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Project Summary

Evaluation of Pollution Prevention Techniques to Reduce Styrene Emissions from Open Contact Molding Processes

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This study evaluated several pollution prevention techniques that could be used to reduce styrene emissions from open molding processes in fiberglass-reinforced plastics/composites (FRP/C) and fiberglass boat building industries. Styrene emissions using standard industry techniques, materials, and equipment were evaluated in a controlled environment and compared to a baseline condition to determine the effects of these pollution prevention techniques on styrene emissions. The study found that using controlled spraying (i.e., reducing overspray), low-styrene and styrene-suppressed materials, and non-atomizing application equipment can reduce styrene emissions by from 11 to 52%. Facilities should investigate the applicability and feasibility of these pollution prevention options to reduce their styrene emissions. The calculated emission factors were from 1.6 to 2.5 times the mid-range AP-42 emission factors for the corresponding gel coat and resin application. These results indicate that facilities using AP-42 emission factors to estimate emissions in open molding processes are likely to underestimate actual emissions.

This Project Summary was developed by EPA's Air Pollution Prevention and Control Division of the National Risk Management Research Laboratory, 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

Gel coat and resin sprayup are commonly used in open molding processes in the fiber-reinforced plastics/composites (FRP/C) and boat building industries. However, styrene, a compound listed as a hazardous air pollutant, is emitted during the application and postapplication (roll-out and curing) stages. These emissions are coming under increasingly stringent regulations as the maximum achievable control technology (MACT) standards are developed by the U.S. Environmental Protection Agency (EPA). The MACT regulations are to be promulgated in November 1997 for the FRP/C industry and in November 2000 for the boat building industry. To help industry meet future emission requirements, pollution prevention options such as new materials and equipment have been developed by various vendors. However, information is needed about the percentage of reduction in emissions that these options can achieve. To meet this need, Research Triangle Institute (RTI), working with the EPA's Air Pollution Prevention and Control Division, evaluated several of these pollution prevention options. Also, emission factors calculated from the results of a prior EPA test in an FRP facility indicated that they were higher than those reported in the EPA AP-42 document. Since the AP-42 emission factors have been used by the facilities to estimate their styrene emissions, a comparison of the emission factors calculated from this test result with the existing AP-42 emission factors for gel coat sprayup and resin applications would verify the accuracy of the existing AP-42 emission factors.

Background

During the gel coat and resin sprayup operations, polyester resins are atomized and projected onto a mold. Gel coat and resin materials contain styrene, which cross-links the resin molecules under the effects of a promoter and an initiator to form a solid polymer. An initiator such as methyl ethyl ketone peroxide (MEKP) is mixed with the resin material to initiate the cross-linking process. The initiator is mixed with resin material within the spray gun or application equipment (internal mixing) or just outside the spray tip (external mixing). Wet resin material cures on the mold. For resin lamination, a roll-out step follows the application step to remove air bubbles entrained in the laminate. During the application and postapplication (i.e., rolling-out and curing) stages, excess styrene not cross-linked in polymerization is emitted from atomized resin particles and from wet laminate.

Testing Approaches

For the pollution prevention technique evaluation, RTI quantified styrene emissions from test runs using standard industry techniques, materials, and equipment. All the formulations and application equipment tested are available commercially. Cook Composites and Polymers (CCP) supplied all gel coats. Reichhold Chemicals provided the facility, all resins and catalysts, and laboratory analyses for resin properties. Catalyst ratios suggested by CCP and Reichhold were used for the gel coat and resin materials. Magnum Industries provided all application equipment and an experienced operator. PPG Industries supplied all fiberglass materials.

Styrene emissions during the test runs were measured and compared to a baseline condition to examine reduction achieved using various pollution prevention options. The baseline test conditions and the various options examined are summarized in Table 1. Six factors were examined in three separate experiments to determine their impact on styrene emissions.

Pilot Experiment

- Operator spraying technique - normal vs. controlled spraying
- Linear air flow velocity in the spray area - 12 vs. 30 m/min (40 vs. 100 ft/min)

Operator techniques affect the amount of overspray and the associated excess emissions. Spraying technique was expected to affect styrene emissions because poor technique creates more overspray (i.e., sprayed material that does not end up on the mold but on the surrounding area). More overspray means more material is used and more surface area is created for styrene emissions. Normal spraying (i.e., spraying without consciously controlling the spray pattern) was compared with controlled spraying (i.e., spraying in a manner that consciously reduces overspray by projecting the spray pattern more precisely on the mold and flange).

Air flow velocity in the spray area was expected to influence styrene emissions from a pure diffusion transfer point of view. Styrene emission is expected to increase with increasing air flow velocity; therefore, tests at these two air flow velocities would reveal their effects on styrene emission. Based on the results of this experiment, a low air flow velocity and a controlled spraying technique were used for subsequent gel coat and resin experiments.

Gel Coat Experiment

- Gel coat formulation - regular vs. low-VOC gel coats
- Gel coat application equipment - air-assisted airless (AAA) vs. high-volume, low-pressure (HVLP) spray guns

Styrene content in the gel coat formulation affects styrene emissions. Typical gel coat materials contain 35 to 50% of styrene monomer; low-VOC gel coat material contains less than 35% styrene. A comparison between a regular gel coat and a low-VOC gel coat would reveal the effect of styrene content on emissions. The low-VOC gel coat formulation was first introduced by CCP in late 1994, and its sprayup emission has not been compared with that of a regular gel coat.

AAA and HVLP spray guns (either internal or external catalyst mixing) are commonly used for gel coat application. Certain

Table 1. Baseline Test Conditions and Pollution Prevention Options Evaluated

Factor	Base Conditions	Pollution Prevention Option
Spray technique	Experienced operator, normal technique (i.e., without consciously controlling overspray)	Experienced operator, controlled spraying technique (very careful spraying to prevent significant overspray)
Air flow velocity in spraying area[a]	30 m/min (100 ft/min)	12 m/min (40 ft/min)
Gel coat formulation	Regular, isophthalic acid-based gel coat[b] (styrene content 38.7%)/initiated by 1.8% MEKP; 17 min gel time;18 to 24 mil gel coat thickness	Low-VOC, isophthalic acid/neopentyl glycol-based gel coat (styrene content 25.4%)/initiated by 1.8% MEKP; 27 min gel time
Gel coat application equipment	AAA spray (external catalyst mixing)	1. HVLP spray gun (internal catalyst mixing) 2. HVLP spray gun (external catalyst mixing)
Resin formulations	Regular (low-profile), dicyclopentadiene-based resin (styrene content 38.3%); initiated by 1.5% MEKP; 20 min gel time; 70 to 100 mil laminate thickness	1. Low-styrene, dicyclopentadiene-based (styrene content 35.3%)/initiated by 1.4% MEKP; 30 min gel time 2. Styrene-suppressed, orthophthalic acid-based resin (styrene content 43.5%)/initiated by 1.5% MEKP; 17 min gel time 3. Orthophthalic acid-based styrene-suppressed resin plus 0.1% wax/initiated by 1.5% MEKP; 17 min gel time
Resin application equipment	AAA spray (external catalyst mixing)	1. Flow coater (internal catalyst mixing) 2. Pressure-fed roller (internal catalyst mixing)

[a]Air velocity in the spraying area was controlled by a baffle upwind of the spraying area.
[b]Gel coats contained no methyl methacrylate to allow assumption that total emissions were styrene.

spray gun designs were said to have a more confined spray fan or improved catalyst mixing, thereby reducing overspray and styrene emissions. Three different spray guns were evaluated to determine the effects of spray gun designs and catalyst mixing on styrene emissions.

Resin Experiment

- Resin formulation - regular vs. low-styrene and styrene-suppressed resins
- Resin application equipment - AAA spray gun vs. flow coater and pressure-fed roller

The effects of a low-styrene resin and a styrene suppressant on resin sprayup emissions were evaluated using the AAA spray gun. A low-styrene resin contains less than 35% of styrene by weight vs. a regular resin containing 35 to 50% of styrene. A styrene suppressant typically is a paraffin or wax additive in the resin formulation, which migrates outward to the surface of the wet laminate during the curing stage and forms a waxy layer that prevents styrene from further evaporation. The styrene suppressant is not expected to have a significant effect on emissions during the application and roll-out stages, because a stagnant condition is necessary for the styrene suppressant to work.

Other resin application equipment (i.e., flow coater and pressure-fed roller) that do not atomize resin materials were compared with the AAA spray gun using a regular low-profile resin. A spray gun atomizes resin material into small droplets that create a large surface area for styrene to evaporate. RTI evaluated a flow coater and a pressure-fed roller to reveal the effects of non-atomizing application equipment and identify pollution prevention options for resin application.

Test Setup

Gel coat sprayup or resin application was conducted in an isolated spray booth of dimensions typically used in FRP/C facilities. Emissions in the spray booth were exhausted through a stack. Emissions resulting from gel coat or resin application and curing were quantified using EPA methods. Styrene emission concentrations were continuously monitored and recorded every 2 seconds at the exhaust stack during a test run. A test run started when gel coat or resin was applied to the mold surface and ended when the material was completely cured and the monitored concentration returned to the baseline concentration. The exhaust flow rate was monitored for each test run so that the emission quantities could be calculated. Environmental conditions (i.e., temperature and relative humidity) were maintained at constant levels, and background concentrations of volatile organic compounds (VOCs) were recorded before the test run.

Gel coat or resin materials were applied onto a box-shaped, male FRP mold by an experienced operator. The same operator applied the materials during a 5-week period to ensure that a consistent technique was used and to reduce any possible variability in operation. The mold measures 0.61 m (2 ft) high, 0.76 m (2.5 ft) long, and 0.61 m (2 ft) wide. A 5.1-cm (2-in.) wide flange surrounds the bottom of the mold. The amount of gel coat or resin material used in each test run was measured using a high precision balance with a 150,000-g (331-lb) capacity and 1-g (0.002-lb) readability. Emissions from gel coat sprayup test runs were compared based on similar gel coat thicknesses of 18 to 24 mils. Emissions from resin application test runs were compared based on similar laminate thicknesses of 70 to 100 mils. Chopped strand mats were used for the flow coater and pressure-fed roller, and fiberglass roving was used for the AAA spray gun.

Results and Conclusions

All tests were conducted in triplicate to permit statistical analysis of the results. Percent emission reductions in the following discussions are based on total grams of styrene emitted or grams of styrene emitted per unit mold surface area. Percent emission reductions are different when emissions are expressed as a percentage of available styrene, because styrene contents in the gel coat and resin materials are different. Using the emission concentration profile and the duration of the application stage, emissions from the application and postapplication stages could be determined separately. These separate emission quantities aided the analysis of emission characteristics resulting from different materials and equipment.

The pilot experiment (shown in Table 2) indicated that:

- Over the velocity range examined, 12 vs. 30 m/min (40 vs. 100 ft/min), linear air velocity had no significant effect on styrene emissions.
- Controlled gel coat spraying technique reduced total styrene emissions by 24% compared to normal spraying technique.
- Controlled spraying on the male mold reduced gel coat usage by 12% due to less overspray.
- Under normal spraying, 48% of total emissions were emitted during gel coat spraying; the remainder were emitted during curing.
- Under controlled spraying, 38% of total emissions were emitted during gel coat spraying; the remainder were emitted during curing.

The gel coat experiment (shown in Table 3) indicated that:

- The low-VOC gel coat reduced total styrene emissions by 28% when compared to the regular gel coat.
- The low-VOC gel coat required a higher air pressure and larger spray tip to achieve the same spray fan as the regular gel coat.
- The AAA (external catalyst mixing) and HVLP (internal and external catalyst mixing) gel coat spray guns made no difference in terms of total emissions.

Evaluation of resin formulations under controlled spraying (shown in Table 4) indicated that:

- The low-styrene resin reduced total emissions by 11% compared to the regular low-profile resin.
- The styrene-suppressed resin emitted 36% less styrene than the regular low-profile resin and the majority of the reduction was achieved during the postapplication stage.

Table 2. Summary of Emissions Using Normal and Controlled Gel Coat Spraying

Spraying technique	Materials used		Total emissions		Emission factor		Emission factor	
	g	Reduc. (%)	g	Reduc. (%)	%AS	Reduc. (%)	g/g	Reduc. (%)
Normal (6 runs)	2,119	BL	513	BL	62.5	BL	0.242	BL
Controlled (6 runs)	1,868	12	391	24	54.1	13	0.210	13

BL = Baseline condition for emission reduction calculation.
Note: Material usage and emission quantities are the averages of the number of test runs for that condition.

Table 3. Summary of Emissions Using Regular and Low-VOC Gel Coats

Type of gel coat	Materials used	Total emissions		Emission factor		Emission factor	
	g	g	Reduc. (%)	%AS	Reduc. (%)	g/g	Reduc. (%)
Regular gel coat (9 runs)	1,783	387	BL	56.0	BL	0.217	BL
Low-VOC gel coat (9 runs)	2,025	278	28	54.2	3	0.137	37

BL = Baseline condition for emission reduction calculation.
Note: Material usage and emission quantities are the averages of the number of test runs for that material.

Table 4. Summary of Emissions Using Different Resin Formulations (Applied by Controlled Spraying)

	Materials used	Total emissions		Emission factor		Emission factor	
Type of resin	g	g	Reduc. (%)	% AS	Reduc. (%)	g/g	Reduc. (%)
Regular, low-profile (5 runs)	6,670	445	BL	17.5	BL	0.067	BL
Low-styrene (3 runs)	6,472	395	11	17.3	1	0.061	9
Styrene-suppressed (3 runs)	6,258	286	36	10.6	39	0.046	31
Styrene-suppressed +wax (3 runs)	5,912	266	40	10.6	39	0.046	31

BL = Baseline condition for emission reduction calculation.
Note: Material usage and emission quantities are the averages of the number of test runs for that material.

- The styrene-suppressed resin with 0.1% wax emitted 40% less styrene than the regular low-profile resin; however, the effect of additional wax on total emissions was not significant.
- For regular and low-styrene resins, 47 to 48% of total emissions occurred during spraying; the remainder were emitted during postapplication.
- For the styrene-suppressed resin with or without additional wax, 63% of total emissions occurred during spraying, which implies that styrene suppressant was effective in reducing curing emissions in the postapplication stage.

Evaluations of resin application techniques and equipment (as shown in Table 5) indicated that:

- **Controlled** resin sprayup emitted 30% less styrene than **normal** resin sprayup.
- Flow coating and pressure-fed roller equipment resulted in 52 to 53% lower emissions than **normal** spraying.
- Flow coating and pressure-fed roller equipment resulted in 31 to 33% lower emissions than **controlled** spraying.

Comparison of Test Results with Existing EPA AP-42 Emission Factors

Table 6 compares emission factors from the EPA AP-42 document and from the test results. Emission factors are expressed as a percentage of available styrene. It is important to note that the styrene emission factors calculated from the test results were from 1.6 to 2.5 times greater than the mid-range AP-42 emission factors for the corresponding gel coat and resin application. The deviation of RTI's measured emission factors from AP-42 emission factors is consistent with the findings of the recent Open Molding Styrene Emission Study conducted by the Composites Fabricators Association at Dow Chemical. These results indicate that facilities using current AP-42 emission factors to estimate gel coat and resin application emissions in open molding processes are likely to substantially underestimate actual styrene emissions.

Recommendations

The results of this study show that different materials, application equipment, and techniques can reduce styrene emissions to varying degrees. Each facility should investigate the applicability and feasibility of the available pollution prevention options to reduce its styrene emissions.

Based on the results of this study, RTI recommends the following pollution prevention options for open molding operations:

- Use operator training to improve application technique and reduce overspray.
- Use low-styrene or styrene-suppressed materials, where feasible.
- Use non-atomizing application equipment, where feasible.

Emission factors and the percent of emission reductions presented in this paper were determined under specific study conditions (e.g., gel coat and resin properties, equipment setup, environmental conditions), which may not represent the conditions in all facilities. Therefore, the results presented in this paper provide general trends, not absolute values, of the effectiveness of various pollution prevention options.

Table 5. Summary of Emissions Using Different Resin Application Techniques and Equipment

Type of equipment	Materials used	Total emissions			Emission factor			Emission factor		
	g	g	Reduc. (%)		%AS	Reduc. (%)		g/g	Reduc. (%)	
AAA spray gun (normal spraying, 1 run)	6,133	634	BL	—	27.1	BL	—	0.104	BL	—
AAA spray gun (controlled spraying, 5 runs)	6,670	445	30	BL	17.5	35	BL	0.067	36	BL
Flow coater (3 runs)	5,619	306	52	31	14.2	48	19	0.055	47	18
Pressure-fed roller (3 runs)	5,096	299	53	33	15.3	44	13	0.059	43	12

BL = Baseline condition for emission reduction calculation.
Note: Material usage and emission quantities are the averages of the number of test runs for that equipment.

Table 6. Comparison of Emission Factors (in % available styrene) from EPA AP-42 and Test Results

Type of material and operation	AP-42 emission factor range	AP-42 EF midpoint	Emission factors from test results	Ratio
Gel coat sprayup (NVS)	26-35	30.5	62.5 (normal spraying)	2.0
			56 (controlled spraying)	1.8
			54.2 (low-VOC gel coat, controlled spraying)	1.8
Resin sprayup (NVS)	9-13	11	17.5 (controlled spraying)	1.6
			27.1 (normal spraying)	2.5
Resin sprayup (VS)	3-9	6	10.6 (styrene-suppressed resin, controlled spraying)	1.8
Resin hand layup (NVS)	5-10	7.5	15.3 (pressure-fed roller)	2.0

NVS=non-vapor-suppressed.
VS=vapor-suppressed.

As shown in Tables 2 through 5, the percentage of reduction varies when emission factors are expressed as a percentage of available styrene and the calculated emission factors are substantially higher than the current AP-42 emission factors; therefore, facilities should not apply the percentage reductions reported in this paper to emission estimates calculated using current AP-42 factors. Doing so could enormously underestimate actual emissions. Facilities should check with the governing agencies or trade associations to determine the appropriate procedures for estimating their current emissions.

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The complete report, entitled "Evaluation of Pollution Prevention Techniques to Reduce Styrene Emissions from Open Contact Molding Processes," consists of two volumes:
Volume 1 is the final report (Order No. PB97-181440; Cost: $21.50, subject to change);
Volume 2 is the appendices (Order No. PB97-181457; Cost: $31.00, subject to change). Both volumes will be available only from

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