United States Environmental Protection Agency

€PA

Research and Development

EVALUATION OF POLLUTION PREVENTION TECHNIQUES TO REDUCE STYRENE EMISSIONS FROM OPEN CONTACT MOLDING PROCESSES Volume I, Final Report

Prepared for

Office of Air Quality Planning and Standards

Prepared by

National Risk Management Research Laboratory Research Triangle Park, NC 27711 EPA-600/R-97-018a March 1997

FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and groundwater; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

'This publication has been produced as part of the Laboratory's strategic longterm research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

> E. Timothy Oppelt, Director National Risk Management Research Laboratory

EPA REVIEW NOTICE

This report has been peer and administratively reviewed by the U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/R-97-018a March 1997

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

Volume I, Final Report

By

Emery J. Kong, Mark A. Bahner, Robert S. Wright, and C. Andrew Clayton Research Triangle Institute P.O. Box 12194 Research Triangle Park, NC 27709

EPA Cooperative Agreement CR 818419-03

EPA Project Officer: Geddes Ramsey Air Pollution Prevention and Control Division National Risk Management Research Laboratory U.S. Environmental Protection Agency Research Triangle Park, NC 27711

> Prepared for U.S. Environmental Protection Agency Office of Research and Development Washington, DC 20460

Abstract

Pollution prevention options to reduce styrene emissions, such as new materials and application equipment, are commercially available to the operators of open molding processes. However, information is needed about the percent reduction in emissions that is achievable with these options.

To meet this need, several of these pollution prevention options were examined. Options examined were operator techniques, air flow velocities in the spraying area, gel coat and resin formulations, and application equipment. Styrene emission factors calculated from this test result were compared with the existing AP-42 emission factors for gel coat sprayup and resin applications.

The study found that using controlled spraying (i.e., reducing overspray), low-styrene and styrene-suppressed materials, and nonatomizing application equipment can reduce styrene emissions from 11 to 52 percent. 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 existing AP-42 emission factors to estimate emissions in open molding processes are likely to underestimate actual emissions.

. . .

Contents

•

.

.

•

Section	Page
Abstract	ii
Figures	
Tables	vi
Acronyms and	l Abbreviations vii
Conversion Ta	able
Acknowledgm	nentsix
Chapter 1	Introduction
1.1	Background1
1.2	Objectives
1.3	Approach
1.4	Report Outline
	References
Chapter 2	Experimental Test Design
2.1	Pilot Experiment
2.2	Gel Coat Experiment
2.3	Resin Experiment
Chapter 3	Facility and Experimental Setup
- 3.1	Total Enclosure System
3.2	Emission Sampling Location
3.3	Experimental Setup
	3.3.1 FRP Mold
	3.3.2 Air Flow Baffle
	3.3.3 Glass Veil and Kraft Paper to Capture Overspray
	3.3.4 Protective Equipment and Clothing for Operator
3.4	Resin Property Testing Laboratory 12
Chapter 4	Materials and Equipment
4.1	Properties of Gel Coat and Resin Materials
4.2	Setting of Gel Coat and Resin Application Equipment
4.3	Reinforcements 17
Chapter 5	Determination of Emission Quantities
- 5.1	Emission Measurement Method
	5.1.1 Determination of Styrene Concentrations in Exhausted Air
	5.1.2 Exhaust Air Flow Rate Measurement
	5.1.3 Emissions Determined by Emission Measurement Method
5.2	Mass Balance Calculation Method Using Gravimetric Measurements

.

Contents (continued)

Section		Page
Chapter 6	Test Results and Discussion	27
6.1	Distribution of Total Emissions During Application and Curing Stages	32
6.2	Pilot Experiment Results	
6.3	Gel Coat Experiment Results	39
6.4	Resin Experiment Results	43
6.5	Comparison of Test Results with EPA AP-42 Emission Factors	49
6.6	Comparison of Emission Measurement Method and Mass Balance	
	Calculation Method	52
	6.6.1 Pure Styrene Evaporation Test	52
	6.6.2 Comparison of Emissions Measured by Two Test Methods	52
Chapter 7	Data Quality Issues	58
7.1	Summation of Project QA Activities	58
7.2	RTI Internal Technical System Audit (TSA) Results	58
7.3	EPA Performance Evaluation	59
Chapter 8	Conclusions and Recommendations	60
- 8.1	Conclusions	60
. 8.2	Recommendations	61

Appendixes (in Volume 2)

- A. A Category III Quality Assurance Project Plan for the Evaluation of Pollution Prevention Techniques to Reduce Styrene Emissions from Open Contact Molding Processes
- B. Reichhold Standard Test Methods
- C. Verification and Intercomparison of Compressed Gas Calibration Standards
- D. Summary of Calibration Data, Calibration Error Tests, and Drift Checks
- E. A Summary of Emission Measurements, Gravimetric Measurements, and Calculated Emission Quantities and Emission Factors for the Test
- F. Statistical Analyses of Test Results
- G. THC Analyzer Evaluation: Sampling Line Loss and Pressure Effect
- H. An RTI Technical System Audit Report
- I. EPA Performance Evaluation of Total Hydrocarbon Analyzer

Figures

<u>No.</u>	Page
3-1	Side view of the Reichhold Chemicals spray booth and the experimental setup in
	a permanent total enclosure
3-2	Sketch of a male mold
5-1	Data recording sheet for mass balance calculation
6-1	Distribution of emissions in the pilot and gel coat experiments
6-2	Distribution of emissions in the resin experiment
6-3	Typical emission concentration profiles for normal and controlled gel coat spraying 37
6-4	Emission reductions observed in the pilot experiment
6-5	Typical emission concentration profiles for regular and low-VOC gel coats
6-6	Typical emission concentration profiles for three types of gel coat spray guns
6-7	Emission reductions observed in the gel coat experiment
6-8	Emission concentration profiles observed for different resin application techniques
	and equipment
6-9	Typical emission concentration profiles for various resin formulations
6-10	Typical emission concentration profiles for low-profile, neat BPO, and modified
	BPO resins
6-11	Emission reductions observed in the resin experiment: "controlled spraying"
	technique baseline
6-12	Emission reductions observed in the resin experiment: "normal spraying"
	technique baseline
6-13	Comparison of mass balance with EPA Method 25A emissions measurements,
	during pure (100 percent) styrene evaporation tests
6-14	Comparison of emission measurement methods

Tables

<u>190.</u>	<u> </u>	age
2-1	Test Runs for Pilot Experiment	5
2-2	Test Runs for Gel Coat Experiment	6
2-3	Test Runs for Resin Experiment	7
4-1	Gel Coat Properties Measured at Reichhold	. 13
4-2	Resin Properties Measured at Reichhold	. 14
4-3	Summary of Gel Coat Equipment Setting	. 15
4-4	Summary of Resin Application Equipment Setting	. 16
6-1	Summary of Emission Measurements and Calculated Emission Factors	. 28
6-2	Significance of Variables Affecting Total Styrene Emissions	. 31
6-3	Distribution of Emissions in Pilot and Gel Coat Experiments	. 32
6-4	Distribution of Emissions in Resin Experiment	. 33
6-5	Summary of Emissions for Normal and Controlled Gel Coat Spraying	. 36
6-6	Summary of Emissions for Regular and Low-VOC Gel Coats	. 39
6-7	Summary of Emissions for Resin Application Equipment	43
6-8	Comparison of Emissions among Various Resin Application Equipment and Normal	
	Spraying	. 44
6-9	Summary of Emissions for Various Resin Formulations	48
6-10	Comparison of EPA AP-42 Emission Factors and Test Results	. 49
6-11	Comparison of Mass Balance Method and Emission Measurements for Pure	
	Styrene Evaporation Tests	53
6-12	Comparison of Mass Balance Method and Emission Measurements	. 55
6-13	Comparison of Mass Balance and Emission Measurement Test Results	. 57

. ۰

No

•

.

.

n

Acronyms and Abbreviations

AAA	air-assisted airless
ANOVA	analysis of variance
AP-42	EPA's Compilation of Air Pollutant Emissions Factors
APPCD	Air Pollution Prevention and Control Division
AS	available styrene
BPO	benzoyl peroxide
CCP	Cook Composites and Polymers
DCPD	dicyclopentadiene
EPA	Environmental Protection Agency
FID	flame ionization detector
FRP/C	fiberglass-reinforced plastics/composites
FS	full scale
HVLP	high volume, low pressure
ISO	isophthalic acid
MACT	maximum achievable control technology
МЕКР	methyl ethyl ketone peroxide
MMA	methyl methacrylate
MnTAP	Minnesota Technical Assistance Program
NDO	natural draft opening
NRMRL	National Risk Management Research Laboratory
NV	nonvolatile
NVS	non-vapor-suppressed
ORTHO	orthophthalic
OSHA	Occupational Safety and Health Administration
PFA ·	perfluoroalkoxy
QA	quality assurance
QAPP	Quality Assurance Project Plan
THC	total hydrocarbon
TRI	Toxics Release Inventory
TSA	technical system audit
VOC	volatile organic compound
VS	vapor-suppressed

Conversion Table

٢.

The U.S. Environmental Protection Agency policy is to express all measurements in Agency documents in metric units. In this report, however, to conform to industry convention, English units are used. Conversion factors from English to metric units are given below.

English Unit	Multiply by	To Obtain
ft³/min	0.028314	m³/min
۴	(°F-32)/1.8	°C
ft	0.304	m
ft ²	0.0929	m ²
gal/min	.3.79	L/min
in. H ₂ O	1.87 [.]	. mm Hg
lb	0.454	kġ
psia	6.895	kilopascal
ton	0.907	Mg

Acknowledgments

During the research period, the authors received valuable information from Bob Lacovara of the Composites Fabricators Association and many representatives in the fiberglass-reinforced plastics/composites industry. The information helped the authors to design a focused test.

The authors would like to acknowledge the invaluable support and assistance of the following organizations:

- Reichhold Chemicals for providing a spray booth and all resin materials for the test and the laboratory support for gel coat and resin properties determination
- Magnum Industries for providing equipment and an experienced operator (Charles Stard) to conduct the actual gel coat and resin application during the entire test period
- Cook Composites and Polymers for providing all gel coat materials
- PPG Industries, Inc., for providing all the fiberglass materials for the test.

Without their generous support, the testing described in this report would not have been possible.

Chapter 1 Introduction

1.1 Background

The open contact molding process is one of the most common production processes used by the fiberglass reinforced plastics/composites (FRP/C) and FRP boat building industry. This process is used to manufacture boats, bathtubs, shower stalls, truck cabs, body panels for recreational vehicles and trucks, swimming pools, etc. It is one of the FRP/C processes that consumes the most polyester resins. It also has the greatest potential of emitting styrene due to the spraying equipment used and the openness of the process. According to the 1990 Toxics Release Inventory (TRI) database, 10,600 tons of styrene were emitted from the FRP/C and boat building industries. More than 50 percent of the total styrene emissions was emitted from the open molding process.

Styrene is emitted during the application stage when a catalyzed gel coat or resin is applied to the surface of an open mold. Styrene continues to be emitted from wet gel coat or resin during gelation and curing. The open contact molding process usually is conducted in a facility with ample ventilation to maintain the ambient styrene concentrations under the current Occupational Safety and Health Administration (OSHA) standard of 100 ppm. Therefore, styrene emissions from the open contact molding process are difficult to capture and control.

The maximum achievable control technology (MACT) standards for the reinforced plastics/composites source category and boat building source category are scheduled to be promulgated by November 15, 1997, and November 15, 2000, respectively. For some open contact molding processes, pollution prevention techniques could be used to reduce styrene emissions. These pollution prevention techniques include changing application equipment and environment and using different gel coat or resin formulations. Existing information indicates that using nonspraying equipment or low-emitting/high-transfer efficiency spray guns, such as air-assisted airless (AAA) or high-volume, low-pressure (HVLP) spray guns, can reduce emissions from the application stage. Gel coat and resin manufacturers also have developed different gel coat and resin formulations. The effects of these pollution prevention techniques and resin manufactures also have not been compared systematically.

Limited studies provide some indications that low-styrene resins can reduce emissions when compared to regular general-purpose resin. A demonstration project entitled Reducing Styrene Emissions in Fiber Reinforced Plastics Operations¹ was conducted by the Minnesota Technical Assistance Program in the early 1990s. The study found that styrene emissions from low-styrene resins were reduced by 25 to 45 percent compared to a conventional orthophthalic (ORTHO)-based general-purpose resin. However, the emissions measured from the simulated production trials were not a typical open molding process, and the emissions quantified may not directly apply to actual operations to estimate styrene emissions. A Finland research group² reports that low-styrene resin reduced total styrene evaporation by 30 to 60 percent compared to

•1

۱

standard resin. However, their test was conducted for hand layup operation under a laboratory hood, and the results cannot be applied to sprayup operations.

1.2 Objectives

This research project has three objectives. The first objective is to quantify and validate the effectiveness of several pollution prevention techniques, specifically operator techniques, air flow velocity in the spraying zone, different gel coat and resin formulations, and application equipment, on styrene emissions from the open contact molding process. The second objective is to compare a mass balance calculation method with an emission measurement method to quantify emissions. The third objective is to compare emission factors calculated from this test with the emission factors for gel coat sprayup and resin applications reported in the U.S. Environmental Protection Agency (EPA) AP-42 document³ to determine the accuracy of the AP-42 emission factors. The results of this study are to be presented to the FRP/C and boat building industries so that individual facilities can identify the most effective and practical pollution prevention techniques to reduce their styrene emissions.

1.3 Approach

This test determined the styrene emission reduction from baseline conditions for several pollution prevention techniques on open contact molding processes. The baseline emissions were determined for a typical gel coat and a general purpose resin using a AAA spray gun under typical environmental and operating conditions. Pollution prevention techniques were evaluated for gel coat and resin applications under the same environmental conditions. The effectiveness of these pollution prevention techniques is determined by comparing total styrene emissions (in grams) and styrene emission factors, expressed as the weight percent of available styrene (% AS) and as mass per unit mold surface area (g/m²). The former unit (%AS) is the unit used in EPA's AP-42 emission factors. The EPA Air Pollution Prevention and Control Division (APPCD) Category III quality assurance (QA) procedures were followed to ensure that the data quality is sufficient to evaluate the effectiveness of these materials and equipment. The QA project plan (QAPP) for this testing is included in Appendix A (Volume II).

1.4 Report Outline

This report in divided into two volumes. Volume I documents the planning, execution, and findings of the pollution prevention technique evaluation test. Chapter 2 presents the experimental design. Chapter 3 describes the facility and the setup for the testing. Chapter 4 describes the testing procedures used to quantify emissions from the operation. Chapter 5 presents the materials and equipment used in the testing. Chapters 6 and 7 present the results of the testing and the associated data quality issues, respectively. Chapter 8 summarizes the conclusions from the research and presents the recommendations to the industry. Volume II contains the appendixes to this report detailed supporting documents that are related to data quality and emission measurement issues.

2

ŋ

References

- 1. Minnesota Office of Waste Management. Reducing Styrene Emissions in Fiber Reinforced Plastics Operations. Minnesota Technical Assistance Program (MnTAP), Minneapolis, Minnesota, 1993.
- 2. Saamamen, A.J., R.I. Miemela, T.K. Blomqvist, and E.M. Nikander. Emission of Styrene During the Hand Lay-up Molding of Reinforced Polyester. *Applied Occupation Environmental Hygiene*, 6(9): 790-793, September 1991.
- 3. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Compilation of Air Pollutant Emission Factors (AP-42). Research Triangle Park, NC. p. 4.12-1, September 1988.

Chapter 2 Experimental Test Design

This testing included a pilot experiment, a gel coat experiment, and a resin experiment. From the pilot experiment, the linear air flow velocity in the spraying zone and the spraying technique were evaluated and a set of conditions was selected for the subsequent gel coat and resin experiments. The gel coat experiment examined two gel coat formulations with three pieces of gel coating equipment (i.e., spray guns). The resin experiment examined five resin formulations and three pieces of resin application equipment. Except for a styrene-suppressed resin with additional wax, the rest of the gel coat and resin formulations and application equipment selected for the testing are commercially available to the FRP/C and boat building industries. Each of the experiments is described in the following subsections.

2.1 Pilot Experiment

Before these formulations and equipment were examined, the effects on styrene emission of the air flow velocity in the spray zone and the spraying technique of the operator were evaluated in the pilot experiment. The pilot experiment was conducted by spraying a regular isophthalic acid (ISO)-based gel coat using a AAA spray gun. The gel coat was catalyzed with methyl ethyl ketone peroxide (MEKP). A low (40 to 50 ft/min) and a high (100 ft/min) air flow velocity in the spray zone were examined. Air velocities were measured by a hot-wire anemometer at several locations across the spraying zone. This range represents the low and high ends of air flow velocity found in an open molding area or in a spray booth. The spraying technique of the operator was evaluated by asking the operator to spray normally (without consciously controlling the spray fan beyond the mold surface and flange) and in a controlled pattern. Controlled spraying was done by consciously minimizing overspray beyond the flange of the mold. The effects of spraying techniques were quantified by transfer efficiency, which is the percentage of gel coat material deposited on the mold right after application. Spraying techniques, shape of mold (male or female), and size of mold all affect the transfer efficiency of the material applied.

The number of test runs for air flow velocity and spraying method are summarized as follows and presented in Table 2-1.

A. Air flow velocity (as measured by a hot-wire anemometer across the spraying zone)

- A1. Low air flow velocity (30 to 50 ft/min)
- A2. High air flow velocity (90 to 120 ft/min)

B. Spraying method

M1. Normal technique without conscious control of overspray from flanges

M2. Controlled spraying technique with more conscious control to reduce overspray

4

4

	A1-Low air flow velocity	A2-High air flow velocity
M1-Normal technique	3	3
M2-Controlled technique	3	3

Table 2-1. Test Runs for Pilot Experiment

The results were analyzed to determine whether there are any differences in styrene emissions resulting from different air flow velocities and spraying techniques. Following the pilot experiment, the low air flow velocity and controlled spraying technique were selected for the subsequent gel coat and resin experiments.

2.2 Gel Coat Experiment

The gel coat formulations selected were one regular ISO-based gel coat and a low-volatile organic chemical (VOC), isophthalic acid/neopentyl glycol (ISO/NPG®)-based gel coat. Cook Composites and Polymers (CCP) provided these two gel coats. For the purpose of this testing, both gel coats contained straight styrene without any methyl methacrylate (MMA). Typical gel coats contain only a low percentage of MMA while the styrene content may range from 35 to 50 percent. This minor modification allowed the assumption that total emissions quantified were styrene emissions. A Reichhold Superox[®] 46709 MEKP catalyst was used and the catalyst ratios followed those suggested by CCP.

The gel coat spraying equipment selected included: one AAA spray gun with external catalyst mixing, one HVLP spray gun with internal catalyst mixing, and one HVLP spray gun with external catalyst mixing. According to the Composites Fabricators Association's industry survey, the AAA external mixing spray gun is the major spray gun used by the industry; therefore, it is treated as the baseline condition. The AAA spray gun was compared with the HVLP spray gun. The effects of internal and external catalyst mixing were evaluated for the HVLP spray guns. Magnum provided all three spray guns. A pump ratio of 20:1 was selected for the gel coat pump systems. The spray guns were compared at similar gel coat thicknesses (about 18 to 24 mil) sprayed on an FRP mold.

The gel coat formulations and application equipment are denoted as follows:

- A: Formulations
 - GF1. Regular ISO-based gel coat (baseline condition)
 - GF2. Low-VOC, ISO/NPG[®]-based gel coat

B. Equipment

GE1. AAA spray gun with external catalyst mixing (baseline condition)

GE2. HVLP spray gun with internal catalyst mixing

GE3. HVLP spray gun with external catalyst mixing.

Table 2-2 shows the number of test runs for each of the gel coat formulation and equipment combinations in the gel coat experiment.

	Equipment type			
Formulation	GE1-AAA(ext)	GE2-HVLP(int)	GE3-HVLP(ext)	
GF1 Regular gel coat	3	3	3	
GF2 Low-VOC gel coat	3	3	3	

Table 2-2. Test Runs for Gel Coat Experiment

ext=External catalyst mixing. int=Internal catalyst mixing.

2.3 Resin Experiment

The resin experiment examined five resin formulations with a AAA spray gun and three pieces of application equipment with a regular low-profile resin.

The resin formulations selected were one dicyclopentadiene (DCPD)-based low-profile resin catalyzed with MEKP, one DCPD-based low-styrene resin, one ORTHO-based styrenesuppressed resin, one DCPD-based resin catalyzed with benzoyl peroxide (BPO), and the same ORTHO-based styrene-suppressed resin with an additional wax content. All the resin formulations were sprayed by a AAA spray gun. Reichhold Chemicals, Inc., provided all resin formulations and catalysts. Reichhold's Superox[®] 46709 MEKP solution has 9 percent active oxygen. Reichhold's Superox[®] 46744 BPO catalyst is a 40 percent BPO dispersion in nonvolatile plasticizer that has 2.6 percent active oxygen. The catalyst ratios for each of the resins followed those suggested by Reichhold.

The pieces of resin application equipment selected were one AAA spray gun with external catalyst mixing, a flow coater with internal catalyst mixing, and a pressure-fed roller with internal catalyst mixing. The AAA spray gun has a valve that allows the operator to use either MEKP or BPO catalyst solution. The AAA external mixing spray gun is considered the baseline condition of the industry. The AAA spray gun was compared with other nonspraying equipment (i.e., the flow coater and the pressure-fed roller). Magnum provided all the equipment for evaluation. A pump ratio of 11:1 was selected for the resin pump systems. The equipment was compared at similar resin laminate thicknesses (about 70 to 100 mil). Fiberglass roving was used for the AAA spray gun and 1.5-oz/ft² chopped strand mat was used for the flow coater and pressure-fed roller. Two layers of the chopped strand mat were used for nonspraying lamination; multiple passes of sprayup were used to give similar laminate thicknesses.

Resin formulations and application equipment are denoted as follows:

A. Formulations

RF1. DCPD-based low-profile resin catalyzed with MEKP (baseline condition)

RF2. DCPD-based low-styrene resin catalyzed with MEKP

RF3. ORTHO-based styrene-suppressed resin catalyzed with MEKP

- RF4. DCPD-based resin catalyzed with BPO
- RF5. Water-emulsified resin (included in the test plan but the manufacturer withdrew from the test)
- RF6. Same ORTHO-based styrene-suppressed resin (RF3) with an additional 0.1 percent wax

B. Equipment

- RE1. AAA spray gun with external catalyst mixing (baseline condition)
- RE2. Flow coater with internal catalyst mixing
- RE3. Pressure-fed roller with internal catalyst mixing
- RE4. Same AAA with external BPO catalyst mixing for the resin catalyzed with BPO

Table 2-3 shows the number of test runs for the resin formulation and equipment examined in the resin experiment.

	Equipment type				
Formulation	RE1-AAA(ext) RE2-flow RE3-pressure- coater(int) fed roller(int)		RE3-pressure- fed roller(int)	RE4-AAA (ext)	
RF1. DCPD-based low-profile resin with MEKP catalyst	6	3	3	NA	
RF2. DCPD-based low-styrene resin with MEKP catalyst	3	NA	NA	NA	
RF3. ORTHO-based styrene- suppressed resin with MEKP catalyst	3	NA	NA	NA	
RF4. DCPD-based low-profile resin with BPO catalyst	NA	NA	NA	. 3	
RF6. ORTHO-based styrene- suppressed resin + 0.1% of wax with MEKP catalyst	3	NA	NA	NA	

 Table 2-3. Test Runs for Resin Experiment

• ext=External catalyst mixing.

int=Internal catalyst mixing.

NA = Not included in the experiment.

Note: RF5 is a water-emulsified resin that was not tested because the manufacturer withdrew from the test.

Chapter 3 Facility and Experimental Setup

The evaluation test was conducted in an isolated spray booth in Reichhold Chemicals' physical testing laboratory, located in Research Triangle Park, North Carolina. This type of spray booth is commonly used in an FRP/C facility. Reichhold Chemicals' physical testing laboratory is used to perform testing for their resin users. It is not a production facility; therefore, the background VOC concentration can be minimized.

3.1 Total Enclosure System

The spray booth is situated in an enclosed room with a double door leading to the physical testing laboratory. The laboratory is air-conditioned; therefore, the room temperature and humidity were very stable during the entire period of testing. The stable conditions reduced the variability of temperature effect. Most facilities are not air-conditioned in the summer, however, they do have winter heating to maintain product quality.

Figure 3-1 shows the side view of the spray booth. The room is 12 feet wide, 19 feet high, and 15 feet deep, which can be considered a permanent total enclosure. The double door measures 6 feet wide by 7 feet high, which can be considered the natural draft opening (NDO) to the enclosure. Inward linear air flow velocity at the door (i.e., NDO) during the testing was always above 200 ft/min. The spray booth and the enclosed room meet the criteria for a total enclosure as prescribed in EPA Method 204--Criteria for and Verification of a Permanent or Temporary Total Enclosure. Therefore, the emissions from the operations in the spray booth can be assumed 100 percent captured.

The spray booth is 7 feet high, 11.5 feet wide, and 7.5 feet deep from the front edge to the filter bank. The filter bank is 6 feet high by 11 feet wide. The distance between the front edge of the spray booth to the double door is 4 feet 10 inches. The air-conditioned makeup air flows through the double door. The exhaust air flows through the filter bank at the end of the spray booth and is exhausted upward by a duct 34 inches in diameter. The exhaust flow rate from the spray booth averaged 8,670 ft³/min during the testing.

3.2 Emission Sampling Location

Emission measurements and exhaust air flow rate were monitored from the exhaust duct. The sampling location is 6 diameters downstream of the last bend as shown in Figure 3-1. EPA Methods 1 and 2 were used to determine the exhaust gas velocity and volumetric flow rate. EPA Method 25A was used to determine total gaseous organic emissions. The emission sampling procedures are outlined in Section 5.1.



Figure 3-1. Side view of the Reichhold Chemicals spray booth and the experimental setup in a permanent total enclosure (19'H x 12'W x 15'L).

3.3 Experimental Setup

3.3.1 FRP Mold

Three identical FRP molds were used for this evaluation test. Figure 3-2 shows a sketch of the male FRP mold. The male mold has five exposed smooth surfaces similar to a rectangular box. The mold measures 2 feet high, 2.5 feet long, and 2 feet wide. A 2-inch wide flange surrounds the bottom of the mold for ease of part removal. The total surface area, including flange, equals $24.5 \text{ ft}^2 (2.28 \text{ m}^2)$. The mold is constructed of traditional reinforced plastics material to represent actual tooling material used by the industry. These empty molds weighed about 34 kg. The mold was placed on a turntable mounted on a cart with casters. The turntable allows the operator to spray on all mold surfaces by turning the mold and without moving his position to the downwind location. The cart allows easy transfer of the mold from a preparation area to the spray booth.

3.3.2 Air Flow Baffle

The exhaust flow rate from the spray booth could not be adjusted because the spray booth had a constant speed exhaust fan. Therefore, a baffle was used between the double door and the spraying zone to divert the air flow to the sides of the spray booth so that the air flow velocity in the spraying zone could be reduced. The 6.5-foot by 4-foot baffle was constructed from lattice board on a frame built from 2-inch by 4-inch studs. It has two additional pieces measuring 6.5 feet by 2 feet on either side of the baffle. These two side pieces can swing open like a screen. Two layers of 15-mil-thick glass veil were attached to the centerpiece of the baffle to reduce the air flow velocity through the baffle. In the pilot experiment, the baffle was used to maintain the low air flow velocity and was removed for the high air flow velocity. Using this baffle, the linear air flow velocity in the spraying zone can be reduced from more than 100 ft/min to 40 ft/min. The baffle was used throughout the gel coat and resin experiments to maintain a low air velocity in the spraying zone.

3.3.3 Glass Veil and Kraft Paper to Capture Overspray

Gel coat and resin sprayup generate overspray. To account for the materials not adhered to the mold, glass veil was used on the filter bank and kraft paper was used on the ground surface and side walls to capture overspray. The veil is 15 mils thick of A-type glass with non-styrenesoluble binder. Two layers of the veil were used on the filter bank. The test results showed that almost all airborne droplets were trapped on the first layer of veil. The kraft paper used for ground cover was 50# weight. These veil and kraft papers were replaced every test run so that overspray for each test run could be accounted for accurately.



Figure 3-2. Sketch of a male mold.

3.3.4 Protective Equipment and Clothing for Operator

The operator wore a respirator with activated carbon cartridges to protect him from exposure to styrene during the application stage of a test run. The operator also wore safety glasses at all times. In order to account for any materials that might come into contact with the operator, clean disposable gloves, coveralls, and shoecovers were used in each test run. This protective gear was weighed before and after the test run to determine the amount of materials on them.

3.4 Resin Property Testing Laboratory

Reichhold Chemicals has a resin property testing laboratory located in the same building as the spray booth. The laboratory has all the instrument and equipment necessary to determine the styrene contents and curing characteristics for the gel coat and resin formulations. Reichhold personnel followed their standard procedures to measure properties for every gel coat and resin formulation examined in the test. These Reichhold Standard Test Procedures are No. 18-001, Determination of Non-Volatile Content of Polyester Resins; No. 18-021, Determination of Brookfield Viscosity & Thixotropic Index of Polyester Resins; No. 18-501, Determination of Room Temperature Gel, Time to Peak, and Peak Exotherm Characteristics of Polymer Resin; and No. 18-152, Determination of Static Styrene Emissions for Compliance with SCAQMD Rule 1162. Copies of these Reichhold standard test procedures are provided in Appendix B (Volume II).

Chapter 4 **Materials and Equipment**

4.1 **Properties of Gel Coat and Resin Materials**

The properties of the gel coats and resins were analyzed by Reichhold personnel in their laboratory using Reichhold standard test methods. These properties are shown in Table 4-1 for gel coats and Table 4-2 for resins. A large sample (about 200 g) was collected for each material when it was first used and a smaller sample (about 20 g) was collected when the material was last used. At the end of the testing, the large samples were analyzed for the listed properties and the small samples for percent nonvolatile (%NV). The final %NV measurement was to verify whether the material lost styrene over the test period or not. The results indicated that no noticeable styrene was lost from the container because proper procedures were used to minimize styrene evaporation loss.

Generally, the measured properties were in agreement with the properties listed in the manufacturers' data sheets. However, major differences were found for the low-VOC gel coat, the low-styrene resin, and the BPO resin. At the same catalyst ratio, the measured cup gel time for the low-VOC gel coat (27 min) is longer than CCP's listed gel time (14-17 min). Measured gel time for low-styrene resin (30 min) is also longer than a typical gel time (15 min) listed in the Reichhold data sheet. The longer gel time might have an effect on total emissions because the wet surface had a longer time to emit styrene.

Table 4-1. Gei Coat Properties ivieasured at Keichnold				
	GF1 Regular gel coat	GF2 Low-VOC gel coat		
CCP product code (color)	944-W-005SP (base white)	962-WA-196SP (pink)		
Density, lb/gal	10.6-10.9	11.3-11.6		
% NV, average (range)	61.3 (61.1-61.4)	74.6 (74.6-74.7)		
% Styrene (by difference)	38.7	25.4		
Viscosity, cps (LVF #4 @ 60 rpm)	3,040	2,970		
Thix index	6.1	3.9		
Catalyst Superox [®] No. and type	46709 MEKP	46709 MEKP		
Catalyst ratio, weight %	1.8	1.8		
Cup gel time, min	17	27		
Total time to peak, min	35	51		
Peak exotherm, °F	353	251		
Rule 1162 static emissions, g/m ²	133	83		

Table 4-1. Gel Coat Properties Mea	sured at Reichhold
------------------------------------	--------------------

	RF1 Low- profile	RF2 Low- styrene	RF3 Styrene- suppressed	RF6 Styrene- suppressed+ 0.1% wax	RF4 Neat BPO	RF4 (modified) BPO+0.5% fume silica as thickening agent
Reichhold's Polylite [®] No.	33233-05	33234-17	33099-08	33099-08	33146-17	33146-17
Density, lb/gal	9.0	9.2	9.1	9.1	9.1	9.1
% NV, average (range)	61.7 (60.9-62.2)	64.7 (63.8-65.5)	56.5 (56.5-56.6)	56.7 (56.7-56.7)	57.4 (57.3-57.4)	57.4 (57.3-57.4)
% Styrene (by difference)	38.3	35.3	43.5	43.3 ·	42.6	42.6
Viscosity, cps (Brookfield LVF #3 @ 6/60 rpm)	585	421	534	394	163	386
Thix index	3.5	2.3	2.6	2.5	2.2	3.8
Catalyst Superox [®] No. and type	46709 MEKP	46709 MEKP	46709 MEKP	46709 MEKP	46744 BPO	46744 BPO
Catalyst ratio, weight %	1.5	1.4	1.5	1.5	2.1 (slow gel)	3.1 (fast gel)
Cup gel time, min	20	30	17	17	30	17
Total time to peak, min	31 .	40	32	33	39	26
Peak exotherm, °F	333	316	309	318	231	277
Rule 1162 static emissions, g/m ²	69.0	73.6	54.0	49.4	160.9	96.6

.

.

Table 4-2. Resin Properties Measured at Reichhold

When the neat (unfilled) BPO resin was first used, it had a much longer gel time (30 min) than the listed gel time (12 min). Its viscosity was also low, so the resin did not stay on the mold until it cured. After two test runs on the neat BPO resin, a 0.5 weight percent of fume silica was added to thicken the resin and the BPO catalyst ratio was increased from 2.1 to 3.1 percent to shorten the gel time. Two additional test runs were conducted for the modified BPO resin. The test results for neat BPO resin and modified BPO resin were analyzed separately.

4.2 Setting of Gel Coat and Resin Application Equipment

The application equipment was prepared for each test run in a separate spray booth. An experienced operator from Magnum Industries operated the application equipment for the entire 5-week period. He adjusted the setting on the equipment in the preparation area until a good spray pattern was acquired. Then the equipment was disconnected from the central compressed-air line, moved to the spray booth where the test was conducted, and reattached to the central compressed-air line. The setting on the equipment was recorded after the application was completed. Tables 4-3 and 4-4 show the range of the setting for the gel coat and resin application equipment, respectively. Table 4-3 shows that the low-VOC gel coat required more air pressure and larger spray tips to achieve a spray pattern similar to the regular gel coat.

Equipment type	GE1-AAA (external catalyst mixing)		GE2-HVLP (internal catalyst mixing)		GE3-HVLP (external catalyst mixing)	
Magnum model No.	ATG-3500		HVLPF-5500		HVLPF-5500	
Pump ratio	20:1		20:1		20:1	
Type of gel coat	GF1 Regular	GF2 Low-VOC	GF1 Regular	GF2 Low-VOC	GF1 Regular	GF2 Low-VOC
Air supply pressure, psi	42-44	52-60	38-45	60-68	42-44	54-64
Catalyst atomizing pressure, psi	26	26	NA	NA	26	26
Spray tip No.	418	518/718	418	518/718	418	518/718
Catalyst ratio setting, volume %	2.1	2.1-2.4	2.1	2.1-2.4	2.1	2.1-2.4
Deliver rate, g/min	784-794	746-839	670-760	779-933	780-809	774-927
Deliver rate, gal/min	0.16	0.14-0.16	0.14-0.16	0.15-0.18	0.16-0.17	0.15-0.18

Table 4-3. Summary of Gel Coat Equipment Setting	· · · · ·
--	-----------

1.19

15

Equipment type	RE1-AAA (external MEKP catalyst mixing)			RE4-AAA (external BPO catalyst mixing)		RE2-Flow coater (internal catalyst mixing)	RE3-Pressure- fed roller (internal catalyst mixing)	
Magnum model No.	ATC-4000			ATC-4000		Flo-6000	MRD resin roller	
Pump ratio	11:1			11:1		11:1	11:1	
Type of resin	RF1 low- profile	RF2 low- styrene	RF3 styrene- suppress.	RF6 styrene- suppress. + wax	RF4 neat BPO	RF4 BPO with thickener	RF1 low-profile	RF1 low-profile
Air supply pressure, psi	37-39	37-38	37-41	36-38	26	24-25	40-42	40-42
Catalyst atomizing pressure, psi	18-19	18	17-18	18-26	43-45	41-43	NA	NA
Spray tip No.	443	443	443	443 ·	443	443	#2	NA
Catalyst ratio setting, volume %	1.5-1.6	1.6	1.5-1.6	1.6	2.0-3.0	3.5	1.5-1.6	1.6
Deliver rate, g/min	2332- 2559	2316- 2335	2254- 2409	2286- 2569	2065- 2376	2205-2269	3388-3605	Not measured
Deliver rate, gal/min	0.57-0.63	0.56-0.56	0.55-0.58	0.55-0.62	0.50-0.58	0.53-0.55	0.83-0.88	Not measured

Table 4-4. Summary of Resin Application Equipment Setting

4.3 Reinforcements

PPG Industries, Inc., provided all the reinforcements for the testing. The HYBON[®] 700 HTX roving material was used for resin sprayup and a GPM chopped strand mat (1.5 oz/ft^2) was used for nonspraying resin lamination. The chopped strand mat was cut into proper sizes before the test so that the operator could apply the mat, piece by piece, on the mold surface.

Chapter 5 Determination of Emission Quantities

Two separate test methods were used to quantify emissions from the test. The first test method was an emission measurement method that uses EPA Method 25A to determine a realtime, continuous emission concentration in the stack and EPA Methods 1 through 4 to determine the exhaust flow rate. Because the enclosed room with the spray booth met the criteria for a total enclosure, the emissions within the enclosed room could be assumed 100 percent captured. The emission quantities were calculated from the product of an average emission concentration and an average exhaust flow rate during a test run.

The second test method was a mass balance calculation method using gravimetric measurements. This method measures the weights of all materials, overspray, mold, and part at the beginning and end of each test run. The difference between the total initial weight and the total final weight is considered the weight loss due to emissions.

Before and during the test campaign, pure styrene evaporation tests were used to compare the emission quantities determined by these two test methods. This involved measuring weight loss due to evaporation from terry cloth towels soaked in pure styrene using a highprecision scale. The measured weight loss was compared with emissions determined by the emission measurement method. If the results are close, it implies that the emission measurement method was accurate.

Both test methods determine total emissions. Because these gel coat and resin materials contained only styrene monomer, the total emissions measured could be considered styrene emissions. Other VOC emissions were excluded from the surrounding environment. The background (i.e., baseline) VOC concentration in the laboratory was measured before each test run and subtracted from the average emission concentration so the net increase in concentration could be attributed to the test. A test run began when gel coat or resin application started and ended when curing was complete and the monitored concentration returned to the baseline concentration. Most of the test runs lasted from 60 to 90 minutes, depending on the time required for complete curing. Two test runs for the neat BPO resin were longer than 100 minutes because of unusually long curing time.

5.1 Emission Measurement Method

The emission measurement method determines styrene concentrations in the exhaust air and exhaust air flow rate, then uses these results to calculate total emissions during the test run.

5.1.1 Determination of Styrene Concentrations in Exhausted Air

Styrene emissions in the exhaust stack of the total enclosure were measured according to EPA Method 25A as given in *Code of Federal Regulations*, Chapter 40, Part 60. The

measurements were made using a Ratfisch Instruments model RS55CA total hydrocarbon (THC) analyzer. This analyzer has a flame ionization detector (FID) that responds to hydrocarbons approximately in proportion to the number of carbon atoms entering the detector. The total hydrocarbon measurements can be attributed to the styrene emissions because the only hydrocarbon emission source was the gel coat or resin application and styrene is the only monomer used in the formulations. Measurements were made immediately before gel coat or resin application started to determine the levels of background hydrocarbons (e.g., natural methane and other trace VOCs) in ambient air. These background levels were subtracted from the levels measured during the test run.

The THC analyzer was connected to the exhaust stack by a sampling line fabricated from a 12-foot length of 1/4-inch ID perfluoroalkoxy (PFA) Teflon tubing. The tubing was capped inside the exhaust stack. Eight holes were drilled in the tubing at various points across the 34inch diameter of the exhaust stack to obtain a representative sample of its contents. Sample was drawn through the sampling line into the analyzer at a flow rate of 7 L/min. Most of the sample was vented to the atmosphere, but a small portion of the sample entered the FID through a capillary. A backpressure regulator maintained a constant sample pressure, which maintained a constant sample flow rate in the capillary. The sample was oxidized by a hydrogen/air flame and the ionized carbon atoms produced in the flame were detected by an electrometer.

The output signal (0 to 10 V dc full scale [FS]) from the analyzer was recorded by an Omega Engineering model OM-170 microprocessor-based portable data logger and a Hewlett-Packard model 7132A strip chart recorder. Both instruments were operated on their 0- to 10-V FS ranges. The data logger recorded the voltages at 2-second intervals throughout each test run. At the end of each day, the voltage measurements were transferred to a laptop computer containing a spreadsheet program. The strip chart recorder provided a visual indication of the styrene emissions measurements during each test run and provided physical documentation for each test run.

The THC analyzer was operated on Range 2 (0 to 200 ppm styrene) for most of the test runs, but was operated on Range 1 (0 to 20 ppm styrene) for three resin experiment runs in which low styrene concentrations were expected. These ranges are also equivalent to 0 to 53 ppm propane and 0 to 533 ppm propane. The THC analyzer was calibrated prior to each test run using compressed gas calibration standards. A calibration drift check was done at the end of each test run. Styrene calibration standards could not be used directly for routine calibrations during test runs because of cylinder pressure limitations associated with styrene's dewpoint. Instead, propane in air calibration standards without such pressure limitations were used for the routine calibrations. The calibration gases were 16, 27, 45, 160, 267, and 453 ppm propane. These calibration gases corresponded to 30 percent, 50 percent, and 85 percent of the two full-scale ranges, as called for in EPA Method 25A.

Calibration data obtained from measurements of propane calibration standards could be used for the styrene emissions determination because RTI developed a correction factor for converting propane concentrations into the equivalent styrene concentrations prior to the testing. A styrene molecule has eight carbon atoms and a propane molecule has three carbon atoms. As a first approximation, one would expect the propane-to-styrene correction factor to equal the ratio of the carbon atoms (i.e., 8/3 = 2.667). The measured propane-to-styrene correction factor was 2.686 for the 0- to 200-ppm styrene range on the THC analyzer. This measured correction factor was used in emission calculations.

The propane calibration standards were verified by RTI using propane analytical reference standards. They were intercompared with styrene calibration standards to obtain the propane-to-styrene correction factor. The styrene calibration standards were verified by RTI using styrene analytical reference standards. The details of these measurements are presented in Appendix C (Volume II).

In general, six propane calibration standards, including the high-level, mid-level, and low-level calibration standards for the selected analyzer range, and zero air were measured during the calibration for the first test run of each day. The three propane calibration standards for the selected analyzer range and zero air were measured during the calibrations for subsequent test runs. Calibration data for one test run were used for the preceding test run's drift check, except for the last test run of the day when a separate drift check was conducted. The analyzer's zero and span pots were not adjusted during the entire 5-week testing period. The details of these calibrations are presented in Appendix D (Volume II).

The propane calibration standards were connected to the analyzer's calibration port via an 8-foot length of 1/8-inch ID PFA Teflon tubing. An in-line pressure regulator set to 5 psig and a needle valve maintained a constant flow rate in the tubing. Quick-connect fittings were used to switch from one calibration standard to the next. The analyzer required 15 minutes or more to yield a stable analyzer response for the first standard to be analyzed during a calibration. However, the stabilization period for subsequent calibration standards was only a few minutes. The cause for this long initial stabilization period was never determined, but it represented only a minor impediment to the calibrations.

After the voltage readings from the styrene emissions measurements were transferred to the computer-based spreadsheet, they were converted into an average voltage for the test run. The voltage associated with the background air measurement from the start of the test run was subtracted to yield a net average voltage. An average styrene concentration for the test run was obtained by multiplying the net average voltage by a styrene calibration factor. This calibration factor was obtained by dividing the equivalent styrene concentration for the high-level calibration standard by the difference between the voltages from the measurements of the high-level calibration standard and zero air.

RTI checked for concentration stratification inside the exhaust stack during a pure styrene evaporation test by sampling the exhaust stream across two perpendicular traverses. These measurements were made at 10 points on each traverse at distances corresponding to equal

subdivisions of the exhaust stack's area. The sampling line was modified so that sample was collected from a single point in the exhaust stack. The styrene concentration was not stable during this pure styrene evaporation test, and the analyzer response declined from 2.17 to 1.32 V. Least squares regression was used to fit these data to an exponential decay curve with a coefficient of determination (i.e., r-squared) equal to 0.98. Individual measurements deviated from the regression curve by an average of 1.6 percent of the predicted value. The maximum deviation was 5.2 percent. This statistical analysis suggests that there is little concentration stratification in the exhaust stack.

5.1.2 Exhaust Air Flow Rate Measurement

Air velocity in the 34-inch diameter circular exhaust stack of the total enclosure was measured according to EPA Methods 1 and 2 as given in *Code of Federal Regulations*, Chapter 40, Part 60. The measurements were made using a Dwyer series 160 stainless steel pitot tube (standard type) and a Dwyer series 2000 Magnehelic differential pressure gauge. The Magnehelic gauge was compared to an inclined manometer (a primary standard). Magnehelic readings were 95 percent (0.95) of manometer readings. This 0.95 correction factor was used in air flow rate calculations. The velocity was measured at a distance of approximately five to six stack diameters downstream of two right-angle bends in the exhaust stack.

Velocity across two perpendicular traverses was measured weekly. These measurements were made at 12 points on each traverse at distances corresponding to equal subdivisions of the exhaust stack's area. These data were recorded in a data sheet and were transcribed into a computer-based spreadsheet for data reduction. In general, the weekly velocity measurements indicated that the exhaust air flow rate remained relatively constant for the entire 5-week testing period. The average exhaust air flow rate was 8,685 ft³/min for the entire testing period and individual weekly measurements varied from 8,358 to 9,034 ft³/min. The Reynolds number for the air flow in the 34-inch diameter exhaust stack was 3.97x10⁵, which places the flow in the turbulent regime. Therefore, any concentration stratifications were not likely to persist for long distances inside the exhaust stack. This conclusion is consistent with the negative results of the concentration stratification measurements.

RTI checked for off-axis flow on one occasion by rotating the pitot tube inside the exhaust stack and recording the velocity head at various angles. The results of these measurements indicate that off-axis flow was not a problem in the exhaust stack.

Velocity head (Δp) measurements at the centerline of the exhaust stack were usually performed at 15-minute intervals during each test run. The Magnehelic differential pressure gauge was used to obtain these measurements. In general, the centerline Δp remained relatively constant throughout each test run although there were short-term fluctuations on the Δp . The 15minute data were recorded in a data sheet and in a laboratory notebook during each test run and were transcribed into a computer-based spreadsheet for data reduction. The average centerline Δp for a test run was used as a scaling factor for calculating an estimated average exhaust air flow rate for that test run. In general, the average centerline Δp remained relatively constant for the entire testing period. Individual values ranged from 0.109 to 0.133 inch of water with an overall average value of 0.120 inch of water.

The exhaust flow rate during the test run was calculated according to the following formula:

$$Q \operatorname{run} = [\operatorname{avg} (\Delta p \operatorname{run})^{0.5} / (\Delta p \operatorname{weekly})^{0.5}] \times Q \operatorname{weekly}$$
(5-1)

where

Q run = exhaust flow rate during a test run (acfm) Q weekly = exhaust flow rate determined by weekly velocity traverse (acfm) avg (Δp run)^{0.5} = average square root of 15-minute Δps recorded at centerline during the test run (Δp weekly)^{0.5} = square root of Δps recorded during weekly velocity traverse.

The relative humidity and temperature of the air in the spray booth were measured by a sling psychrometer during each test run. The measurements showed that the ambient air temperature and relative humidity were very stable at 73 ± 1 °F and 58 ± 2 percent, respectively.

5.1.3 Emissions Determined by Emission Measurement Method

Styrene emission quantity (Em) for each test run was calculated by the following equation:

Em, $lb = 2.6 \times 10^{-9} \times Q \times MW \times C \times T$	(5-2)
Em, $g = 1.18 \times 10^{-6} \times Q \times MW \times C \times T$	(5-3)

where

2.6x10 ⁻⁹ , 1.18x10 ⁻⁶	= conversion factors to standard conditions (68° F and 29.92 inches mercury) in English and metric units, respectively
Q	= average exhaust air flow rate (actual cubic feet per minute)
MW	= molecular weight of styrene (104)
С	= average styrene emission concentration during the entire test run (ppmv actual)
Т	= duration of test run (minutes).

Using the emission concentration profile and the exact duration of the application stage (Ta), an average emission concentration (Ca) could be calculated for the application stage in each test run. The total emissions during the application stage (Ea) could be calculated from the same equation:

22

Ea, $lb = 2.6 \times 10^{-9} \times Q \times MW \times Ca \times Ta$	(5-4)
$Ea, g = 1.18 \times 10^{-6} \times Q \times MW \times Ca \times Ta$	(5-5)

The difference between total emissions and emissions during the application stage is the emissions from the wet-out stage (for resin lamination), stagnant (curing) stage, and overspray.

5.2 Mass Balance Calculation Method Using Gravimetric Measurements

The mass balance calculation method involves weighing all materials, overspray, mold, and part in the beginning and at the end of a test run. The difference between the total initial weight and the total final weight is the weight loss due to emissions.

Weight losses due to styrene emissions were determined using two floor-type, highprecision scales (Sartorius Corporation, Model F150S). The scales have a 150,000-g capacity and 1-g readability. These two scales were calibrated with subsequent additions of standard weights - 1 g, 5 g, 10 g, 20 g, 50 g, 100 g, 500 g, 1,000 g, and 2,000 g - daily. The calibration procedures were performed on an empty scale and with a heavy object (i.e., an empty mold) on the scale. This dual calibration procedure ensured that the scales had the same sensitivity in the range of weights encountered in the tests. These calibration procedures showed that the scales precisely indicate the standard weights added. Scale drift was checked periodically by leaving a 1,000-g or 2,000-g standard weight on the scale overnight. The drift check showed that these two scales were very stable and the overnight drifts were within ± 2 g.

The first scale was used to measure the initial and final weights of gel coat or resin materials, catalyst, fiberglass reinforcement, glass veil, protective clothing, and kraft paper for ground cover. A second scale was specifically used for the mold and cart. The mold and cart were left on the second scale for the entire test run.

The gravimetric measurement procedures for the mass balance calculation method are outlined as follows:

- A. Before Application
 - 1. Determine the initial weight of ground cover (e.g., kraft paper) and thin glass veil (used to capture overspray droplets on filter bank) W1.
 - 2. Determine the initial weight of tools and other items (e.g., wet-out rollers, gloves, booties, coverall) that will come into contact with the materials during the application W2.
 - 3. Determine the initial weights of materials (i.e., gel coat, resin, catalyst, fiberglass roving, or chopped strand mat) to be used for part production. Weigh the pump

system including gel coat or resin container on the first scale to determine the initial weight of gel coat or resin material and catalyst - W3.

- 4. Determine the initial weight of the empty mold with the cart and protective skirt on the second scale W4.
- B. Preparation for Gel Coat or Resin Application
 - 1. Place ground cover on the floor around the second scale in the spray booth and attach glass veil on the filter bank to capture droplets from overspray.
 - 2. Place the empty mold and the cart (with protective skirt attached) on the second scale in the center of the spray booth.
 - 3. Apply gel coat or resin in a manner consistent with a typical operation.
- C. After Application
 - 1. Determine the final weights of materials (i.e., gel coat, resin, catalyst, fiberglass roving, or chopped strand mat) used for application. Take the reading of the whole pump system from the first scale to determine the final weight of gel coat or resin material and catalyst W5.
 - 2. Take a measurement reading of the second scale for the mold with the wet gel coat or resin after application is completed W6.
 - 3. For resin lamination, take another measurement reading of the second scale for the mold with the part, after wet-out rolling is completed W7.
- D. After Complete Curing
 - 1. Determine the final weight of the mold with cured gel coat or resin laminate on the second scale W8.
 - 2. Determine the final weight of ground cover and thin glass veil W9.
 - 3. Determine the final weight of tools and items (e.g., wet-out rollers, gloves, booties, coverall) that came into contact with the materials during the application. (Wet-out rollers can be weighed right after they are used so that resin residue can be cleaned from the rollers) W10.

E. Transfer Efficiency

From the weights of materials used and materials applied on the mold, calculate the transfer efficiency for each test run. Transfer efficiency = (W6-W4)/(W3-W5).

F. Emissions from Part During Stagnant (Curing) Period

Emissions from the gel coat on the mold during the stagnant (curing) period can be determined from the weight loss after the spraying and complete curing = W6-W8.

Emissions from the resin laminate during the stagnant (curing) period can be determined from the weight loss between when the wet-out rolling was completed and curing was completed. During this period the mold remained on the second scale. Emissions from the resin laminate only during the stagnant period = W7-W8.

G. Total Emissions

Total emissions (including emissions from the application stage, the wet-out rolling stage, the stagnant [curing] period, and overspray) = Materials used (W3-W5) - Materials on the mold (W8-W4) - Materials not on the mold (W9+W10-W1-W2).

A data recording sheet used for the testing is shown in Figure 5-1. This data recording sheet records more detailed measurements so that glass ratio and catalyst ratio can also be calculated.
Data Recording Sheet for Mass Balance Calculation Time: Date: **Recorded by:** Material/container #: Application technique: normal/controlled Test run#: Equipment: Wet buib: Dry bulb: **RH%:** Air velocity: low/high Baffle: with/without Initial (g) Final (g) Change (g) Mass of rear veil with a roll of wide masking tape 1 Mass of ground cover/front veil/masking tape/booties/gloves/pants/stool 2. 2a. Mass of ground cover and a roll of narrow masking tape 2b. Mass of front veil with existing masking tape 2c. Mass of booties/gloves/pants/stool Mass of wet-out rollers in container 3. 4. Mass of fiberglass roving or chopped strand mat Mass of resin or gel coat material Sp.gr. 5. Volume of catalyst, ml (catalyst type/#: 6a. Mass of catalyst 6b. Weight(g) Time 7a. Mass of scale cover + empty mold + skirt + duct tape (fan off) Mass of scale cover + empty mold + skirt + duct tape (fan on before application) 7b. Mass of scale cover + wet mold + skirt + duct tape (at the end of application) 8a. Mass of scale cover + wet mold + skirt + duct tape (at the end of rolling) 8b. Mass of scale cover + cured mold + skirt + duct tape (fan on) 9a. Mass of scale cover + cured mold + skirt + duct tape (fan off) 9b. 10. Mass of material used (M4+M5+M6b) Mass of cured material on mold + skirt + scale cover (M9b-M7a) 11. Mass of cured materials deposited elsewhere (M1 + M2 + M3) 12. 13. Total emissions (M10-M11-M12) Curing emissions from mold and skirt (M8a-M9a) 14. Glass ratio (M4/(M4 + M5))15. Catalyst ratio (M6b/M5) 16. 17. Transfer efficiency [(M8a-M7b)/M10]

Note:

26

Figure 5-1. Data recording sheet for mass balance calculation (used in the testing at Reichhold).

Chapter 6 Test Results and Discussions

A spreadsheet containing the emission measurements, gravimetric measurements, and calculated emission quantities and emission factors is provided in Appendix E (Volume II). Table 6-1 summarizes the emission measurements and calculated emission factors for three experiments. The test results were subject to analysis of variance (ANOVA) to determine the significance of variables on styrene emissions. The detailed results of this statistical analysis are included in Appendix F (Volume II). Table 6-2 compares variables that affect total emissions as measured by THC. Information in Table 6-2 is extracted from Table 17 in Appendix F.

The level of significance of the comparison is presented by the number of asterisks -- the more asterisks, the more confidence that there is a significant difference in the comparison. The majority of the comparisons are significant at the 0.001 level (or 99.9 percent confidence interval), noted by ***. This means that if the test is repeated 100 times, 99.9 percent of the test results will show a difference between the two variables compared. A few variables are significant at 0.01 or 0.05 levels (99 or 95 percent confidence intervals), noted by ** and *, respectively. If the comparison is not statistically significant at the 0.05 level, it is noted by "ns."

Table 6-2 shows that, in the pilot experiment, normal and controlled spraying techniques caused a difference in total emissions and the difference is significant at the 0.001 level. The high and low air velocity in the spray booth did not make a difference in total emission and the difference was not significant at the 0.05 level.

The gel coat experiment shows that the regular and low-VOC gel coat made a difference in total emissions and the difference is significant at the 0.001 level. The total emissions from three gel coat spray guns are not significantly different at the 0.05 level.

In the resin experiment, the difference in total emissions from low-profile (general purpose) resin and low-styrene resin is significant at the 0.01 level. The differences between low-profile resin and styrene-suppressed resin or styrene-suppressed resin with additional wax are significant at the 0.001 level. This implies that emission reductions achieved by using low-styrene resin, styrene-suppressed resin, and styrene-suppressed resin with additional wax are statistically significant. However, total emissions between styrene-suppressed resin and styrene-suppressed resin with additional wax are suppressed resin with additional wax are statistically significant. However, total emissions between styrene-suppressed resin and styrene-suppressed resin and styrene-suppressed resin with additional wax are not significantly different. This implies that the emission reduction achieved by adding wax to the styrene-suppressed resin is not statistically significant at the 0.05 level.

Similarly, emissions generated from the flow coater and pressure-fed roller are significantly different from those from the AAA spray gun at the 0.001 level. However, the emissions generated from the flow coater and the pressure-fed roller are not significantly different.

		1	Total	Emissions	Total				Emission	Factors	
	Application	Air	emissions	during	emissions	Material	· Transfer	Styrene	% AS	2/m2	9/9
Test run #1MateEquin	Method	Vel	by THC. g	application, g	by MB. g	used, g	eff. %	content. %	by THC	by THC	by THC
container #				(by THC)							
EXPERIMENTAL RUN	S										
1											
RFI-EXP RFI REI	Normal	High	631	328	886	9287	90.1	38.33	17.7	277	0.068
GFI-EXP GF1 GE1	Normai	High	456	228	478	1564	75.5	38.75	75.2	200	0.291
PILOT EXPERIMENT	1										
PI GFI GEI	Controlled	Low	322	134	380	1564	79.8	38.75	53.1	· 141	0.206
P2 GFIIGEI	Normal	High	536	310	607	2261	66.1	38.75	61.2	236	· 0.237
P3 GF1 GE1	Controlled	High	382	138	442	1695	80.0	38.75	58.2	168	0.225
P4 GF1 GE1	Normal	High	526	253	415	2067	74.0	38.75	-65.7	231	0.254
P5 GF1/GE1	Controlled	Low	397	134	412	1964	85.1	38.75	52.2	175	0.202
P6 GF1IGE1	Normal	Low	506	-219	506	2204	75.7	38.75	.59.2	222	0.230
P7 GFIIGEI	Controlled	High	427	157	466	1900	81.2	38.75	58.0	1881	0.225
P8 GF1 GE1	Normal	Low	554	271	499	2056	73.8	38.75	69.6	244	0.270
P9 GF1 GE1	Controlled	High	. 422	176	389	2064	85.0	38.75	52.7	-185	0.204
PIO GFIIGEI	Controlled	Low	396	145	457	2021	82.6	38.75	50.6	174	0.196
PII GFIGEI	Normal	High	479	214	535	2077	74.5	38.75	59.5	210	0.231
P12 GF1 GE1	Normal	Low	476	· 204	442	2049	77.7	38.75	60.0	209	0.232
				•							
Average (12 runs)			452	196	463	1994	78.0	38.75	58.3	199	0.226
M1-Normal spraying (6 ru	ns)		513	245	501	2119	73.6	38.75	-62.5	225	0.242
M2-Controlled spraying (6	nins)		391	147	424	1868	82.3	38.75	54.1	172	0.210
					· ·						
A2-High air velocity (6 ru	15)		462	208	476	2011	76.8	38.75	59.2	203	0.229
Al-Low air velocity (6 run	s)		442	184	449	1976	79.1	38.75	57.4	194	0.223
	ļ										
M1/A1 (3 runs)	·		512	231	482	2103	75.7	38.75	62.9	225	0.244
M2/A1 (3 runs)			· 372	138	416	1850	82.5	38.75	52.0	163	0.201
M1/A2 (3 runs)			514	259	519	2135	71.5	38.75	62.1	226	0.241
M2/A2 (3 runs)	!	ļ	410	157	432	1886	82.1	38.75	56.3	180	0.218
		ليبيها		L	<u> </u>						
Note: THC=THC emission	n measuremen	nt, MB=n	nass balance	measurement, E	r=emission [actor, %A	S=% avail	able styrene.			
g/g=g of emission per g of	material used			1		1					

Table 6-1. Summary of Emission Measurements and Calculated Emission Factors

(con.)

l				Totali	Emissions	Total				Emission	Factors (
1	1	Application	Air	emissions	during	emissions	Material	Transfer	Styrene	% AS	g/m2	. g/g
Test run #	Mate Equip.	Method	Vel.	by THC. gi	application. g	by MB, g	used, g	eff. %	content, %	by THC	by THC	by THC
1	container #				(by THC)							
GELCOA	T EXPERIME	TV TV	1	:	1				,			
1		r										
GI	GFIIGE3	Controlled	Low	3951	154	348	1723	84.6	38.75	59.2	174	0.229
G2	GF1IGE2	Controlled	Low	3951	164	406	1808	81.4	38.75	56.4	174	0.218
G3	GFIJGEI	Controlled	Low	4091	158	404	1756	79.0	38.75	60.2	180	0.233
'G4	GF2IGEI	Controlled	Low	2731	91	227	1929	88.8	25.35	55.8	120	0.141
GS	GFIIGEI	Controlled	Low	4031	154	355	1765	84.3	38.75	58.9	177	0.228
G6	GFIIGEI	Controlled	Low	387	142	410	1817	82.9	38.75	54.9	170	0.213
G7	GF2IGE3	Controlled	Low	271		273	1876	87.3	25.35	56.9	119	0.144
G8	GFI GE3	Controlled	Low	3821	143	472	1891	80.0	38.75	52.1	168	0.202
G9	GFIIGE2	Controlled	Low	3861	155	398	1787	82.4	38.75	55.7	169	0.216
G10	GFI GE3	Controlled	Low	384	134	360	1723	84.7	38.75	57.6	169	0.223
GII	GF2 GE2	Controlled	Low	294	94	327	1940	83.3	25.35	59.8	129	0.152
G12	GF2 GE2	Controlled	Low	2491	94	346	1940	81.9	25.35	50.6	109	0.128
G13	GF2 GE2	Controlled	Low	291 !	. 112	. 374	2245	81.1	25.35	51.2	128	0.130
G14	GF2 GE1	Controlled	Low	2671	92	332	1933	. 81.9	25.35	54.6	117	0.138
G15	GFI GE2	Controlled	Low	3391	162	387	1776	82.0	38.75	49.2	149	0.191
G16	GF2 GE1	Controlled	Low	274	99	302	2128	87.4	25.35	50.9	120	0.129
G17	GF2 GE3	Controlled	Low	298	100	310	2275	85.7	25.35	51.7	131	0.131
G18	GF2 GE3	Controlled	Low	282	93	286	1963	85.4	25.35	56.6	124	0.144
					·							
Average ()	18 runs)			332	123	351	1904	83.6	32.05	55.1	146	0.177
GF1-Regu	lar gel coat (9 ru	ns)		387	152	393	1783	82.4	38.75	· 56.0	170	0.217
GF2-Low	VOC gel coat (9	runs)		278	95		2025	84.8	-25.35	54.2	122	0.137
GEI-AAA	ext mix gun (6	runs)		336	123	338	1888	84.1	32.05	55.9	· 147	0.180
GE2-HVL	P int mix gun (6	runs)		326	130	373	_1916	. 82.0	32.05	53.8	143	0.172
GE3-HVL	Pext mix gun (6	runs)	· · ·	335	117	342	1909	84.6	· 32.05	55.7	147	0.179
J												
GFI/GEI	(3 runs)	I		400	131	390	1779	82.1	38.75	58.0	176	0.225
GF1/GE2	(3 runs)		Í	373	160	397	1790	81.9	38.75	53.8	164	0.208
GFI/GE3	(3 runs)		ļ	387	143	393	1779	83.1	38.75	56.3	170	0.218
GF2/GE1	(3 runs)	L	ļ	272	94	287	1997	86.0	25.35	53.7	119	0.136
GF2/GE2	(3 runs)			278	100	349	2042	82.1	25.35	53.9	122	0.137
GF2/GE3	(3 runs)	ļ		284	91	290	2038	86.1	25.35	55.1	124	0.140
			<u> </u>	<u> </u>	<u> </u>	<u> </u>			L	L	<u> </u>	
Note: TH	C=THC emissio	n measureme	nt, MB=1	nass balance	measurement, E	r=cmission	actor, %A	S=% avai	able styrene	· · ·		!
g/g=g of e	mission per g of	material used	i.					!	i	1	1	{

Table 6-1. Summary of Emission Measurements and Calculated Emission Factors

(con.)

	(con.)												
1	i	1			Total	Emissions	Total				Emission	Factors	
			Application	Air	emissions	during	emissions	Material	Transfer	Styrene	% AS	g/m2	g/g
Test run #	Mat	Equip.	Method	Vel.	by THC, g	application, g	by MB, g	used, g	eff. %	content, %	by THC	by THC	by THC
	cont	ainer#				(by THC)							
RESIN EX	KPER	IMENT	·	1				{					
RI	RF6	REI	Controlled	Low	316	196	284	7712	92.7	43.29	9.5	138	0.041
R2	RFI	RE2	Controlled	Low	305	169	335	5445	96.2	38.33	14.6	134	0.056
R3	RFI	RE3	Controlled	Low	286	136	267	4919	97.2	38.33	15.2	125	0.058
R4	IRFI	RE3	Controlled	Low	279	142	280	5041	97.3	38.33	14.5	123	0.055
IR5	RFI	REI	Controlled	Low	440	212	434	5978	90.8	38.33	19.2	193	0.074
R6	RF3	REI	Controlled	Low	296	193	302	5663	91.7	43.45	12.0	130	0.052
R7	RFI	REI	Controlled	Low	404	207	424	6160	91.0	38.33	17.1	177	0.066
R8	RF2	REI	Controlled	Low	389	195	361	5979	91.4	35.34	18.4	170	0.065
R9	RF4	RF4	Controlled	Low	743	266	694	6116	88.7	42.61	28.5	· 326	0 122
R10	IRFI	REI	Normal	Low	636	310	607	6133	80.5	38 33	27.1	279	0.104
R11	RFG	REI	Controlled	Low	267	153	247	5152	89.9	43.29	12.0	117	0.052
R12	REG	REI	Controlled	Low	207	155	203	4872	927	43.20	10.3	95	0.032
R12	1887	REI	Controlled	Low	403	192	374	6566	91.7	35 34	17.4	177	0.044
R14	RET	REI	Controlled	Low	304	192	366	6870	03.2	35 34	16.2	173	0.057
RIS	REI	DEI	Controlled	Low	453	278	442	7000	93.2	38 33	16.2	100	0.057
IRI6	IPEI	IDE3	Controlled	Low	433	226	236	5328	92.0	38.33	16.3	146	0.003
R10	DEA	DEA	Controlled	Low	762	356	722	7467	70.7	42.61	23.0	224	0.002
R19	DE1	027	Controlled	Low	. 702	126	752	5371	077	28 32	14.2	120	0.102
R19	RET	REI	Controlled	Low	293	120	203	6680	97.7	43.45	10.0	127	0.033
R20	10PP	PEI	Controlled	Low	271	180	202	6423	02.0	. 13.45	0.0	110	0.043
R21	REI	REI	Controlled	Low	468	216	478	6058	92.9	28 22	175	205	0.042
R22	PEI	PEI	Controlled		400	210	420	7256	02.5	39 33	16.5	205	0.063
R23	RF4	RE4	Controlled	LOW	524	192	451	\$606	93.5	42.61	21.0	201	0.003
R24	REI	022	Controlled	Low	324	134	280	6040	07.9	38 33	13.0	141	0.054
1225	DE4	DEA	Controlled		500	103	488	5608	01.0	42.61	20.6	210	0.033
1125	1		Condoned	1.0.4		135		5070		42.01	20.0		0.000
Average (2	5 000	s w "Norr	al" run P 10)		402	105	384	6008	02.2	30.87	16.5	175	0.065
Average (2	4 mm	s w/o "No	mal" an R1	<u>"</u>	302	193	375	-6096	92.2	39.07	16.0	172	0.005
11101050 (1	}	1		"				0070	,		- 10.1		0.004
REI/REI-A		ext mix gu	1. n (6 mins w/	R10)	477	230	461	6581	90.1	. 38 33	191	200	0.073
REI/REL		ext mix au	n (5 mme w/	0 P10)	411	230	432	6670	92.0	38 33	17.5	195	0.067
RE2-Flow	coate	r (3 runs)			306	143	796	5619	97 3	38 33	14.2	134	0.055
RF3-Pressi	ire-fe	d miler (3)		<u>.</u>	200	145	270	5006	97.1	38 33	15.2	131	0.059
RF4-AAA		ix gun for	RPO system	(see PEA	277	100					13.3		
RE7 J OW S	byren	a Derin (2)	DrO system	(SCC NP4	205	102	367	6472	92.0	25 34	17.3	173	0.061
DET Chime	a cur	c Acsil (J	in (2 mma)		375	192	270	6750	92.0	42.45	17.5	175	0.001
DEA DDO	Cetal	piessed rea	sin (5 runs)	<u>}</u>	200	100	417	6220	92.5	43.43	10.0	277	0.040
DEA PDO	Const	ver Resin	(+ runs)		032	252	100	6702	00.0	42.01	25.1	211	0.101
DEA DDOA		vecu Kesin	(2 runs, siow	r gei)	- /32	311	/13	5652	04.1	42.01	20.2	220	0.001
DEC WAA		vice Kesin	(2 runs, tast	ger)	512	193	468	2022	91.8	42.01 NIA	21.3 NIA	223 NIA	
DEC Chine	emu	silled resil	(INOT TESTED)	(2		NA	NA	NA 6012		AZ 20	104	117	
RPO-Styren	ie sup	pressed re	sin pius wax	(3 runs)	200	149	245	5912	91.8	43.29	10.0		0.040
Note: TLIC) 	Comini-	1		ana halanaa		Ecomicsion 6		S 6 aug 21	able stumps			
alama of the		C CITUSSIOF	measuremet	ы, мв=п I	uass palance i	neasurement, E	r=emission t	acitor, 70 A	5 70 avail	auto styrene,			{
rs=g or en	182210	m per got:	maternal used	J.			· · · · · · · · · · · · · · · · · · ·	l					

Table 6-1. Summary of Emission Measurements and Calculated Emission Factors

Comparison	Significance
Pilot experiment	
Normal vs. Controlled spraying	***
High vs. Low air velocity	ns
Gel coat experiment	·
Regular vs. Low-VOC	***
AAA (ext) vs. HVLP (int)	ns
AAA (ext) vs. HVLP (ext)	ns .
HVLP (int) vs. HVLP (ext)	ns
Resin experiment	
Low-profile vs. Low-styrene	*
Low-profile vs. Styrene-suppressed	***
Low-profile vs. Styrene-suppressed+wax	. ** *
Low-styrene vs. Styrene-suppressed	***
Low-styrene vs. Styrene-suppressed+wax	***
Styrene-suppressed vs. Styrene-suppressed+wax	ns
AAA vs. Flow coater	***
AAA vs. Pressure-fed roller	***
Flow coater vs. Pressure-fed roller	ns
Pequier up PPO entelymed (fact cel)	**
Regular vs. BPO-catalyzed (last gel) Regular vs. BPO-catalyzed (slow gel)	***
BPO-catalyzed slow gel vs. fast gel	***

 Table 6-2. Significance of Variables Affecting Total Styrene Emissions

ns = Not statistically significant at 0.05 level.

* = Statistically significant at the 0.05 level.

****** = Statistically significant at the 0.01 level.

******* = Statistically significant at the 0.001 level.

The emissions from the BPO-catalyzed resin (either neat resin with slow gel or modified resin with fast gel) are different from the regular resin under controlled spraying. The emissions from the neat BPO-catalyzed resin are also significantly different from those from the modified BPO-catalyzed resin.

The following results and discussions are based on total emissions quantified by the emission measurement method. The percent reduction is based on the averages of total emissions for the number of test runs conducted under the same conditions. The same percentage of reduction is also achieved when the emissions are expressed in grams/square meter because the same mold surface area is used in the denominator to calculate the emission factors.

6.1 Distribution of Total Emissions During Application and Curing Stages

Tables 6-3 and 6-4 show the distribution of emissions in gel coat and resin experiments. The emission quantities are the averages of the number of test runs conducted for that condition. Total emissions and emissions during the application stage were determined by emission measurement method using the procedures outlined in Section 5.1.3. The difference between total emissions and emissions during the application stage is postapplication emissions. The postapplication emissions included emissions from the wet-out rolling (for resin lamination), stagnant (curing) period, and the curing of overspray.

	Total emissions	Emis durir appli	sions 1g Ication	Post- application emissions		
Gel coat application condition	g	g	% total	g	% total	
Pilot experiment (gel coat spraying)						
Normal spraying/high air velocity (3 runs)	514	259	50	255	50	
Controlled spraying/high air velocity (3 runs)	410	157	38	253	62	
Normal spraying/low air velocity (3 runs)	512	231	45	281	· 55	
Controlled spraying/low air velocity (3 runs)	372	138	37	234	63	
Gel coat experiment (controlled spraying)						
Regular gel coat/AAA-external mix (3 runs)	400	151	38	249	62	
Regular gel coat/HVLP-internal mix (3 runs)	373	160	43	213	57 -	
Regular gel coat/HVLP-external mix (3 runs)	387	143	37	244	63	
Low-VOC gel coat/AAA-external mix (3 runs)	272	94	35	178	65	
Low-VOC gel coat/HVLP-internal mix (3 runs)	278	100	36	178	64	
Low-VOC gel coat/HVLP-external mix (3 runs)	284	91	32	193	68	
Range			32-50		50-68	
Average			39		61	

Table 6-3. Distribution of Emissions in Pilot and Gel Coat Experiments

Table 6-3 shows that 32 to 50 percent (average 39 percent) of total emissions was emitted during the gel coat spraying stage and the remainder was emitted during the postapplication (curing) stage. Figure 6-1 shows the amount of styrene emitted for each of the gel coat application conditions. It is apparent that controlled spraying emitted less styrene than normal spraying, and the low-VOC gel coat emitted less styrene than the regular gel coat. The pilot experiment also showed that low and high linear air velocities in the spray booth (between 40 and 100 ft/min) did not have an effect on emissions. Figure 6-1 also shows that there is no significant difference in total emissions for three different spray guns (i.e., AAA spray gun with external catalyst mixing and HVLP spray gun with internal and external catalyst mixing). More detailed discussion is presented in Section 6.3.

Table 6-4 shows that 38 to 63 percent (average 50 percent) of total emissions was emitted during the resin application stage and the remainder was emitted during the postapplication stage. The postapplication stage included wet-out rolling and stagnant (curing) periods. Figure 6-2 shows the styrene emissions quantified for each of the resin application conditions. It is apparent that the flow coater and the pressure-fed roller resulted in less emissions than normal or controlled resin sprayup. Low-styrene and styrene-suppressed resins also emitted less styrene than the low-profile resin. More detailed discussions for the resin experiment are presented in Section 6.4.

	Total emissions	Emissi applica	ons during ation	Postar emissi	oplication ons
Resin application condition	. g	·g	% total	g .	% total
AAA-normal spraying (1 run)	636	310	49	[.] 326	. 51
AAA-controlled spraying (5 runs)	445	214	48	231	52
Flow coater (3 runs)	306	143	47	163	53
Pressure-fed roller (3 runs)	299	166	56	133	44
Low-styrene resin (3 runs)	395	192	49	203	51
Styrene-suppressed resin (3 runs)	286	180	63	106	37
Styrene-suppressed resin + wax (3 runs)	266	149	56	117	44
Neat BPO resin - slow gel (2 runs)	752	311	41	441	59
BPO resin + thickener - fast gel (2 runs)	512	193	38	319	62
Range			38-63		37-62
Average			50		50

 Table 6-4. Distribution of Emissions in Resin Experiment



Figure 6-1. Distribution of emissions in the pilot and gel coat experiments.

Figure 6-2. Distribution of emissions in the resin experiment.



6.2 **Pilot Experiment Results**

Typical emission concentration profiles recorded by the THC analyzer for various test runs are presented and their resultant emission quantities are used in the following discussions. A comparison of typical emission concentration profiles provides a clear picture of what happened when different techniques, equipment, and materials were used. A test run began when spraying or nonspraying application started and ended when the curing was completed. The end of the zigzag-like concentration profile indicates the end of the application stage. The average concentration and the duration of application are used to calculate emissions during the application stage. As soon as the application is completed, the emission concentration gradually returns to the baseline concentration during the wet-out rolling and curing stages.

Figure 6-3 shows the typical emission concentration profiles for normal and controlled spraying test runs for the regular gel coat. Average styrene concentration during the application stage of the normal spraying test run P6 (59 ppm) is higher than that of the controlled spraying test run P10 (41 ppm).

Using the total emissions data presented in Table 6-3 and normal spraying/high air velocity as the baseline condition, Figure 6-4 shows the emission reduction observed in the pilot experiment. Controlled spraying reduced emissions by 27 percent and 20 percent at low and high air velocity conditions, respectively.

Table 6-5 shows the summary of emissions for the pilot experiment. Transfer efficiency increased and gel coat usage decreased when spraying technique improved. Total emissions and emission factors also reduced when spraying technique changed from normal to controlled spraying. However, the effects of air velocity under each spraying technique are not significant.

					the second s					
Spraying	Transfer	Materi	als used	Total e	missions	Emissio	n factor	Emission factor		
velocity	efficiency	g	Reduc. (%)	g	g Reduc. . (%)		Reduc. (%)	g/g	Reduc. (%)	
Normal/High (3 runs)	71.5	2,135		514		62.1		0.241		
Controlled/ High (3 runs)	82.1	1,886	12	410	20	56.3	9	0.218	10	
Normal/Low (3 runs)	75.7	2,103		512		62.9	. 	0.244		
Controlled/ Low (3 runs)	82.5	1,850	12	372	27	52.0	17	0.201	18	

 Table 6-5.
 Summary of Emissions for Normal and Controlled Gel Coat Spraving

Note: Material usage and emission quantities are the averages of the number of test runs for that condition. %AS = percent of available styrene in gel coat.

g/g = gram of styrene emitted per gram of gel coat material used.



Figure 6-3. Typical emission concentration profiles for normal and controlled gel coat spraying.



Condition

Figure 6-4. Emission reductions observed in the pilot experiment (based on total emissions, or emission factors in grams per square meter).

6.3 Gel Coat Experiment Results

Figure 6-5 shows the typical emission concentration profiles for a regular gel coat and a low-VOC gel coat test run. Average styrene concentration during the application stage of the regular gel coat was 45 ppm, which is higher than the 26 ppm for the low-VOC gel coat. The emission reduction from the low-VOC gel coat is evident.

Figure 6-6 shows the emission concentration profiles of the AAA spray gun with external catalyst mixing, the HVLP spray gun with internal catalyst mixing, and the HVLP spray gun with external catalyst mixing. These concentration profiles are similar in magnitude and the total emissions are not significantly different among these three spray guns.

Using the total emissions data presented in Table 6-3 and the regular gel coat/AAA spray gun controlled spraying as the baseline condition, Figure 6-7 shows the emission reductions observed in the gel coat experiment. The low-VOC gel coat reduced total emissions by 28 to 32 percent when compared to the regular gel coat. The changes in emission among these three spray guns are not significant.

Because the effect of spray guns on total emissions was not significant, nine regular and nine low-VOC gel coat test runs were combined to compare the effects of different gel coat formulations. Total emissions and emission factors were calculated from the averages of nine test runs in each gel coat formulation and presented in Table 6-6. Table 6-6 shows that the low-VOC gel coat reduced total emissions by 28 percent when compared to the regular gel coat under controlled spraying conditions. When the emission factors are presented as percent available styrene (%AS), there is a little or insignificant reduction of 3 percent. This is because the styrene contents of the gel coats canceled out the effects of emission reduction in the emission factor calculation. When the emission factors are presented as g of styrene emitted per g of gel coat applied, the low-VOC gel coat achieved 37 percent reduction. SCAQMD Rule 1162 static emission measurements for these two gel coats indicate that there is a 37 percent reduction.

	Materials Total used emissions			Emissio	on factor	Emissi	on factor	Rule 1162 static emissions				
Type of gel coat	. g	g	Reduc. (%)	%AS	Reduc. (%)	g/g	Reduc. (%)	g/m²	Reduc. (%)			
Regular (9 runs)	1,783	387		56.0		0.217		133				
Low-VOC (9 runs)	2,025	278	28	54.2	3	0.137	37	83	37			

Table 6-6. Summary of Emissions for Regular and Low-VOC Gel

Note: Material usage and emission quantities are the averages of the number of test runs for that material. %AS = percent of available styrene in gel coat.

g/g = gram of styrene emitted per gram of gel coat material used.







Figure 6-6. Typical emission concentration profiles for three types of gel coat spray guns.



Condition

Figure 6-7. Emission reductions observed in the gel coat experiment (based on total emissions, or emission factors in grams per square meter).

42

۰.

6.4 **Resin Experiment Results**

Emission quantities for different resin application equipment are summarized and presented in Table 6-7. Nonspraying equipment (i.e., flow coater and pressure-fed roller) reduced total emissions by 31 to 33 percent when compared to controlled resin sprayup. As shown in Table 6-1, the statistical analysis indicates that total emissions between the flow coater and pressure-fed roller are not statistically significant at the 95 percent confidence level.

	Materials used	Total e	missions	Emissi	on factor	Emission factor		
Type of equipment	g	g	g Reduc. (%)		Reduc. (%)	g/g	Reduc. (%)	
AAA spray gun (controlled spraying, 5 runs)	6,670	445	BL	17.5	BL	0.067	BL	
Flow coater (3 runs)	5,619	306	31	14.2	19	0.055	18	
Pressure-fed roller (3 runs)	5,096	299	33	15.3	13	0.059	12	

 Table 6-7. Summary of Emissions for Resin Application Equipment

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

%AS = Percent of available styrene in resin.

g/g = Gram of styrene emitted per gram of resin material used.

The test plan originally called for six runs of controlled spraying. Accidentally, one of the six test runs was conducted in normal spraying. Table 6-8 compares the emission quantities for three types of application equipment to the normal spraying test run. Controlled resin sprayup reduced total emissions by 30 percent when compared to normal (uncontrolled) resin sprayup. Flow coater and pressure-fed roller achieved 52 to 53 percent total emission reduction when compared to normal resin sprayup.

Figure 6-8 shows the typical emission concentration profiles for various resin application techniques and equipment. Average styrene concentration during the application stage of the normal spraying test run R10 was 88 ppm, which is higher than the 60 ppm of the controlled spraying test run R15. The flow coater and the pressure-fed roller took longer to complete the lamination but the magnitude of concentration profiles (less than 10 ppm) is much lower than that of resin sprayup.

	Transfer efficiency	Materials used	Total e	missions	Emissi	on factor	Emission factor		
Type of equipment	%	g	g	Reduc. (%)	%AS	Reduc. (%)	g/g	Reduc. (%)	
AAA spray gun (normal spraying, 1 run)	80.5	6,133	634	BL	27.1	BL	0.104	BL .	
AAA spray gun (controlled spraying, 5 runs)	92.0	6,670	445	30	17.5	35	0.067	36	
Flow coater (3 runs)	97.3	5,619	306	52	14.2	48	0.055	47	
Pressure-fed roller (3 runs)	97.1	5,096	299	53	15.3	44	0.059	43	

 Table 6-8. Comparison of Emissions among Various Resin Application Equipment and Normal Spraying

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

%AS = Percent of available styrene in resin.

g/g = Gram of styrene emitted per gram of resin material used.

Figure 6-9 shows the typical emission concentration profiles for various resin formulation test runs. The magnitude of the emission profiles decreases as the styrene content in the resin decreases or the styrene-suppressant content increases. Figure 6-10 compares emission profiles of the low-profile resin, neat BPO-catalyzed resin, and modified BPO-catalyzed resin. The neat and modified BPO resins had higher and longer concentration profiles than the low-profile resin because of higher styrene content or longer gel time. The BPO-catalyzed resin was formulated for filled application, but it was used in this testing without any filler. Fume silica was added to the BPO resin to keep the resin material on the mold until it was cured.

Emission quantities for different resin formulations are summarized and presented in Table 6-9. Low-styrene resin reduced total emissions by 11 percent when compared to controlled resin sprayup. Styrene-suppressed resin with or without additional wax reduced total emissions from controlled resin sprayup by 36 to 40 percent. Emission reductions are even higher when the comparison is based on the normal spraying test run. Statistical analysis indicates that total emissions from styrene-suppressed resin with and without additional wax are not significantly different at the 95 percent confidence interval. The neat and modified BPO-catalyzed resins



Figure 6-8. Emission concentration profiles observed for different resin application techniques and equipment.



Figure 6-9. Typical emission concentration profiles for various resin formulations (applied by AAA spray gun).



Figure 6-10. Typical emission concentration profiles for low-profile, neat-BPO, and modified BPO resins (applied by AAA spray gun).

Type of resin (applied by controlled	Materials used	Total	Total emissions			Emission factor			ion fact	or	Rule 1162 static emission		
spraying, except as noted)	g	g Reduction (%)		%AS	Reduction (%)		g/g	Redu (*	uction %)	g/m²	Reduction (%)		
Low-profile (normal spraying, 1 run)	7,710	634	BL		27.1	BL		0.104	BL		69	BL	
Low-profile (5 runs)	6,670	445	30	BL	17.5	35	BL	0.067	36	BL	69	BL	
Low-styrene (3 runs)	6,472	395	38	11	17.3	36	1	0.061	41	9	74	-7	
Styrene-suppressed (3 runs)	6,258	286	55	36	10.6	61	39	0.046	56	31	54	22	
Styrene-suppressed +wax (3 runs)	5,912	266	58	· 40	10.6	61	39	. ^{0.046}	56	31	49	29	
Neat BPO resin (2 runs)	6,792	752	-19	-69	26.2	3	-50	0.112	-8	-67	161	-133	
BPO resin + thickener (2 runs)	5,652	512 ·	·19	· -15	21.3	21	-22	0.091	13	-36	97	-41	

Table 6-9. Summary of Emissions for Various Resin Formulations

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

%AS = Percent of available styrene in resin.

.

g/g = Gram of styrene emitted per gram of resin material used.

.

emitted more styrene than the low-profile resin. These results contradict the original assumption that resin catalyzed by BPO might reduce styrene emissions. Possible explanation for this situation is that the BPO resin was developed for filler application, not for neat resin sprayup and the gel time for BPO resin was longer than that of the low-profile resin.

Figure 6-11 shows the overall emission reductions or increases observed in the resin experiment. The reductions or increases are calculated based on the total emission quantities presented in Tables 6-6, 6-7, and 6-8 for each of the conditions. Using low-profile resin and controlled spraying as the baseline, emission reductions or increases for various equipment and materials are presented. Except for the BPO-catalyzed resin, all other resin formulations resulted in emission reduction when compared to the low-profile resin.

Figure 6-12 shows the emission reductions or increases when using low-profile resin and normal spraying as the baseline. Higher emission reductions were achieved by flow coater, pressure-fed roller, low-styrene resin, and styrene-suppressed resin. If the normal spraying technique represents actual practices in the industry, Figure 6-12 shows the potential reduction that could be achieved by changing to flow-coater and pressure-fed roller and other low-styrene or styrene-suppressed resins.

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

Emission factors derived from the test results are compared to relevant EPA AP-42 emission factors in Table 6-10. These emissions factors are 1.6 to 2.5 times the respective midpoints of AP-42 emission factors. The implication of this finding is that current EPA AP-42 emission factors for gel coat and resin sprayup and hand layup operations may underrepresent actual emissions for these operations.

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	27.1 (normal spraying)	2.5
			17.5 (controlled spraying)	1.6
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

Table 6-10. Comparison of EPA AP-42 Emission Factors and Test Results (in %AS)



Condition

Figure 6-11. Emission reductions observed in the resin experiment: "controlled spraying" technique baseline (reductions based on total emissions, or emission factors in grams per square meter).



Condition

Figure 6-12 Emission reductions observed in the resin experiment: "normal spraying" technique baseline

6.6 Comparison of Emission Measurement Method and Mass Balance Calculation Method

6.6.1 Pure Styrene Evaporation Test

Three sets of pure styrene evaporation tests were conducted at Reichhold in June 1995. One set was conducted on June 5, the second set on June 7, and a final set on June 29. Within each set, there were several periods that different styrene evaporation rates were generated. The results of these different test runs are shown in Table 6-11 and Figure 6-13. The agreement between the emission measurements and the mass balance calculation method during the pure styrene evaporation runs was good. Table 6-11 shows that the average ratio of mass balance calculation method to emission measurements for these 15 runs was 0.99. Figure 6-13 indicates that the agreement between the mass balance calculation method and emission measurement method was within ± 10 percent for 12 out of 15 runs.

6.6.2 Comparison of Emissions Measured by Two Test Methods

Mass balance measurements were compared with emission measurements during four experimental test runs and 55 official test runs at the Reichhold Chemicals facility. These 59 test runs can be separated into:

4	Experimental runs
12	Pilot test runs (involving gel coat spraying)
18	Gel coat application runs
<u>25</u>	Resin application runs
59	Total runs

These two methods for these 59 test runs are compared in Table 6-12 and Figure 6-14. Prior to June 22, the pilot and gel coat application test runs were made with only the 5-gallon gel coat supply container on the scale. The amount of material used in each test run was calculated from the weight loss from the 5-gallon container. It was found that the pump system is a singleaction pump that withdraws material from the container only during the upstroke action. Therefore, there was a potential error in estimating the exact amount of material dispensed from the spray gun when the piston pump starts and ends at different positions. In this case, the amount of material in the pump system could not be accounted for by weighing the container only. Beginning in run G16, the project team member made sure that the pump started and ended at the same position, so that the amount of material in the pump system remained the same at the beginning and the end of a test run. This approach improved the accuracy of the mass balance calculation method. Table 6-12 indicates that the ratio between the mass balance calculation method and emission measurement method came close to 1.0 (indicating perfect agreement) much more consistently between test runs G16 and R2.

Date	Start Time	End Time	Emission rate	Average concentration	Exhaust	Emission rate	Emission
			by mass balance (MB)	by THC (FID) analyzer	flowrate	by THC (FID) analyzer	ratio
(m/d/y)	(hr:min)	(hr:min)	(g/min)	· (ppm)	(cfm)	(g/min)	(MB/THC)
							•
6/5/95	15:46	15:59	9.2	8.4	· 8961	9.3	0.99
6/5/95	16:18	16:30	9.9	9.5	8961	10.4	0.95
6/5/95	16:43	16:55	17.4	14.1	8961	15.5	1.12
6/5/95	16:56	17:06	11.8	· 10.6	8961	11.6	1.02
6/5/95	17:09	17:19	12.3	11.8	8961	13.0	0.95
6/7/95	10:25	10:40	40.1	39.0	8924	42.3	0.95
6/7/95	10:42	10:57	15.3	14.8	8924	15.8	0.97
6/7/95	11:06	11:11	43.8	39.0	8924	42.4	1.03
6/7/95	11:14	11:35	9.7	9.4	8924	9.9	0.98
6/7/95	11:43	11:55	3.0	2.6	8924	2.5	1.20
6/7/95	11:58	12:05	34.1	34.0	8924	36.9	0.92
6/29/95	16:42	16:49	48.7	49.1	8646	52.1	0.93
6/29/95	16:52	16:59	21.3	21.5	8646	22.8	0.94
6/29/95	17:00	17:07	50.3	49.9	8646	52.9	0.95
6/29/95	17:32	17:45	. 29.5	31.4	8646	33.3	0.89
		·					
						Average	0.99

Table 6-11. Comparison of Mass Balance Method and Emission Measurements for Pure Styrene Evaporation Tests



Figure 6-13. Comparison of mass balance with EPA Method 25A emissions measurements, during pure (100 percent) styrene evaporation tests.

	-		Exhaust flow	Ava pati	Test our	Total emissions	Total emissions	Emission mile
Date	Time	Test nin #	tate. cfm	CODC., DDM	duration mini	by THC o	by MB. c	IMB/THC
EXPERIMENTA	LRUNS			eutres, ppint		<u> </u>	UT (10, g)	
6/6/95	10:22	RF1-EXP	9124	6.35	88.8	631	888	1.40
6/6/95	14:55	GF1-EXP	9054	7.30	56.2	456	478	1.05
7/7/95	12:19	EXP1	8510	0.58	102.2	62	65	1.05
7/7/95	14:12	EXP2	8681	4.48	31.2	149	152	1.02
PILOT EXPERIN	MENT						·	
6/7/95	14:50	P1	8909	3.85	76.3	322	380	1.18
6/8/95	10:01	P2	8980	7.14	68.2	538	607	1.13
6/8/95	14.40	P3	8681	7 39	66.8	526	442	0.79
6/9/95	10:20	P5	8818	4.72	77.8	397	412	1.04
6/9/95	14:45	P6	8704	6.21	76.3	506	506	1.00
6/12/95	10:36	P7	8864	4.99	78.7	427	468	1.09
6/12/95	13:47	P8	8796	7.53	68.2	554	499	0.90
6/12/95	15:44	P9	8681	5.92	66.9	422	389	0.92
6/13/95	10:37	P10	9034	5.11	70.0	396	457	1.15
6/13/95	12:57	P11	8987	6.04	71,9	479	535	1.12
6/13/95	15:21	P12	8909	6.02	72.3	476	442	0.93
BILLUAT EXP	LINUMENT	G1	9764	E 75	70.0	205	240	
6/14/95	13:46	G2	8680	5.20	70.0	392	348	1 03
6/14/95	16:06	G3	8563	6.46	60.3	409	404	0.99
6/15/95	11:38	G4	8610	3.41	75.7	273	227	0.83
6/15/95	14:03	G5	8609	5.41	70.4	403	355	0.88
6/15/95	15:59	G6 ·	8633	5.13	71.2	387	410	1.06
6/16/95	10:23	G7	8916	3.07	80.7	271	273	1.01
6/16/95	12:49	G8	8887	. 4.97	70.5	382	472	1.24
6/16/95	15:33	G9	8819	. 5.07	70.2	386	398	1.03
6/19/95	10:36	G10	8752	5.14	69.6	384	360	0.94
6/19/95	12:47	G11	8866	3.18	85.1	· 294	327	1,11
6/19/95	15:23	G12	8700	2.74	85.0	-249	346	1.39
6/21/95	13.18	G14	· 8739	2.85	83.7	291	. 374	1.28
6/21/95	16:27	G15	8660	5.25	60.7	339	387	1.14
6/22/95	11:14	G16	8775	3.00	85.0	274	. 302	1.10
6/22/95	13:41	G17	8820	3.21	85.7	298	310	. 1.04
6/22/95	15:55	G18	8722	3.19	82.4	282	286	1.01
RESIN EXPERI	MENT						•	
6/23/95	11:06	R1	8710	2.86	103.1	316	284	0.90
6/23/95	14:30	R2	8683	3.52	81.3		335	1.10
6/23/95	16:35	R3	8399	3.70	75.0	. 286	267	0.93
6/26/95	10:42	85	8563	3.17	83.8	2/9	280	1.00
6/26/95	16:05	R6	8495	3.65	78.0	296	302	1.02
6/27/95	10:46	R7	8613	5.05	75.7	404	424	1.05
6/27/95	13:14	R8	8543	5.16	71.8	389	361	0.93
6/27/95	15:51	R9	8358	4.76	152.4	743	694	0.93
6/28/95	10:21	R10	8501	7.49	81.5	636	607	0.95
6/28/95	12:45	R11	8471	2.81	91.3	267	247	0.93
6/28/95	15:20	R12	8501	2.18	95.2	217	203	0.94
6/29/95	10:22	R13	8566	5.01	76.5	403	374	0.93
6/29/95	12:20	114 1915	8495	5.04	75.1	394	306	0.93
6/30/95	10.14	B16	8033	4 03	70.5	+03 332	336	1.01
6/30/95	13:13	817	8521	7.10	102.6	762	732	0.96
6/30/95	15:51	R18	8457	4.07	69.3	293	265	0.90
7/5/95	11:53	R19	8637	3.63	75.6	291	262	0.90
7/5/95	14:02	R20	8471	3.51	74.7	272	273	1.00
7/5/95	16:19	R21	8419	5.87	77.2	468	428	0.9
7/6/95	10:12	2 R22	8589	5.74	75.9	459	431	0.9
7/6/95	14:34	IR23	8661	5.55	88.9	524	488	0.9
7/6/95	16:41	R24	8492	3.96	78.0	322	289	0.9
111/95	10:10	//1/20	8658	5.53	85.1	500	488	0.9
			1 1				Average	1.0

Table 6-12.	Comparison of M	ass Balance Metho	d and Emission I	Measurements

•



Figure 6-14. Comparison of emission measurement methods.

•

.

.s %

Beginning in run R3, resin usage was measured by placing both the 5-gallon container and the entire piece of application equipment on the scale. This procedure avoided the need to make sure that the pump was returned to its initial position at the end of the run. With the pump and the gun on the scale, all material exiting the gun was directly measured. Figure 6-14 shows that the ratio between mass balance measurements was within +5 percent and -10 percent of 1.0 for runs R3 through R25.

Overall, the mass balance method and emission measurement method were within ± 10 percent for 43 out of 59 runs (i.e., 73 percent of the runs) and the two methods agreed to within ± 10 percent for all 25 resin runs (the last 25 runs). Table 6-12 shows that the average ratio between mass balance calculation measurements and emission measurements was 1.02. These results show that, on average, the two methods agreed to within 2 percent.

Table 6-13 also shows that the mass balance/emission measurement ratio for the resin runs had a smaller standard deviation than the previous pilot and gel coat test runs. This comparison shows that correct measurement of the amount of material used in a test run improved the accuracy of the mass balance calculation method. These test results indicate that, when proper procedures are carefully followed, the mass balance calculation method can provide calculated emissions that are in good agreement with emission measurement using EPA Method 25A and a total enclosure.

Test designation	Number of runs	Average ratio, (mass balance/emission measurement)	Standard deviation
Experimental	4	1.13	0.16
Pilot	12	1.03	0.12
Gel coat	18	1.07	0.14
Resin.	25 .	0.96	0.05
Total runs	59		
Weighted average		1.02	0.10

Table 6-13.	Comparison of Mass Balance and Emission Measurement Test Results
	(Testing at Reichhold, June-July 1995)

Chapter 7 Data Quality Issues

Overall data quality met or exceeded the objectives outlined in the Category III quality assurance project plan (QAPP). Specific QA activities are presented in the following sections. More detailed analyses or evaluations are provided in Appendixes D, G, and H (Volume II).

7.1 Summation of Project QA Activities

A quality assurance project plan, Pollution Prevention Technology Demonstration, Evaluation of Pollution Prevention Techniques to Reduce Styrene Emissions from Open Contact Molding Processes, Category III Quality Assurance Project Plan, was prepared by the RTI project team and submitted to EPA on April 28, 1995, for approval prior to the start of the proposed testing. Responses to comments from EPA were summarized in a memorandum from Emery Kong to Carlos Nunez dated May 25, 1995, which is considered an addendum to the QAPP. Both the QAPP and the addendum are included in Appendix A (Volume II).

As described in the QAPP, the following QA activities were conducted as part of the project. The RTI project QA manager, Cynthia Salmons, and William Yeager conducted an internal technical system audit (TSA) of the project on June 9, 1995.

No formal corrective action requests were necessary for this project. Minor deviations from the QAPP were documented in laboratory notebooks and data sheets, when necessary. Two major deviations were (1) the modification of BPO resin after it was found to have a long gel time and low viscosity and (2) the withdrawal of a water-emulsified resin from the test by the manufacturer.

Other QA and QC activities during the course of this project included daily calibration of the high-precision scale with standard weights ranging from 1 g to 2,000 g (described in Section 5.2), periodic checks for scale drift by leaving a standard weight on the scale overnight, styrene evaporation experiments (described in Section 6.6.1), comparison of the total hydrocarbon analyzer's response to styrene cylinders with its response to the propane calibration cylinders (described in Appendix C), and a comparison of direct injection to the THC analyzer with delivery through the sampling line, as described in Appendix I (Volume II).

7.2 RTI Internal Technical System Audit (TSA) Results

The internal TSA found that the project activities were generally conducted in accordance with the QAPP and that results were carefully documented. More extensive calibrations of the THC analyzer were performed than were described in the QAPP or the EPA method. The measurement point for the exhaust flow rate was approximately five or six diameters downstream of a bend, instead of the eight diameters recommended by the EPA method, but there was no reasonable way of correcting this. The maximum number of traverse points suggested in EPA Method 1 for this type of situation was used. Checks for off-axis flow did not indicate a problem. The records for the total enclosure test indicated that there was considerable fluctuation in the hot wire anemometer readings and that a few of the flow velocity readings at the natural draft opening were slightly less than 200 ft/min, but this did not seem to present a problem, judging from the results of the styrene evaporation experiments. Due to the audit schedule, several aspects of the project were not observed during the TSA. These included sampling and analysis of the gel coat and resin, the styrene evaporation experiment, the demonstration that the spray booth meets the criteria for a total enclosure, the weekly traverse measurements, and the measurement of equipment delivery rate. Records of these activities were reviewed when possible. A memorandum documenting the TSA activities is included in Appendix H (Volume II).

7.3 EPA Performance Evaluation

EPA supplied RTI with a performance evaluation styrene standard gas cylinder, which RTI analyzed on July 7, 1995. The results of this EPA performance evaluation are presented in Appendix I (Volume II). Using the THC analyzer and calibration standards, RTI predicted the styrene concentration in the EPA performance evaluation standard to be 30.4 ppm. The certified value of the styrene standard was 31.0 ppm by the Scott Specialty Gases. There was only a 2 percent difference between the predicted and certified values. Therefore, the data quality objective for emission concentration measurement was met.

Chapter 8 Conclusions and Recommendations

8.1 Conclusions

The results from the **pilot** experiment 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 percent compared to normal spraying technique.
- Controlled spraying on the male mold reduced gel coat usage by 12 percent due to less overspray.
- Under normal spraying, 48 percent of total emissions was emitted during gel coat spraying; the remainder was emitted during curing.
- Under controlled spraying, 38 percent of total emissions was emitted during gel coat spraying; the remainder was emitted during curing.

The results of the gel coat experiment indicated that:

- The low-VOC gel coat reduced total emissions by 28 percent when compared to the regular gel coat.
- The low-VOC gel coat required a higher air supply pressure and larger spray tip to achieve the same spray fan as the regular gel coat.
- The AAA and HVLP (internal and external catalyst mixing) gel coat spray guns made no difference in terms of total emissions.
- The results of the **resin** experiment indicated that:
- **Controlled** resin spraying emitted 30 percent less styrene than **normal** spraying technique.
- Flow coater and pressure-fed roller equipment resulted in 31 to 33 percent less styrene than **controlled** resin sprayup.
- Flow coater and pressure-fed roller equipment resulted in 52 to 53 percent less styrene than **normal** resin sprayup.
- Thirty-eight to 63 percent (average 50 percent) of total emissions was emitted during the resin application stage; the remainder was emitted during the wet-out rolling and curing stages.
- The low-styrene resin emitted 11 percent less styrene than the low-profile resin.
- The styrene-suppressed resin emitted 36 percent less styrene than the low-profile resin.
- The styrene-suppressed resin with 0.1 percent additional wax emitted 40 percent less styrene than the low-profile resin.

- The BPO-catalyzed resin emitted more styrene than the low-profile resin because of higher styrene content and/or longer gel time.
- For the BPO-catalyzed resin, a shorter gel time reduced total emissions.

Other observations made from this testing were:

- On an average of 55 official test runs and 4 experimental test runs, total emissions determined by emission measurements and the mass balance calculation method are in good agreement within 5 percent.
- The mass balance calculation method could potentially be used to determine emissions from open molding processes.
- Emission factors derived from the test results are 1.6 to 2.5 times the respective midrange EPA AP-42 emission factors; this implies that AP-42 emission factors for resin and gel coat sprayup may underrepresent actual emissions for these processes.

8.2 **Recommendations**

in,

17

Based on the findings of this testing, the following recommendations are made to facilities using the open molding process:

- Train operators to improve their spraying technique to reduce overspray, material wasted, and emissions.
- Use nonspraying equipment when feasible to reduce emissions.
- Use low-styrene or styrene-suppressed materials when feasible.
- Reduce gel time when feasible to curtail emissions.
- Combine the effects of operator technique, materials, and application equipment to achieve the maximum emission reduction.
- The mass balance calculation method and in-house personnel can be used to determine emission factors for materials and equipment.
| ۵۲
۱۹ | | |
|--|---|---|
| TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing) | | |
| 1. ПЕРОПТ NO. 2.
ЕРА-600/R-97-018a | 3. RECIPIENT'S ACC | CESSION NO. |
| 4. TITLE AND SUBTITLE
Evaluation of Pollution Prevention Techniques to | 5. REPORT DATE
March 1997 | |
| Reduce Styrene Emissions from Open Con
Molding Processes: Volume L. Final Repo | tact 6. PERFORMING OF | IGANIZATION CODE |
| 7. AUTHOR(S)
Emery Kong, Mark Bahner, Robert Wright | 8. PERFORMING OF | GANIZATION REPORT NO. |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS | 10. PROGRAM ELEI | MENT NO. |
| Research Triangle Institute | | |
| P.O. Box 12194 | 11. CONTRACT/GR | ANT NO. |
| Research Triangle Park, North Carolina | 2///09 CR 818419-0 |)3 |
| 12. SPONSORING AGENCY NAME AND ADDRESS | 13. TYPE OF REPOR | AT AND PERIOD COVERED |
| EPA, Office of Research and Development
Air Pollution Prevention and Control Divis | ion | GENCY CODE |
| Research Triangle Park, NC 27711 | EPA/600/1 | 3 |
| 15. SUPPLEMENTARY NOTES APPCD project officer is Geddes H. Ramsey, Mail Drop 61, 919/
541-7963. Volume II contains appendices. | | |
| building industries. Styrene emissions using standard industry techniques, mater-
ials, and equipment were evaluated in a controlled environment and compared to a
basline 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 nonatomizing appli-
cation 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. | | |
| 17. KEY WORDS AND DOCUMENT ANALYSIS | | |
| a. DESCRIPTORS | b.IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
| Pollution
Styrene Resins
Emission
Molding Techniques
Fiberglass-reinforced Plastics
Boats | Pollution Prevention
Stationary Sources
Boat Building | 13B
111, 11J
14G
13H
11D
13J |
| 18. DISTRIBUTION STATEMENT | 19. SECURITY CLASS (This Report) | 21. NO. OF PAGES |
| Release to Public | 20. SECURITY CLASS (This page)
Unclassified | 22. PRICE |

. ·

. .

.

EPA Form 2220-1 (9-73)

U.S. ENVIRONMENTAL PROTECTION AGENCY

Office of Research and Development National Risk Management Research Laboratory Technology Transfer and Support Division Cincinnati, Ohio 45268

OFFICIAL BUSINESS PENALTY FOR PRIVATE USE. \$300 AN EQUAL OPPORTUNITY EMPLOYER

> If your address is incorrect, please change on the above label tear off; and return to the above address.

If you do not desire to continue receiving these technical reports, CHECK HERE ; tear off label, and return it to the above address,

Publication No. EPA- 600 / R-97-018 a