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Project Summary

Evaluation of Styrene Emissions from a Shower Stall/ Bathtub Manufacturing Facility

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Current EPA emission factors (AP-42) for styrene emissions from the production of polyester-resin-reinforced plastic products represent a composite of spraying and post-spraying emissions (from curing molds) from shower stall/bathtub manufacturing plants that use compressed-air-powered spray guns to apply catalyzed styrene resins to prepared molds. Because each step of manufacture (gel coating, first-stage spray lay-up, and second-stage spray lay-up) creates large surface areas from which volatile styrene monomer can evaporate, non-spraying emissions can constitute a large fraction of the styrene emitted to the atmosphere. Thus, it is of interest to quantify the level of non-spraying styrene emissions characteristic of this industry to validate current emission factors for spraying, as well as to develop emission factors for emissions not directly related to a spraying activity.

In this study, emissions were measured at a representative facility (Eljer Plumbingware in Wilson, NC) that manufactures polyester-resin-reinforced shower stalls and bathtubs by spraying styrene-based resins onto molds in vented, open, spray booths. Styrene emissions were characterized for the three stages of manufacture by measuring styrene concentrations at the vents of spray booths used in each part of the process. In addition, styrene concentrations were measured at each ventilation fan exhaust. Emission levels were determined using EPA Method 18 to obtain integrated emissions samples and total hydrocarbon analyzers to measure continuous emissions levels during the EPA Method 18 sampling.

Analysis of the EPA Reference Method data indicates that: (1) styrene monomer is the only volatile organic compound released in this process; (2) overall, approximately 4% of all material sprayed is lost to atmospheric emissions as styrene (approximately 19% of styrene sprayed); and (3) emissions vary for each phase of manufacture, with post-spraying emissions of styrene (from curing molds) constituting a large part, approximately 29%, of all emissions.

This Project Summary was developed by EPA's National Risk Management Research Laboratory's Air Pollution Prevention and Control Division, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Current EPA emission factors (AP-42) for styrene emissions from the production of polyester-resin-reinforced plastic products do not specifically account for post-spraying emissions (from curing molds) from shower stall/bathtub manufacturing plants that use compressed-air-powered spray guns to apply catalyzed styrene resins to prepared molds. Because each step of manufacture creates large surface areas from which volatile styrene monomer can evaporate, post-spraying emissions can constitute a large fraction of the styrene emitted to the atmosphere. Thus, it is of interest to quantify the level of spraying and post-spraying styrene emissions characteristic of this industry to validate current emission factors for spraying, as well as to develop emission factors for post-spraying emissions.

Shower stalls and bathtubs are among the many products fabricated from liquid polyester resin that have been extended with various inorganic filler materials and reinforced with glass fibers. These composite materials are often referred to collectively as fiberglass-reinforced plastic or "fiberglass." Depending on the size, shape, and intended use, any one of several manufacturing processes can be used for fabrication. For the manufacture of shower stalls and bathtubs, the preferred technique is spray lay-up or sprayup. All of these processes involve the application of a liquid resin that is mixed with a catalyst to initiate polymerization. In polymerization, a liquid unsaturated polyester is cross-linked with a vinyl-type monomer, usually styrene, by the action of the catalyst. Common catalysts are organic peroxides, typically methyl ethyl ketone peroxide or benzoyl peroxide. Resins may contain inhibitors to avoid self-curing during resin storage, and promoters to allow polymerization to occur at lower temperatures.

In the production of fiberglass shower stalls and bathtubs exhaust air from the spray booths used for mold-coating and plant ventilation air outlets represent the major point sources of VOC emissions. Thus, at a particular facility, the number of manufacturing steps that involve the spraying of styrene-based resins, the amount of styrene sprayed in each step of manufacture, and the amount of styrene that is volatilized during the spraying and curing of molds determine the amount of styrene emitted to the atmosphere.

This study was undertaken to quantify styrene emission factors at a shower stall/bathtub manufacturing plant determined by the EPA to be a representative facility. Once styrene emissions were measured, the emissions measurements and raw material usage data from the plant were used to determine emission factors for each phase in the manufacturing process.

Testing was carried out at Eljer Plumbingware, Wilson, NC, and was part of a larger effort that also involved the evaluation of a pilot-scale liquid chemical scrubber for styrene removal. Styrene emissions measurements were originally scheduled for the week of June 14, 1993, and the liquid chemical scrubber evaluation was originally scheduled for the following week. Because the plant was operating on a 4-day production week during this time (Monday through Thursday), instead of the 5-day production week that had been expected, emissions testing had to be extended through Monday, June 21, 1993, to obtain a suitable set of emissions data. A full day of testing could not be carried out on Monday because portions of that day had to be devoted to preparing for the upcoming liquid chemical scrubber evaluation.

Section 2 of the full project report contains a detailed description of the facility and sampling locations. Detailed descriptions of the sampling methodology are presented in Section 3 and the results of this evaluation along with a discussion of these results are presented in Section 4.

The quality assurance and quality control measures taken during this evaluation, as well as the results of these measures, are contained in the Quality Control Evaluation Report as Appendix A. This project summary briefly addresses the methodology and emission rate conclusions from the study. More detailed information can be obtained from the report sections described above.

Two methods were used to measure styrene emissions. A heated Tedlar™ bag sampler was used to obtain an integrated sample of the contaminated air exiting a representative point in each process exhaust vent. Concurrently, styrene emissions were measured on a continuous basis using a total hydrocarbon (THC) analyzer equipped with flame ionization detectors. Sample times ranged from 40 to 45 minutes, typically the time required to spray eight to ten molds. Sample times were dictated by the plant production rate and the time available for sampling during a particular period of spraying.

Table 1 presents average styrene emissions as a function of the area sprayed, the total mass that was sprayed, and the total amount of styrene that was sprayed. Styrene emissions based on measurements with the THC analyzers were generally greater than those determined by Method 18. This result is somewhat unexpected because one might suspect that some styrene would be lost in the long heated sampling lines used to convey the ventilation air samples to the THC analyzers. Apparently, that was not the case for these measurements. However, as Table 1 shows, within the uncertainty of the data, styrene emissions as determined from THC data and from Method 18 data do overlap. It should be emphasized that because of the lack of multiple measurements, no uncertainty could be determined for styrene emissions not captured by spray booth exhaust fans (based on THC analyzer data). Therefore, the uncertainties in Table 1 are *minimum* values. The lack of multiple measurements for such emissions is especially unfortunate because styrene emissions not captured by active spray booth exhaust fans are one of the largest sources of styrene emissions.

Research conducted subsequent to the above analysis of test results has also shown differences between EPA Method 18 measurements of styrene emissions and those using THC analyzers. However, the reason for these differences remains the subject of research. It has been suggested that in the Method 18 procedure styrene can polymerize before analysis and may also have a very low vapor pressure at stack or instrument conditions. Both of these conditions would result in a lower measurement for styrene.

Although it is not specifically noted in AP-42, it is reasonable to assume that styrene emission factors cited in this standard for polyester resin plastics products fabrication include emissions not captured by active spray booths. Thus, in order to compare the results obtained in this study with those cited in AP-42, it is necessary to apportion non-spray booth emissions to those parts of the process associated with spraying operations: gel coating, lay-up, and back-up. When such an apportionment is carried out, with the data obtained at Eljer, the following emission factors are obtained:

- Gel Coat - 47.5% of the styrene sprayed in that phase of manufacture
- Lay-Up - 20.0% of the styrene sprayed in that phase of manufacture
- Back-Up - 12.1% of the styrene sprayed in that phase of manufacture

These data suggest that spray booth emissions are higher than those cited in AP-42 for gel coating and spray lay-up. AP-42 cites a value from 26% to 35% of styrene monomer being emitted for gel coat that contains no vapor suppressing additives (as was the case at Eljer). Likewise, these results show that when non-spraying emissions are apportioned to each part of the manufacturing process nearly 48% of the styrene in the gel coat mix is lost to the atmosphere.

As might be expected AP-42 makes no distinction between styrene emissions from lay-up booths or from back-up booths, and indicates that with vapor suppressing additives in the mix, from 3% to 9% of the styrene sprayed in this operation is emitted. If vapor-suppressing additives are not added to the mix, emissions rise to from 9% to 13% of the styrene sprayed. At Eljer, vapor suppressants are added to the lay-up and back-up mix. However,

Table 1. Styrene Emissions for Each Part of the Manufacturing Process

(a) Styrene Emissions per Unit Area of Mold Sprayed

	THC Analyzer		EPA Method 18	
Emissions from:	*Styrene (g/m^2)*	*Pop. Std. Dev. (g/m^2)*	*Styrene (g/m^2)*	*Pop. Std. Dev. (g/m^2)*
Gel Coat Booths	*110.5*	*21.2*	*69.5*	*26.4*
Lay-Up Booths	*116.0*	*43.1*	*85.5*	*28.3*
Back-Up Booths	*68.7*	*3.8*	*51.9*	*12.6*
Non-Spray Booth Emissions	*83.7*	*N/A*	*83.7*	*N/A*
All Emissions	*378.9*	*48.1**	*290.6*	*40.7**

(b) Percent of Total Mass Used in Each Stage of Manufacture That Was Emitted as Styrene

	THC Analyzer		EPA Method 18	
Emissions from:	*Styrene (%)*	*Rel. Std. Dev. (%)*	*Sytrene (%)*	*Rel. Std. Dev. (%)*
Gel Coat Booths	*14.3*	*2.7*	*9.0*	*3.4*
Lay-Up Booths	*3.4*	*1.3*	*2.5*	*0.8*
Back-Up Booths	*2.4*	*1.5*	*1.8*	*0.4*
Non-Spray Booth Emissions	*1.2*	*N/A*	*1.2*	*N/A*
All Emissions	*5.4*	*0.7**	*4.2*	*0.6**

c) Percent of Styrene Used in Each Stage of Manufacture That Was Emitted

	THC Analyzer		EPA Method 18	
Emissions from:	*Styrene (%)*	*Rel. Std. Dev. (%)*	*Styrene (%)*	*Rel. Std. Dev. (%)*
Gel Coat Booths	*44.4*	*8.5*	*27.9*	*10.6*
Lay-Up Booths	*16.1*	*6.0*	*11.9*	*3.9*
Back-Up Booths	*11.4*	*0.6*	*8.6*	*2.1*
Non-Spray Booth Emissions	*5.3*	*N/A*	*5.3*	*N/A*
All Emissions	*24.2*	*3.3**	*18.6*	*2.8**

**Minimum estimate. Assumes each process independent with no contribution from the non-spraying emissions component.*

the levels of styrene emissions measured there suggest that the emissions levels are probably higher than what AP-42 cites as typical for non-vapor suppressed emissions, particularly for the lay-up phase of manufacture. Thus, results calculated according to the above apportioning procedure show that styrene emissions to the atmosphere averaged 20% of the styrene sprayed in the lay-up booths and 12% of the styrene sprayed in the single back-up booth.

These generally higher-than-expected emission levels may be due, at least in part, to the nature of the process. At the Eljer facility (determined by the EPA to be a representative facility) molds that have been sprayed are frequently left near the mouths of spray booths where spraying is in progress. Hence, styrene evolved from a curing mold can be captured by an adjacent spray booth. While this practice is not common in the gel coat booths (because of limited space in front of the booths at the Eljer facility), this practice is an integral part of the manufacturing process for the latter two stages of spraying. In fact, at any one time, it is common for as many 15 molds to be in various stages of manufacture in the general vicinity of the lay-up and back-up booths. Also, molds are generally left in a lay-up booth between sprayings where the surface of the mold is rolled flat. In AP-42 it is noted that styrene emissions are increased by such manual rolling.

Finally, AP-42 provides no separate estimate of styrene emissions not captured by spray booths. While such emissions are certainly a function of ventilation system design and the specific equipment at a given facility, at Eljer it was found that 6% of all the styrene sprayed exits the facility through openings other than spray booth exhausts. As noted in Table 2, this corresponds to from 22 to 29% (depending on the measurement method) of all styrene emitted to the atmosphere; thus, styrene emissions not captured by spray booths represent a source of styrene emissions as great as (or possibly greater than) styrene emissions associated with any one of the spraying operations.

Table 2. *Distribution of Styrene Emissions from Each Part of the Manufacturing Process, Including Styrene Emissions Not Captured by Spray Booths*

	From THC Analyzer Measurements					*From Method 18 Measurements*				
Date	*Gel Coat Booths (%)*	*Lay-Up Booths (%)*	*Back-Up Booths (%)*	*Non-Spraying (%)*	*All Sources (%)*	*Gel Coat Booths (%)*	*Lay-Up Booths (%)*	*Back-Up Booths (%)*	*Non-Spraying (%)*	*All Sources (%)*
6/15/93	*29.9*	*30.2*	*17.9*	*22.0*	*100.0*	*24.5*	*29.1*	*17.6*	*28.8*	*100.0*
6/16/93	*29.2*	*30.5*	*18.1*	*22.2*	*100.0*	*24.0*	*29.3*	*17.8*	*28.9*	*100.0*
6/17/93	*29.2*	*30.6*	*18.2*	*22.0*	*100.0*	*24.0*	*29.5*	*17.9*	*28.6*	*100.0*
Average	*29.4*	*30.5*	*18.0*	*22.1*	*100.0*	*24.2*	*29.3*	*17.7*	*28.8*	*100.0*

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The complete report, entitled "Evaluation of Styrene Emissions from a Shower Stall/ Bathtub Manufacturing Facility," (Order No. PB97-125439; Cost: $21.50, subject to change) will be available only from:
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