information and, of these, one reported an overall uncontrolled VOC emission rate of 9.8 g/kg of product. For the other, an overall uncontrolled VOC emission rate of 7.7 g/kg is indicated, by back-calculating two emission streams controlled by condensers.

The information on emission rates for individual streams varied greatly from plant to plant. For example, one plant reported a VOC emission rate for the suspension reactor of 0.027 g/kg of product, while another reported a rate of 1.9 g/kg of product. This inconsistency in emission rates may be because of differences in process reactors, operating temperatures, and/or reaction times, but sufficient data to determine this are not available. Therefore, individual stream emission rates for the post-impregnation process are not given here.

Particulate emissions (emissions of fines from dryers, storage, and pneumatic transfer of the polymer) usually are controlled by either cyclones alone or cyclones followed by baghouses. Overall, controlled particulate emissions are relatively small, approximately 0.18 g particulate/kg of product or less. Control efficiencies of 99 percent were indicated and, thus, uncontrolled particulate emissions might be around 18 g particulate/kg of product.

Table 6.6.3-3 summarizes uncontrolled VOC emissions factors for the in-situ process, based on a study of a single plant. An uncontrolled emission rate of about 5.4 gVOC/kg of product is estimated for this suspension EPS process. Most emission streams are uncontrolled at this plant. However, reactor emissions are vented to the boiler as primary fuel, and some of the dryer emissions are vented to the boiler as supplementary fuel, thereby resulting in some VOC control.

The blowing agent, which continually diffuses out of the bead both in manufacturing and during storage, constitutes almost all VOCs emitted from both processes. A small amount of styrene is emitted from the suspension reactors in the post-impregnation process and from the mix tanks and reactors in the in-situ process.
Figure 6.6.3-4. Simplified flow diagram of the expandable polystyrene in-situ suspension process.
Table 6.6.3-3 (Metric Units). EMISSION FACTORS FOR IN-SITU PROCESS EXPANDABLE POLYSTYRENE

EMISSION FACTOR RATING: C

<table>
<thead>
<tr>
<th>Stream Identification</th>
<th>Emission Stream</th>
<th>Nonmethane VOC</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Mix tank vents</td>
<td>0.13</td>
<td>16</td>
</tr>
<tr>
<td>B</td>
<td>Regranulator hoppers</td>
<td>negligible</td>
<td>16</td>
</tr>
<tr>
<td>C</td>
<td>Reactor vents</td>
<td>1.09 b</td>
<td>17</td>
</tr>
<tr>
<td>D</td>
<td>Holding tank vents</td>
<td>0.053</td>
<td>16</td>
</tr>
<tr>
<td>E</td>
<td>Wash tank vents</td>
<td>0.023</td>
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</tr>
<tr>
<td>F</td>
<td>Dryer vents</td>
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</tr>
<tr>
<td>G</td>
<td>Product improvement vents</td>
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</tr>
<tr>
<td>H</td>
<td>Storage vents and conveying losses</td>
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</tr>
<tr>
<td>Total Plant</td>
<td></td>
<td>5.37 c</td>
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</tbody>
</table>

* Stream identification refers to Figure 6.6.3-4. Units are grams VOC per kilogram of product.
* Reference 16. All reactor vents and some dryer vents are controlled in a boiler. Rates are before control.
* At plant where all reactor vents and some dryer vents are controlled in a boiler (and assuming 99% reduction), an overall emission rate of 3.75 is estimated.

Because of the diffusing of the blowing agent, the EPS bead is unstable for long periods of time. Figure 6.6.3-5 shows the loss of blowing agent over time when beads are stored under standard conditions. This diffusion means that the stock of beads must be rotated. An up-to-date analysis of the blowing agent content of the bead (measured as percent volatiles at 100°C [212°F]) also needs to be maintained, because the blowing agent content determines processing characteristics, ultimate density, and economics. Expandable beads should be stored below 32°C (90°F) and in full containers (to reduce gas volume space).

Since pentane, a typical blowing agent, forms explosive mixtures, precautions must be taken whenever it is used. For example, after storage containers are opened, a time lag of 10 minutes is suggested to allow fumes or pentane vapors to dissipate out of the containers. Care must be taken to prevent static electricity and sparks from igniting the blowing agent vapors.
References For Section 6.6.3


7. Written communication from R. Symuleski, Standard Oil Company (Indiana), Chicago, IL, to A. Limpiti, Energy And Environmental Analysis, Inc., Durham, NC, July 2, 1981.


Figure 6.6.3-5. EPS beads stored in fiber drum at 21 - 24°C (70 - 75°F).


15. Written communication from T. M. Nairn, Cosden Oil And Chemical Company, Big Spring, TX, to J. R. Farmer, U. S. Environmental Protection Agency, Research Triangle Park, NC, March 30, 1983.
