

Project Summary

Addendum to Assessment of Styrene Emission Controls for FRP/C and Boat Building Industries

Emery J. Kong, Mark A. Bahner, and Sonji L. Turner

Abstract

This report is an addendum to a 1996 EPA report entitled *Assessment of Styrene Emission Controls for FRP/C and Boat Building Industries*. This addendum presents additional evaluation of the biological treatment of styrene emissions, Dow Chemical Company's SORBATHENE[®] solvent vapor recovery system, Occupational Safety and Health Administration regulations and other policies that affect the fiber reinforced plastics/composites (FRP/C) and boat building industries, and secondary pollution and natural gas usage resulting from various emission control options.

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

Introduction

In 1995 and 1996, Research Triangle Institute (RTI), under contract to the U.S. Environmental Protection Agency's (EPA's) Office of Research and Development, investigated end-of-pipe controls to reduce styrene emissions from the fiber-reinforced plastic/composite (FRP/C) and boat building industries. The types of controls that were evaluated included thermal oxidation (also called incineration), catalytic oxidation, biofiltration, and preconcentration/oxidation systems. In preconcentration/oxidation systems, styrene is typically adsorbed onto materials such as activated carbon, zeolite, or proprietary polymers, then desorbed (in a concentrated stream) for catalytic oxidation. Preconcentration/oxidation allows the oxidizer to run nearly autothermally (without additional fuel), even for the low styrene inlet concentrations typically found in the FRP/C and boat building industries. The results of RTI's research were published in a 1996 EPA report, *Assessment of Styrene Emission Controls for FRP/C and Boat Building Industries*.

Objectives

Subsequent to completion of the original report, several additional issues regarding end-of-pipe controls for styrene were identified. The goals of this project were to address four specific additional issues:

- 1) Recently, studies on biofiltration/bioscrubbing of styrene have been identified that were not discussed in the original EPA report. The EPA requested further in-depth investigation of these studies.
- 2) The EPA also identified Dow Chemical's SORBATHENE® vapor recovery system as a possible styrene removal technology, and requested an evaluation of the SORBATHENE process for removal of styrene emitted from FRP/C and boat building facilities.
- 3) The EPA requested further documentation and interpretation of Occupational Safety and Health Administration (OSHA) regulations that can affect the viability of end-of-pipe controls for styrene removal. The original report contained cost calculations that showed that, for a given styrene mass input to a control device, cost can be substantially reduced if concentration to the control device can be increased (i.e., if air flow rate can be reduced). The EPA requested exploration of issues including operating spray booths above the allowable Permissible Exposure Limit (PEL) for styrene, with respirators being worn by the operators, and use of fresh air supplied to the operators in a "space suit".
- 4) In May 1996, a report containing calculations of the noneconomic impacts of incineration was prepared by Dr. Robert Haberlein (a consultant) for the Society of the Plastics Industry/Composites Institute (SPI/CI), a trade organization for the FRP/C industry. Noneconomic impacts, including energy usage and the generation of secondary pollutants (e.g., nitrogen oxides, sulfur dioxide, and carbon dioxide), were calculated, assuming thermal oxidation of an exhaust stream containing 20 parts per million of styrene. The EPA requested an analysis of the assumptions in the report, and calculation of noneconomic impacts for other types of controls (such as preconcentration/catalytic oxidation).

Analyses and Results

RTI's further investigation of biofiltration/bioscrubbing included contacts with six biofiltration/bioscrubbing researchers and suppliers. Four researchers/suppliers provided information, including data on flow rates, emission sources, concentrations, control efficiencies, frequency of regeneration, and costs (capital and operating). Most of the installations that were identified were bench-scale or pilot-scale in size, with flow

rates of less than 1,700 m³/h (1,000 cfm). The largest system controlling styrene was a bioscrubber, operating on an automotive parts plant in Germany, with a flow rate of 20,000 m³/h (11,774 cfm). The system capital costs for this application were given as \$450,000 to \$700,000. This can be compared to an estimated equipment cost and total capital investment of \$301,000 and \$619,000, respectively, from the biofiltration cost spreadsheet developed in the original styrene controls assessment. Most of the biofiltration systems were able to achieve a control efficiency of 90% or greater, except during acclimation periods (periods after prolonged shutdown), or process upsets.

Dow Chemical Company's SORBATHENE process was evaluated as a means for controlling styrene emissions from FRP/C and boat building operations. The SORBATHENE process is typically applied to recover organic vapors from process vents, storage tanks, and loading/unloading operations. The process can be designed to achieve 99.9% removal from vent streams ranging in flow rate from 34 to 5,100 m³/h (20 to 3,000 cfm), with volatile organic compound feed concentrations between 1,000 and 500,000 ppm. RTI's investigation indicated that the SORBATHENE process would not be economically feasible for the large flow rates and low styrene concentrations typically associated with FRP/C fabrication and boat building.

The principle OSHA regulations affecting the design and economics of end-of-pipe controls in the FRP/C industry are regulations dealing with allowable employee exposure to styrene. Various organizations in the reinforced plastics industry voluntarily committed to meeting a 50-ppm 8-hour time-weighted average (TWA) concentration in July 1997. OSHA regulations require that administrative or engineering controls (e.g. enclosure or confinement of the operation, general and local ventilation, and substitution of less toxic materials) must be considered and implemented, if feasible. If these controls are determined to be infeasible, or while these controls are being implemented, respiratory protection is required. RTI identified one boat building facility operating a paint booth where "space suits" with fresh air supply are used to protect spray gun operators.

Calculations of the noneconomic (energy and environmental) impacts of incineration were presented in a May 1996 report for the SPI/CI. These calculations were based on incineration (thermal oxidation) of an exhaust stream with a styrene concentration of 20 ppm. RTI's investigation indicated that a styrene concentration of 20 ppm would be uncharacteristically low for an FRP/C facility performing open mold spraying, and with annual polyester resin usage greater than 900 Mg (1000 tons, corresponding to a medium-to-large plant). Further, RTI's previous economic analysis indicated that preconcentration/catalytic oxidation systems have lower annualized costs than straight thermal oxidation, for styrene inlet concentrations below approximately 300 ppm. Therefore, it would be unlikely that a FRP/C company would choose a thermal oxidizer for an exhaust stream containing 20 ppm of styrene.

RTI conducted non-economic impact analyses for three types of control devices (thermal oxidizer, catalytic oxidizer, and preconcentrator/catalytic oxidizer), over styrene inlet concentrations ranging from 20 to 260 ppm (the highest known exhaust concentration for any existing facility with spraying operations). It was found that natural gas usage and secondary pollutant generation were much lower for preconcentration/oxidation systems than for straight thermal oxidation. Since preconcentration/oxidation systems also appear to have lower annualized costs than straight thermal oxidation (below approximately 300 ppm), the choice of preconcentration/oxidation systems in this range lowers both economic and noneconomic impacts.

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The complete report, entitled "Addendum to Assessment of Styrene Emission Controls for FRP/C and Boat Building Industries," (Order No. ; Cost: \$, subject to change) will be available only from:

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Addendum to Assessment of Styrene Emission Controls for FRP/C and Boat Building Industries

Final Report

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Abstract

This report is an addendum to a 1996 EPA report entitled *Assessment of Styrene Emission Controls for FRP/C and Boat Building Industries*. This addendum presents additional evaluation of the biological treatment of styrene emissions, Dow Chemical Company's SORBATHENE[®] solvent vapor recovery system, Occupational Safety and Health Administration regulations and other policies that affect the fiber reinforced plastics/composites (FRP/C) and boat building industries, and secondary pollution and natural gas usage resulting from various emission control options.

This study concludes that:

- Based on available results from bench- and pilot-scale studies and full-size operation, biofiltration or a bioscrubber could be a viable control option for treatment of styrene emissions.
- Dow Chemical's SORBATHENE[®] vapor recovery system was developed for high-concentration, low-flow exhaust from storage vents and would not be economically feasible for low-concentration, high-volume flow typically found in the most prominent processing techniques in the FRP/C and boat building industries.
- Employers should comply with current or future permissible exposure limits (PELs) for styrene using feasible engineering controls and should provide respiratory protection to employees when worker exposure cannot meet PELs after feasible engineering controls have been implemented. It is also an industrial practice for employers to provide additional respiratory protection to the employees even though the PELs are met.
- Direct thermal oxidation or catalytic oxidation would be less economical than preconcentration/oxidation technologies for low-concentration, high-volume emissions typically found in the industries. Secondary pollution and natural gas usage could be reduced significantly when using preconcentration technologies followed by catalytic oxidation.

Contents

| | |
|--|------|
| Abstract | ii |
| Figures | v |
| Tables | v |
| Acronyms and Abbreviations | vi |
| Conversion Table | viii |
| Chapter 1 | |
| Introduction | 1 |
| References | 1 |
| Chapter 2 | |
| Biological Treatment | 2 |
| 2.1 System Information Requested | 2 |
| 2.2 Descriptions of Biological Treatment Systems | 2 |
| References | 8 |
| Chapter 3 | |
| Novel Styrene Emission Control Technology | 9 |
| 3.1 Dow Chemical SORBATHENE® Solvent Vapor Recovery Unit | 9 |
| References | 11 |
| Chapter 4 | |
| OSHA Regulations and Policies Affecting Worker Exposures in the FRP/C and Boat Building Industries | 12 |
| 4.1 Summary and Implication of OSHA Regulations | 12 |
| 4.2 De Minimis Violations | 13 |
| 4.3 Local Air Flow Management and Spray Booth Modifications | 14 |
| References | 15 |
| Chapter 5 | |
| Assumptions in the Society of Plastics Industry/Composites Institute's (SPI/CI) Study on Noneconomic Impacts of Incineration Controls | 17 |
| 5.1 Use of Thermal Oxidizer | 17 |
| 5.2 Control Device Inlet Concentration of 20 ppm | 17 |
| 5.2.1 Economic Incentives for Maximizing Inlet Concentrations | 19 |
| 5.2.2 Exhaust Concentrations at Existing Plants | 19 |
| 5.2.3 Recent and Potential Future Changes in Allowable Exposures to Styrene | 21 |
| 5.2.4 Existing Relationships Between Worker Exposure and Exhaust Concentration | 21 |
| 5.2.5 Potential Methods to Increase Concentration to Downstream Controls . | 21 |
| 5.2.6 Conclusions on Assumption of Control Device Inlet Concentration of 20 ppm | 23 |
| References | 24 |
| Chapter 6 | |
| RTI Analysis of Noneconomic Impacts of Controls | 25 |
| 6.1 Normalized Curves for Natural Gas Usage and Secondary Pollutant Emissions | 25 |
| 6.1.1 Natural Gas Usage | 25 |

Contents (continued)

| | | |
|-------|---------------------------------|----|
| 6.1.2 | Carbon Dioxide Emissions | 27 |
| 6.1.3 | Nitrogen Oxide Emissions | 27 |
| 6.2 | Calculations for Specific Plant | 29 |
| 6.2.1 | Natural Gas Usage | 31 |
| 6.2.2 | Carbon Dioxide Emissions | 31 |
| 6.2.3 | Nitrogen Oxide Emissions | 34 |
| 6.2.4 | Radon Emissions | 34 |
| 6.3 | Conclusions | 37 |
| | References | 37 |

APPENDIXES

| | | |
|---|---|----|
| A | Comments on Individual Statements in the SPI/CI Study | 39 |
| B | Revision of the Styrene Control Cost Spreadsheet Model and Cost Figures | 43 |

Figures

| <u>No.</u> | <u>Page</u> |
|---|-------------|
| 2-1 VVK Weege GmbH bioscrubber system | 7 |
| 3-1 Process diagram of a SORBATHENE solvent vapor recovery unit | 10 |
| 5-1 Cost curves for a large plant (400 tons per year inlet) | 18 |
| 5-2 Typical open molding operation in a spray booth | 22 |
| 6-1 Normalized natural gas usage for various control options and for sensible heating of exhaust stream | 26 |
| 6-2 Normalized additional carbon dioxide generated by natural gas combustion for various control options | 28 |
| 6-3 Normalized NO _x emissions for various control options | 30 |
| 6-4 Natural gas usage for various control options and for sensible heating at a typical plant | 32 |
| 6-5 Carbon dioxide emissions for various control options at a typical plant | 33 |
| 6-6 NO _x emissions for various control options at a typical plant | 35 |
| 6-7 Radon emissions due to natural gas combustion for various control options at a typical plant | 36 |

Tables

| <u>No.</u> | <u>Page</u> |
|--|-------------|
| 2-1 Properties for Styrene Abatement Biosystems | 4 |
| 5-1 Styrene Exhaust Concentrations at Existing Open Molding Plants with Resin/Gel Coat Usage Greater than 1,000 ton/yr | 20 |
| 5-2 Comparison of average styrene exhaust concentration (290 ppm) with worker exposure levels at Lasco Bathware, South Boston, VA | 23 |
| 6-1 Characteristics for Specific Plant (Universal Rundle, in Ottumwa, Iowa) | 31 |

Acronyms and Abbreviations

| | |
|-----------------|---|
| ACGIH | American Council of Government Industrial Hygienists |
| BACT | best available control technology |
| Btu | British thermal unit |
| CAAA | Clean Air Act Amendments of 1990 |
| CE | capital equipment (cost) |
| CEFIC | Unsaturated Polyesters Sector Group of European Chemical Industry Council |
| CFCs | chlorofluorocarbons |
| CO | carbon monoxide |
| CO ₂ | carbon dioxide |
| EC | equipment cost |
| EC&C | Environmental C&C, Inc. |
| EPA | Environmental Protection Agency |
| FID | flame ionization detector |
| FRP/C | fiber-reinforced plastics/composites |
| ft | feet |
| ft/min | feet per minute |
| GPRMC | European Organization of Reinforced Plastics/Composite Materials |
| HAP | hazardous air pollutants |
| H.R. | heat recovery |
| kW | kilowatt |
| kWh | kilowatt-hour |
| lb | pound |
| lb/h | pounds per hour |
| LEL | lower explosive limit |
| MACT | maximum achievable control technology |
| MIAB | Molnbacka Industri, AB |
| NFPA | National Fire Protection Association |
| NO _x | nitrogen oxides |
| OAQPS | Office of Air Quality Planning and Standards |
| OSHA | Occupational Safety and Health Administration |
| PADRE | Polymer Adsorption and Removal |
| PC | personal computer |
| PEC | purchased equipment cost |
| PEL | permissible exposure limits |
| ppm | parts per million (by volume) |
| PSA | pressure swing adsorption |
| psig | pounds per square inch, gage |
| REECO | Regenerative Environmental Equipment Co., Inc. |
| RPC | reinforced plastic composites |
| RTI | Research Triangle Institute |
| SIC | Standard Industrial Classification |
| SMC | sheet molding compound |

| | |
|--------|---|
| SPI/CI | Society of the Plastics Industry/Composites Institute |
| STC | Southeastern Technology Center |
| STEL | short-term exposure limit |
| TCI | total capital investment |
| TDC | total direct cost |
| TLV | threshold limit value |
| ton/yr | tons per year |
| TRI | Toxics Release Inventory |
| TVA | Tennessee Valley Authority |
| TWA | time-weighted average |
| VOC | volatile organic compound |
| yr | year |
| °C | degrees Celsius |
| °F | degrees Fahrenheit |

Conversion Table

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 industrial convention, English units are used. Conversion factors from English to metric units are given below.

| English Unit | Multiply by | To Obtain |
|----------------------------|-------------------------------|---------------------|
| Btu | 1.055×10^3 | joule |
| °F | $(^{\circ}\text{F} - 32)/1.8$ | °C |
| ft | 0.3048 | m |
| ft ² | 0.0929 | m ² |
| ft ³ | 0.0283 | m ³ |
| ft ³ /min (cfm) | 0.028314 | m ³ /min |
| gal/min | 3.79 | l/min |
| inch | 2.54 | cm |
| in. H ₂ O | 1.87 | mm Hg |
| lb | 0.454 | kg |
| psia | 6.895 | kilopascal |
| ton | 0.907 | Mg |

Chapter 1

Introduction

The 1990 Clean Air Act Amendments (CAAA) mandate the development and promulgation of standards for hazardous air pollutants (HAP) emitted from a multitude of source categories by the year 2000. Styrene is listed as a HAP in the CAAA, and it is known to be emitted from the fiberglass-reinforced plastics/composites (FRP/C) and boat building industries. An earlier study (Kong et al., 1996) assessed the available control technologies, their efficiencies, performance, and cost. That study also reviewed and summarized Occupational Safety and Health Administration (OSHA) regulations governing the worker exposure issues, and presented the air flow management practices that could achieve cost-effective control of styrene emissions.

This report presents additional evaluation of the biological treatment of styrene emissions, Dow Chemical Company's SORBATHENE[®] solvent vapor recovery system, OSHA regulations and other policies that affect the FRP/C and boat building industries, and secondary pollution and natural gas usage resulting from various emission control options.

This study concludes that:

1. Based on available results from bench- and pilot-scale studies and full-size operation, biofiltration or a bioscrubber could be a viable control option for treatment of styrene emissions.
2. Dow Chemical's SORBATHENE[®] vapor recovery system was developed for high-concentration, low-flow exhaust from storage vents and would not be economically feasible for low concentration, high-volume flow typically found in the most prominent processing techniques in the FRP/C and boat building industries.
3. The employers should comply with current or future PELs for styrene using feasible engineering controls and should provide respiratory protection to the employees when worker exposure can not meet PELs after feasible engineering controls have been implemented. It is also an industrial practice for employers to provide additional respiratory protection to the employees even though the PELs are met.
4. Direct thermal oxidation or catalytic oxidation would be less economical than preconcentration/oxidation technologies for low-concentration, high-volume emissions typically found in the industries. Secondary pollution and natural gas usage could be reduced significantly when using preconcentration technologies followed by catalytic oxidation.

References

Kong, E.J., M.A. Bahner, and S.L. Turner. September 1996. *Assessment of Styrene Emission Controls for FRP/C and Boat Building Industries*. EPA-600/R-96-109 (NTIS PB97-104640), Research Triangle Park, NC.

Chapter 2

Biological Treatment

Biological treatment uses microorganisms in a medium, usually a biofilter or bioscrubber, to destroy organic compound emissions in an air stream. Air emissions containing biodegradable constituents pass through a biologically active medium. The microorganisms degrade the organic constituents in the air stream to essentially carbon dioxide and water. Biofiltration has been used for many years in Europe, Japan, and the United States for odor control, but the use of biofiltration to degrade more complex air emissions from chemical plants has occurred only within the last few years. Descriptions of biofiltration and biotrickling filter systems are presented in an EPA report (Kong et al., 1996). Biofiltration and biotrickling filter are similar in principle, but different vendors use different designs and media. This addendum includes another new biological treatment system which comprises a bioscrubber and a bioreactor. This section presents the process descriptions and information for several biological treatment units that have been tested or applied for styrene emissions.

2.1 System Information Requested

The Research Triangle Institute (RTI) contacted seven researchers and suppliers to obtain available information on their various existing and proposed biological treatment systems. The request included but was not limited to information on the following:

- flow rates
- emission source
- concentration
- capture efficiency
- control efficiency
- time of operation (hours/day, days/week)
- number of persons required for operation
- frequency of regeneration
- composition of the bio-medium
- incubation period of the bio-medium
- size of the biofilter
- pressure drop
- acclimation period
- performance during startup
- performance after periods of shutdown
- capital and operating costs

Five facilities responded by the requested deadline to provide information for this report: Envirogen, Tennessee Valley Authority (TVA), VVK Weege GmbH, Southeastern Technology Center (STC), and EnvirOzone, Inc.

2.2 Descriptions of Biological Treatment Systems

Envirogen. Envirogen provided information for two units, a pilot-scale biofilter and a proposed full-scale biotrickling filter. The pilot-scale biofilter was tested on air discharged from a fiberglass spray booth operation. The full-scale biotrickling filter was designed to control styrene emissions generated by a sequence batch reactor in a chemical company's wastewater treatment facility; however, the system was never put into service. Currently, CVT Bioway is conducting a field pilot study with TNO in Europe. This work is confidential and remains unavailable to

Envirogen. (Envirogen and a Dutch company have a joint venture company called CVT America. CVT America has potential access to license TNO's technology through a sister company called CVT Bioway. CVT Bioway is a separate company from CVT America.) As data and information from this field study become available to them, Envirogen will update RTI. Information on the Envirogen biotreatment system is presented in an EPA report (Kong et al., 1996). Properties for their pilot-scale system and design specifications for their full-scale system are listed in Table 2-1.

TVA. In 1989, 1.04×10^6 kg (1,144 tons) of styrene was emitted by manufacturing industries in the Tennessee Valley making styrene the second largest Toxic Release Inventory (TRI) classified toxic chemical released in the region (Lackey et al., 1994). Laura Lackey with TVA conducted bench-scale and pilot-scale studies to eliminate styrene emissions from the air streams of an industrial partner and other varied industrial applications. For bench-scale biofilter experiments, a parallel series of three bench-scale 2.8-L biofilters was constructed. All three biofilters were packed with a 1:1 (v/v) mixture of pine bark and composted chicken litter. A stainless steel screen supported the packing material creating a free space at the bottom of each biofilter. A controlled feed of styrene-contaminated gas entered the free space, and purified air exited the top. For the bench-scale experiments, biofilters were operated continuously for a 7-month period. Biofilter 1, the Control, was autoclaved and served as a sterile control. Biofilter 2 was inoculated with a styrene-degrading consortium of organisms, and Biofilter 3 used only naturally occurring microorganisms. Inlet styrene concentrations ranged from 50 to 4,000 ppmv and the empty bed contact time varied between 1 and 8 minutes. During days 29 to 36, the humidity of the incoming air stream was inadvertently dropped below the normal 99 percent to below 50 percent relative humidity. This drop caused the removal efficiency of Biofilter 2 to decrease to 60 percent. After the humidity was returned to normal, the performance of Biofilter 2 quickly improved and removal efficiency increased to greater than 99 percent. This problem did not occur with Biofilter 3. After the initial acclimation period, the performances of Biofilter 2 and Biofilter 3 were similar, greater than 99 percent (L.W. Lackey, TVA, personal communication, Sept. 4, 1996).

The pilot-scale biofilter that was installed at a boat building manufacturing site was 0.8 meters in diameter with a total packing volume of 1.26 m^3 (Holt and Lackey, 1995). It was also filled with a 1:1 (v/v) mixture of pine bark and composted chicken litter. The pilot-scale biofilter was monitored for 3 months. During normal manufacturing, the spray booth was operated for three shifts each day (20 h/d). Following the first week of operation and microbial acclimation, the manufacturing facility shut down for 1 week. During the shutdown, the biofilter continued to operate, and the system was maintained under aerobic conditions by blowing an uncontaminated air stream through the biofilter. Some styrene breakthrough was noted during the first shift after the week of downtime. However, no styrene was detected in the biofilter effluent for the next 2 months when the empty bed contact time was maintained at a constant rate. Additional information about the properties for both systems is listed in Table 2-1. Lackey plans to design a demonstration-scale $340\text{-m}^3/\text{min}$ ($12,000\text{-ft}^3/\text{min}$) biofiltration system based on the results of the two studies. However, a decision to construct the demonstration-scale system is currently on hold until there are regulatory requirements to build it.

Table 2-1. Properties for Styrene Abatement Biosystems

| Bioreactor Parameters | Companies | | | | |
|---------------------------------|---|--|---|---|-----------------------------|
| | ENVIROGEN | | TVA | | VVK W |
| Unit type | Pilot | Full-scale ^a | Bench ^b | Pilot | Full-sc |
| Reactor type | Biofilter | Biofilter | Biofilter | | Bioscru |
| Reactor size | 0.85 m ³ (30 ft ³) medium | 0.28 m ³ (10 ft ³) | 2.8 x 10 ⁻³ m ³ (0.099 ft ³) | 1.26 m ³ (44.5 ft ³) medium | Designed fo treatment re |
| Emissions source | Fiberglass spray booth operation | Wastewater treatment facility | Controlled contaminated feed | Boat manufacturer | Automotive production |
| Other pollutant(s) | NA | | Acetone | MEK Acetone | NA |
| Flow rate | 7.08 x 10 ⁻³ to 5.66 x 10 ⁻³ m ³ /s (15 to 120 ft ³ /min) | 0.6608 m ³ /s (1,400 ft ³ /min) | NA | 2.83 x 10 ⁻³ to 2.12 x 10 ⁻³ (6 to 45 ft ³ /min) | 20,000 (11,774 ft |
| Styrene concentrations | NA | NA | 50 to 4,000 ppmv (inlet) | 0 to 400 ppmv (inlet) | 50 to 60 pp 5 ppm (c |
| Control efficiency | >95% @ 30+ sec 85% to 95 % @15 sec | 90% removal | >99% removal (Biofilter 2) >99% removal (Biofilter 3) | >98% removal | ~ 90% remc |
| Time of operation | 16 h/d, 5 d/wk, 4 months | 24 h/day | 7 months | 13 months | 8 h/d, 5 d 10.5 m |
| Persons needed for operation | 1 | | None | | Non |
| Media replacement | 5 to 7 years | Life of system | NA | | Life of s |

| Bioreactor Parameters | Companies | | | | |
|-----------------------|---|-------------------------------------|---|---------------------------------|------------------------|
| | ENVIROGEN | | TVA | | VVK W |
| Unit type | Pilot | Full-scale ^a | Bench ^b | Pilot | Full-sc |
| Media composition | Proprietary engineered organic based material | Synthetic packing | 1:1 (v/v) pine bark and composted chicken litter | | Proprietary |
| Acclimation period | ~ 1 week | 1 to 2 weeks (expected) | ~ 5 days (Biofilter 2) ~ 55 days (Biofilter 3) | NA | NA |
| Pressure drop | 1 in. to 2 in. H ₂ O @ start-up 8 in. H ₂ O design | < 1 in. H ₂ O (expected) | 0.003 in. H ₂ O (max) | 0.75 in. H ₂ O (max) | NA |
| Startup performance | 75 % @ 60 sec | NA | NA | | NA |
| Shutdown recovery | 5 to 8 h (weekend shutdown) | NA | NA | | ½ to 1 h (after shut-d |
| Capital cost | NA | Available upon request | NA | | \$450,000 to \$700,000 |
| Operating cost | NA | Available upon request | NA | | \$25/day to \$ |

NA = not available.

a. Design parameters of this systems are listed. The system currently is not in use.

b. A parallel series of three bench-scale biofilters were used for this bench-scale test. Biofilter 1 was autoclaved and served as a inoculated with a styrene-degrading consortium of organisms. Biofilter 3 utilized only naturally occurring microorganisms.

c. Each system is designed to handle specific waste streams. Normal height of filter material is a maximum of 1 to 1.25 m. For estimate approximately 1 m³ of filter material.

d. System can be engineered for specific waste streams of volatile organic compound (VOCs). A series of bioscrubbers can be d to treat a specific VOC.

VVK Weege GmbH. VVK Weege GmbH, an engineering company in Wiesbaden, Germany, developed a bioscrubber system that removes styrene and other volatile organic compounds (VOCs) from industrial waste gases. The bioscrubber system employs a four-step process to treat styrene and VOC emissions from industrial waste gas. As shown in Figure 2-1, industrial waste gases enter a packed absorption tower where styrene is absorbed into the countercurrent flow of the absorbent solution (i.e., water and clean effluent from the bioreactor). The absorption tower consists of packing, a droplet separator, and a liquid distributor. After this step, clean air leaves the tower, and the styrene-laden absorbent solution is pumped into a stirred bioreactor. In the bioreactor, styrene is biologically degraded. After the degradation is complete, proprietary additives are applied to maintain the bacteria population, and the clean effluent from the bioreactor is pumped to the absorption tower for reuse. No sludge or solid waste is generated from the bioscrubber process.

The bioscrubber system is equipped with sensors and measuring devices and a computer to control the operations of the system. VVK Weege sells a service contract to maintain and operate the system. The personal computer (PC) station is the heart of data acquisition for the bioscrubber system. The PC station collects all data and controls various functions of the system, such as refilling water to make up for evaporation loss, replenishing the additives, and controlling the system. Through modern communication methods, these data are communicated back to VVK Weege. This information transfer allows VVK Weege to continually monitor the function of the system and to remotely adjust the system when necessary using a fax modem.

Two bioscrubber systems exist in Germany: one is a laboratory-scale facility, the other is a commercial unit used by a German company using sheet molding compound (SMC) to manufacture automotive parts. The commercial unit operated for one year but is no longer in operation now. Rudi Weege, company president, provided RTI with an overview of the commercial unit. Information for the commercial system is provided in Table 2-1.

The cost data in Table 2-1 for the VVK Weege system are taken from published literature (Modern Plastics, 1996). The capital costs for a system handling 11,766 ft³/min are estimated to be between \$450,000 and \$700,000. This can be compared to estimated equipment costs and total capital investments of \$301,000 and \$619,000, respectively, from the biofiltration cost spreadsheet developed in the original styrene controls assessment. Operating costs are given as approximately \$25 to \$30 per day. This can be compared with an electrical cost estimate of approximately \$15 per day from the biofiltration cost spreadsheet (assuming electricity cost of \$0.06 per kWhr, operating 8 hours per day).

VVK Weege is in the process of establishing a North American subsidiary to introduce and commercialize their technology to the FRP composite industry and other industries emitting VOCs in North America. According to Weege, the system can be designed to treat various VOCs, with each unit dedicated to treating a specific pollutant.

Southeastern Technology Center (STC). STC is a non-profit corporation whose mission is to facilitate the transfer of commercially viable technologies from the government sector to the business sector for the purpose of promoting economic development and creating jobs.

Figure 2-1

Regina Porter at STC is conducting a pilot study for styrene removal from an FRP facility. Her research is being conducted under a Department of Energy (DOE) contract. Delphinus Engineering, Inc. and EnvirOzone, Inc., both in South Carolina, are subcontractors to STC and are responsible for the design and operation of the pilot-scale unit. Delphinus and EnvirOzone provided preliminary information for this report for a 21.62-m³ (764-ft³) pilot-scale unit that has been designed to treat gaseous exhausts from an FRP facility. The flow rates of the exhaust streams range from 0.472 to 0.944 m³/s (1,000 to 2,000 ft³/min). The biofilter media contains 10 tons (9,070 kg) of chicken compost (80 percent chicken manure and 20 percent granular activated carbon) that requires a 2- to 3-week incubation period. Additional information for this pilot unit can be found in Table 2-1 (A. Saha, Delphinus Engineering, personal communication, Sept. 11, 1996).

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Chapter 3

Novel Styrene Emission Control Technology

3.1 Dow Chemical SORBATHENE® Solvent Vapor Recovery Unit

The Dow Chemical Company developed the SORBATHENE® pressure swing adsorption (PSA) process in the late 1980s to recover VOCs and other valuable chemical products from storage, loading, and process vents. Since 1988, the Dow Chemical Company has installed 19 SORBATHENE® units to recover hydrocarbon, chlorofluorocarbons (CFCs), chlorinated solvents, aromatics, and monomers. Dow Chemical has two SORBATHENE® units for recovery of styrene vapors from storage vents. A SORBATHENE® unit can be designed to achieve 99.9% VOC removal from vent streams ranging in flow rate from 20 to 3,000 ft³/min with feed concentrations between 1,000 and 500,000 ppm (Collick et al., 1996). The chemical components are recovered as a condensed liquid. Based on the evaluation of this technology and a follow-up conversation with Larry Larrinaga (Radian International, personal communication, September 9, 1996), the SORBATHENE® technology would be expensive to treat the low-styrene concentration (less than 200 ppm) at high flow rates (greater than 5,000 ft³/min) typically found in the most prominent processing technologies (e.g., sprayup and hand layup in open molding processes) in the FRP/C facilities.

Process Description. The SORBATHENE® process is typically applied to recover organic vapors from process vents, storage tanks, and loading/unloading operations. The process uses PSA and the heat generated during adsorption to desorb the VOCs collected on the adsorbent. Adsorption is carried out at atmospheric pressure and the heat of adsorption is retained in the adsorption bed, then the adsorbate is desorbed at a lower pressure (i.e., under vacuum) using the retained heat. Optimal desorption pressures are selected between 50 and 300 mm Hg (1 and 5.8 psig). As shown in Figure 3-1, the adsorption and desorption steps are batch processes that occur simultaneously in alternating twin beds to maintain steady state operation of the unit. During the desorption step, a fraction of the clean gas leaving the adsorbing bed is used as the backpurge gas for desorption. The concentrated stream of desorbed VOC is drawn through a vacuum system then passes through a condenser where the VOC condenses and is removed as a liquid. The cooling medium is selected based on the temperature required to condense the vapor. Control valves switch the beds over short cycle times to avoid an excessive temperature rise caused by the heat of adsorption. The SORBATHENE® unit is designed for the maximum instantaneous feed concentration and flow rate that would be expected during operation of the unit. The unit would not require adjustment as the inlet flow rate and concentration vary due to tank filling operation.

Standard Operating Conditions. The process has been applied for vent streams ranging from 20 to 3,000 ft³/min concentrations between 1,000 and 500,000 ppm. The adsorbent, operating pressures and temperatures, and cycle time of the unit are determined in a pilot study

based on the characteristics of the VOC to be recovered. Each unit is tailored to the specific VOC and the characteristics of the exhaust stream.

Figure 3-1. The process diagram of a SORBATHENE[®] vapor solvent recovery unit.

Control Efficiency. A SORBATHENE[®] unit has been tested for styrene vapor recovery from storage vents and its recovery efficiency was 99.78 percent for an inlet concentration of 5,742 ppm and an outlet concentration of 13.3 ppm (Hall, 1993). The flow rate was not reported for this tested unit; however, exhaust flow rates from storage vents are probably in the several-hundred-ft³/min range when being filled. Polymerization was not encountered for the adsorbent used in these applications.

Applicability to FRP/C/C Processes. The SORBATHENE[®] technology would not be economically feasible for the typical low-concentration and high-flow rate exhaust encountered in the FRP/C facilities. A SORBATHENE[®] unit might be used after the exhaust stream has been concentrated and its flow rate reduced by a preconcentration unit; however, its feasibility will be determined by the economic value, quantity, and reusability of the recovered styrene.

Cost. Larry Larrinaga (Radian International, personal communication, September 9, 1996) estimated that the equipment costs for a SORBATHENE unit treating an optimal flow rate of 300 to 500 ft³/min would range from \$600,000 to \$800,000. The SORBATHENE[®] unit is very sensitive to flow rate and the equipment cost increases dramatically as the flow rate increases. Operating costs include electricity cost to operate the adsorbers, vacuum pump, condenser, and separator.

References

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Chapter 4

OSHA Regulations and Policies Affecting Worker Exposures in FRP/C and Boat Building Industries

OSHA regulations governing the permissible exposure limit (PEL) for styrene and the ventilation system design in the FRP industry were summarized and presented in an RTI report (Kong et al., 1996). That report also concluded that concentrating the exhaust air stream and reducing the exhaust flow would reduce the cost of control. However, the worker exposure is bounded by OSHA's PEL for styrene. The current 8-hour time-weighted-average (TWA) PEL for styrene is 100 ppm. The TWA short-term exposure limit (STEL) is 200 ppm for 15 minutes during a work day and 600 ppm for 5 minutes in any 3 hours.

John B. Jenks, the Chairman of the Society of the Plastics Industry, Inc.'s Styrene Information & Research Center, and several industry officials sent a letter to Joseph A. Dear, the Assistant Secretary of Labor for OSHA, on January 29, 1996, and declared a willingness to voluntarily comply with lower exposure limits than those set by OSHA in its January 1989 rule on PEL for styrene and other air contaminants (OSHA, 1996). The lower limits are 50 ppm for an 8-hour TWA and 100 ppm for short-term exposure. The industry groups volunteering to lower exposure limits are the Society of the Plastics Industry, Inc.'s Composites Institute, Composites Fabricators Association, National Marine Manufacturers Association, and International Cast Polymer Association. These industry groups use polyester resins that emit styrene in the production processes. The goal is for these industry groups to comply with the lower exposure limits by July 1997.

As the worker exposure limits are lowered, more efficient exhaust systems will be needed to remove the same amount of emissions or employees who may not presently be wearing respirators will need to wear them. General ventilation, also called dilution ventilation because it uses fresh air to achieve lower worker exposure levels, is not practical and would be expensive in the winter when makeup air is heated to maintain a constant temperature for product quality. Therefore, new air flow management practices to remove styrene emissions effectively or a respiratory protection program will be necessary to comply with lower exposure limits.

This section presents (1) the summary and implication of OSHA regulations related to styrene emissions and ventilation in the FRP industry, (2) the explanation for "de minimis violations" under the OSHA policy, and (3) local air flow management practices and modifications to spray booths that could be considered for the ventilation and worker exposure issues.

4.1 Summary and Implication of OSHA Regulations

If a facility does not have a designated booth or area for gel coating and resin application in an open molding process, the emissions from these operations will be dispersed in the work area and the surrounding open space. Under these conditions, the worker exposures are limited to the styrene PELs listed in Table Z-2 in 29 CFR § 1910.1000 (OSHA, 1993) or as shown above. Title 29 CFR § 1910.1000 (e) states that administrative or engineering controls (e.g., enclosure or confinement of the operation, general and local ventilation, and substitution of less toxic materials) must first be determined and implemented whenever feasible. When such engineering controls are not feasible to achieve full compliance or while they are being instituted, protective equipment or any other protective measures should be used to keep the exposure of employees to air contaminants within the limits prescribed in the section. Whenever respirators are used, their use should comply with requirements in 29 CFR § 1910.134 “Respiratory Protection.”

When a facility uses a spray booth, its design must comply with regulations in 29 CFR § 1910.94 (c) and § 1910.107. Section § 1910.94 (c) lists the design and construction of the spray booth and the minimum air flow velocities that must be designed and maintained at the entrance to the spray booth under various operating conditions in order to meet health and safety requirements. Section § 1910.107 is adopted by OSHA from National Fire Protection Association (NFPA) 33-1969 (NFPA, 1969) “Standard for Spray Finishing Using Flammable and Combustible Materials.” The NFPA-33 standard is explicitly a fire and explosion safety standard. Therefore, the OSHA standard at 29 CFR § 1910.107 pertains to the prevention of workplace fire and explosion hazards and does not pertain to health considerations.

Because the industry has volunteered to comply with lower PELs, facilities having difficulty meeting the lower limits will have to build spray booths for their styrene-emitting operation, apply air flow management to exhaust styrene emissions, or provide respirators for employees who could be exposed to styrene concentrations above the PELs. These facilities will choose one of these options based on the feasibility of using engineering controls, building spray booths, applying air flow management practices, changing material/equipment/process, or providing personal respirators. When the employee exposures are above the PELs, as determined by personal sampling, the employer can work with the OSHA compliance officer to determine a schedule for an interim abatement system (e.g., providing respirators to employees) and a long term abatement system (e.g., building a ventilation system). Feasibility of the abatement systems will be considered by the facility operator and the compliance officer in meeting the PELs. If worker exposures still can not meet PELs after engineering controls have been employed, then the respiratory program will become a permanent program (Smith, OSHA, personal communication, October 15, 1996).

4.2 De Minimis Violations

According to the OSHA policy (Shepich, 1990), de minimis violations are violations of standards that have no direct or immediate relationship to employee safety or health. Whenever de minimis conditions are found during an inspection, they are documented the same way as any

other violation but are not included on the citation. De minimis violations result in no penalty and no required abatement. The criteria for finding a de minimis violation are as follows:

An employer complies with the clear intent of the standard but deviates from its particular requirements in a manner that has no direct or immediate relationship to employee safety and health. These deviations may involve distance specifications, construction materials requirements, use of incorrect color, minor variations from recordkeeping, testing, or inspection regulations, or the like.

An employer complies with a proposed standard or amendment or a consensus standard rather than with the standard in effect at the time of the inspection when the employer's action provides equal or greater employee protection.

An employer's workplace is at the "state of the art" that is technically beyond the requirement of the applicable standard and provides equivalent or more effective employee safety or health protection.

Under an OSHA policy for de minimis violations, employers are encouraged to abide by the standard applicable to their operations that provides equal or greater employee protection rather than with the OSHA standard in effect at the time of the inspection.

4.3 Local Air Flow Management and Spray Booth Modifications

The most effective way to reduce worker exposure is to directly remove styrene emissions from the source before the pollutants have a chance to disperse. Local air flow management, such as local extraction ventilation or a spray booth, removes emissions at the source and therefore reduces the amount of air to be exhausted and the amount of makeup air to be heated. Several local extraction ventilation systems are presented in the earlier report (Kong et al., 1996). These local extraction ventilation systems apply the push-pull ventilation principle in that fresh makeup air is admitted at one end of the work area and the air current picking up the emissions is exhausted at the other end of the work area. An operator can reduce unnecessary exposure by staying in the upwind side of the ventilated work area.

As the EPA Office of Air Quality Planning and Standards (OAQPS) develops maximum achievable control technology (MACT) standards for the FRP industry, new facilities using greater than a certain quantity of resin and gel coat in an open molding process may be required to reduce their emissions. Emissions from concentrated sources in certain operations, such as continuous lamination, pultrusion, and SMC production, can be captured and exhausted using a vent hood. Emissions from other open molding processes, such as gel coating and resin sprayup, need to be confined in a spray booth that meet OSHA's requirements. A spray booth can be designed to meet the requirements of a total enclosure so that the emissions can be completely captured. In this case, fresh makeup air should be supplied to the operator's breathing zone in the spray booth.

If the worker exposures are still higher than the PELs after proper engineering controls (i.e., confinement, local extraction, or general ventilation) have been implemented, then the operator should wear a respirator or a positive-pressure respirator with fresh uncontaminated air supply. The fresh air supplied to a positive-pressure respirator should meet certain air quality requirements and if the air is supplied by an oil-based compressor there must be a CO alarm to detect CO in the air (Smith, OSHA, personal communication, October 15, 1996).

It is common for the employers of some large FRP and boat building facilities to provide respirators to their employees for additional protection even though they may be in compliance with the PELs. Positive-pressure respirator with full body protection and fresh air supply is not common in the FRP and boat building industries; however, such a system is used in an enclosed paint booth in Hatteras Yachts in New Bern, North Carolina.

Modifications to spray booths, such as a split flow recirculation, have been examined in a large painting booth at a military installation (Hughes et al., 1994). A portion of the exhaust from the spray booth that contains less pollutants is recirculated to the front of the spray booth after mixing with fresh makeup air. The concentration in the return air is less than the PELs. The balance of the exhaust, which is at a higher concentration, is vented to an add-on emission control device. The purpose of recirculation is to increase the outlet concentration and reduce the exhaust flow so that the capital and operating costs of the add-on control can be minimized. The recirculating air can be returned to the spray booth at any point, either mixed with fresh makeup air or not mixed with fresh makeup air. In the latter case, the fresh makeup air can be supplied to the breathing zone of the operator to provide the most protection. Although recirculation in the spray booth is not recommended by OSHA, the bottom line is that worker exposures should not exceed the PELs (R. Fairfax, Health Compliance Program, Occupational Safety and Health Administration, personal communication, September 9, 1996).

If all forms of air flow management are not feasible, a facility should consider preconcentrating the exhaust stream to reduce the flow rate and to increase the concentration of the exhaust stream for an add-on control. Preconcentration reduces not only the capital cost but also the operating cost of the add-on control; it also reduces natural gas usage and generates fewer secondary pollutants than straight thermal oxidation of the entire exhaust stream. An analysis of secondary pollution and natural gas usage for various control options is presented in Chapter 5.

References

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Chapter 5

Assumptions in the Society of Plastics Industry/Composites Institute's (SPI/CI) Study on Noneconomic Impacts of Incineration Controls

Energy use and generation of secondary pollution for control devices are dependent on the type of control device selected and the flow rate into the control device. The SPI/CI Study on Non-Economic Impacts of Incineration Controls (Haberlein, 1996) was based on thermal oxidation of a 30,000 ft³/min exhaust stream containing 20 ppm of styrene. The following sections discuss the assumptions of a thermal oxidizer operating on a stream containing 20 ppm of styrene. Appendix A contains a discussion of other assumptions in the SPI/CI study.

5.1 Use of Thermal Oxidizer

The SPI/CI study assumes a thermal oxidizer operating on a stream containing 20 ppm of styrene. However, previous RTI analyses of the costs of controls has indicated that pre-concentration/oxidation systems have lower annualized costs than straight thermal oxidation for control device inlet concentrations below approximately 300 ppm. For example, Figure 5-1 shows RTI-calculated control costs for thermal oxidation, catalytic oxidation, and three pre-concentration/oxidation systems, for a plant with uncontrolled emissions of 400 ton/yr (operating 4,000 h/yr).¹ Figure 5-1 shows that the three preconcentration/oxidation technologies (MIAB, Polyad, and Durr rotary concentrator systems) have lower total costs per unit of styrene removed than straight thermal oxidation or catalytic oxidation. Therefore, it is likely that an FRP company would choose a preconcentration/oxidation system over straight thermal oxidation for an exhaust stream containing 20 ppm styrene based on lower total annualized cost. It is also likely that an FRP company would attempt to increase the styrene concentration (i.e., lower the flow rate), compared to the 20-ppm assumption in the SPI/CI study. This point is discussed in the following section.

5.2 Control Device Inlet Concentration of 20 ppm

Noneconomic impact analyses in the SPI/CI study are based on an assumed styrene concentration of 20 ppm to a thermal oxidizer. To evaluate this assumption, RTI reviewed the following: (1) economic incentives for maximizing inlet concentrations (minimizing flow rates) to end-of-pipe controls, (2) plant-wide average exhaust concentrations currently found at FRP plants, (3) recent and possible future changes to allowable exposure levels for employees of FRP plants, (4) existing relationships between employee exposures to styrene and exhaust concentrations at FRP plants, and (5) possible methods for new plants to increase concentrations (decrease flow rates) to controls while maintaining or lowering employee exposures.

¹ Figure 5-1 is based on a cost curve presented in a previous EPA report (Kong et al., 1996), with corrections as discussed in Appendix B to this report.

Figure 5-1.

5.2.1 *Economic Incentives for Maximizing Inlet Concentrations*

Previous RTI research demonstrated the economic desirability for a plant considering installation of end-of-pipe controls to evaluate methods to minimize flow rate prior to choosing any form of end-of-pipe controls. This is demonstrated by Figure 5-1, where the total annualized cost per unit of styrene removed decreases for all control choices as flow rate is reduced (i.e., as concentration increases). This trend is true even for preconcentration/oxidation systems (i.e., even for preconcentration/oxidation systems, the total annualized cost is reduced when design flow rate is reduced). Therefore, companies that contemplate end-of-pipe controls would find significant economic benefits in increasing control device inlet concentration above 20 ppm, with the associated reduction in total flow to the control device.

5.2.2 *Exhaust Concentrations at Existing Plants*

The SPI/CI study was based on a hypothetical exhaust stream averaging 20 ppm. One way to evaluate the appropriateness of this concentration is to look at average facility-wide exhaust concentrations at existing facilities. Research Triangle Institute and Pacific Environmental Services conducted an evaluation of facility-wide styrene exhaust concentrations currently found at fiber-reinforced plastics facilities with open-mold spraying operations. The results of this evaluation are presented in Table 5-1. Table 5-1 contains only facilities with annual (neat, or unfilled) resin-plus-gel-coat usage of greater than approximately 1,000 tons per year.

Average facility-wide exhaust concentrations in Table 5-1 are calculated based on facility-wide emissions (in mass per year), total facility exhaust flow rate, and facility operating schedule (hours per year). Where possible, values in Table 5-1 for emissions and flow rates are based on testing data. Otherwise, resin/gel coat usage and emission factors are used to calculate emissions for subsequent exhaust concentration calculations.

Table 5-1 shows that all eight facilities evaluated currently have average exhaust concentrations above 20 ppm. The mean value for the eight facilities is 120 ppm, and the median value is 82 ppm.

Two of the eight facilities listed in Table 5-1 have controls. The A.R.E. facility in Massillon, Ohio, which has a thermal oxidizer, has a calculated average styrene concentration of 231 ppm in the flow stream to the control device. The American Standard facility in Salem, Ohio, which has a Polyad preconcentration/catalytic oxidation system, has an average styrene concentration of 75 ppm flow stream to preconcentrator.

In summary, existing facilities with open-mold spraying and combined resin/gel coat usage above 1,000 ton/yr typically have average exhaust concentrations that are above the 20 ppm assumed in the SPI/CI study.

Table 5-1.

5.2.3 *Recent and Potential Future Changes in Allowable Exposures to Styrene*

Currently, OSHA PELs for styrene are 100 ppm as an 8-hour time-weighted-average (TWA) and 200 ppm as a 15-minute short-term-exposure-limit (STEL). The SPI/CI study notes that the reinforced plastics industry has voluntarily agreed to meet a 50-ppm TWA and a 100-ppm STEL. Compliance with the agreement will go into effect in July 1997. The SPI/CI study further notes that the American Council of Government Industrial Hygienists (ACGIH) has placed styrene on the Notice of Intended Change list to lower the styrene threshold limit value (TLV) to 20 ppm, with a STEL of 40 ppm.

The SPI/CI study uses a control device inlet concentration of 20 ppm. This is equal to the TLV being proposed by the ACGIH. RTI has no information to indicate that OSHA currently plans to lower the TWA to 20 ppm.

5.2.4 *Existing Relationships Between Worker Exposure and Exhaust Concentration*

Even if the OSHA TWA were lowered to 20 ppm, it would be reasonable to assume that a company building a new facility would have an average exhaust concentration to an end-of-pipe control that would be above 20 ppm. One reason for this is the strong economic incentive to maximize concentration (minimize flow rate), as discussed in Section 6.1. Another reason for this is that most capture systems would logically be oriented to draw styrene away from the worker, rather than drawing styrene into the worker's breathing zone. This concept is illustrated in Figure 5-2.

Currently, there is little available data relating average exhaust concentrations to worker exposures. Some data are available from the Lasco-South Boston (Virginia) tub-and-shower facility, and are presented in Table 5-2. Table 5-2 indicates that gel coat gun operators and lamination rollers had the highest average worker exposures during the measurement period and that the average ratio of exhaust-duct-concentration-to-worker-exposure was 2.36 and 2.42, respectively.

RTI is analyzing data collected at a tub-and-shower facility in which employee exposure and exhaust duct concentration were measured simultaneously. The results of this testing are expected to be published by February 1997 (see Section 5.2.5).

5.2.5 *Potential Methods to Increase Concentration to Downstream Controls*

Previous research by RTI identified several potential methods to decrease required flow rates for end-of-pipe controls while preventing excess employee exposure levels. These methods included: (1) local air flow management, (2) spray booth modifications (such as split-flow spray booths and spray booth recirculation), and (3) enclosures and total enclosures.

RTI is currently analyzing data from proof-of-concept testing at a tub-and-shower facility. This testing is evaluating the ability of spray enclosures and air flow management techniques to increase exhaust duct concentration while

Figure 5-2.

Table 5-2. Comparison of Average Styrene Exhaust Concentration (290 ppm) (Strum, 1995) With Worker Exposure Levels (Boyd, 1995) at Lasco Bathware, South Boston, VA

| Job Category | Number of Measurements* | Exposure Range* (ppm) | Average Exposure* (ppm) | Average Ratio, Exhaust/Exposure |
|------------------------------|--------------------------------|------------------------------|--------------------------------|--|
| 1. Gel Coat Gun Operator | 5 | 88-199 | 123.0 | 2.36 |
| 2. Lamination Gun Operator | 17 | 37-267 | 90.4 | 3.21 |
| 3. Lamination Roller | 6 | 92-142 | 120.0 | 2.42 |
| 4. Barrier Coat Gun Operator | 5 | 61-105 | 79.4 | 3.65 |
| 5. Part Puller | 2 | 32-39 | 35.3 | 8.22 |
| 6. QC Technician | 4 | 23-75 | 37.0 | 7.84 |
| 7. Mixer | 5 | 15-44 | 31.6 | 9.18 |
| 8. Trimmer | 1 | | 46.0 | 6.30 |
| 9. Waxer | 1 | | 25.0 | 11.60 |

* Data provided to Madeleine Strum by Daniel Boyd (Boyd, 1995).

maintaining or lowering worker exposures. The enclosure concept involves placing a part inside an enclosure while the spray gun operator stands outside the enclosure. The air flow management techniques involve the use of a close-capture exhaust panel. In this testing, one flame ionization detector (FID) device continuously measured exhaust duct concentration while another (portable) FID was used to continuously monitor worker exposure. In this manner, the ratio of exhaust duct concentration to worker exposure concentration could be continuously monitored and compared with “baseline” results from an unmodified spray booth. The results of the RTI enclosures/air flow management testing are expected to be available by February 1997.

5.2.6 Conclusions on Assumption of Control Device Inlet Concentration of 20 ppm

There are strong economic incentives for a company to maximize the concentration (minimize the flow rate) to a control device. Most existing facilities with open-mold spraying (even those without controls) currently have exhaust concentrations well above 20 ppm. Lowering allowable worker exposure levels can force lower concentrations to a control device. However, it appears likely that, even for worker exposure levels of 20 ppm, minimum exhaust concentrations on the order of 50-100 ppm could be achieved with current, or slightly improved, air flow management practices. Therefore, the assumption of a control device inlet concentration of 20 ppm appears to be too low.

References

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Chapter 6

RTI Analysis of Noneconomic Impacts of Controls

RTI's analysis of noneconomic impacts of controls includes the development of normalized curves to predict noneconomic impacts. Noneconomic impacts are also calculated for a specific, typical existing facility that has gel coat and sprayup processes.

6.1 Normalized Curves for Natural Gas Usage and Secondary Pollutant Emissions

To compare energy usage and secondary pollutant emissions for various flow rates and styrene mass emission rates, we must “normalize” the data. Data presented in Section 6.1 have been “normalized” to reflect fuel usage and secondary pollutant emissions per ton of styrene removed (based on 95 percent removal efficiency).

Most of the figures in this section include the following control options: (1) a thermal oxidizer, with 95 percent heat recovery, operating at 1,800 °F (as assumed in the SPI/CI study); (2) a thermal oxidizer, with 95 percent heat recovery, operating at 1,500 °F (which could produce a styrene destruction efficiency of 95 percent); (3) a catalytic oxidizer, with 95 percent heat recovery, operating at 650 °F (which could produce a styrene destruction efficiency of 95 percent); and (4) a preconcentrator/catalytic oxidizer, based on the Polyad system, that has a natural gas requirement of 96,000 Btu/h at 30,000 ft³/min. (The Polyad system requires 96,000 Btu/h to desorb styrene, for a system with an inlet flow of 30,000 ft³/min.)

The figures in this section can be used in the following manner: In Figure 6-1, the natural gas usage for a thermal oxidizer operating at 1,800 °F, with an inlet concentration of 20 ppm, is approximately 650,000 ft³ per ton of styrene removed. Therefore, if a thermal oxidizer removed 100 tons of styrene under these conditions, the natural gas usage would be 65 million cubic feet. Similarly, from Figure 6-1, the natural gas usage for a preconcentrator/oxidizer operating with a styrene inlet concentration of 100 ppm is approximately 4,200 ft³/ton of styrene removed. Therefore, if a preconcentrator/oxidizer removed 100 tons of styrene under these conditions, the natural gas usage would be 420,000 ft³.

6.1.1 *Natural Gas Usage*

Figure 6-1 presents normalized curves for natural gas usage for various control options. Figure 6-1 also contains normalized curves for the sensible heat required to raise an exhaust stream from average outdoor temperatures to an indoor temperature of 75 °F for two locations (i.e., Fort Wayne, Indiana, and Los Angeles, California). The curves for sensible heating requirements are included to compare the additional natural gas usage for controls with existing natural gas for heating.

In Figure 6-1, the top left point of the four control-option curves represents the assumptions in the SPI/CI study (i.e., a thermal oxidizer, with 95 percent heat recovery, operating

Figure 6-1.

at 1,800 °F, with an inlet concentration of 20 ppm). The natural gas requirement for this point is approximately 650,000 ft³/ton of styrene removed. In contrast, for a preconcentrator-catalytic oxidizer operating at 88 ppm, the natural gas requirement is approximately 5,000 ft³/ton of styrene removed.

Figure 6-1 illustrates that the natural gas usage for a preconcentrator/catalytic oxidizer is actually less than the sensible heat required to heat an equal flow rate to 75 °F, in Fort Wayne, Indiana, or Los Angeles, California.

6.1.2 Carbon Dioxide Emissions

Figure 6-2 presents normalized carbon dioxide emissions for four control-option curves. In Figure 6-2, the top left point of the four curves represents the assumptions in the SPI/CI study (i.e., a thermal oxidizer, with 95 percent heat recovery, operating at 1,800 °F, with an inlet concentration of 20 ppm). The carbon dioxide generated by natural gas combustion for this point is approximately 41 ton/ton of styrene removed. In contrast, for a preconcentrator-catalytic oxidizer operating at 88 ppm, the carbon dioxide generated by natural gas combustion is approximately 0.33 ton/ton of styrene removed.

All of the curves in Figure 6-2 depict only the carbon dioxide emissions generated by burning natural gas to destroy styrene. These curves do not include the carbon dioxide created naturally by the degradation of styrene. Chemical stoichiometry dictates that every ton of styrene converts to 3.38 tons of carbon dioxide.

6.1.3 Nitrogen Oxide Emissions

The SPI/CI study assumed 15 ppm of nitrogen oxides (NO_x) are emitted from the thermal oxidizer. This was based on the following numerical values, as reported by Haberlein (Haberlein, 1996):

- 50-100 ppm, as reported by CVM
- 10-15 ppm, as reported by Wheelabrator
- 13 ppm, as reported by Tellkamp
- <10 ppm, as reported by Huntington.

RTI's research appears to indicate that values of less than 10 ppm are probably more typical for thermal oxidizers, particularly if the oxidizer operates at approximately 1,500 °F, and especially if the oxidizer uses technology to reduce NO_x emissions, such as low-NO_x burners. Specifically, RTI's research indicates the following:

- Smith Engineering stated that none of the 25 installations for which they have NO_x measurements has an average concentration over 10 ppm.

- Durr Industries provided NO_x emissions test data for two installations. Both installations had average NO_x emissions less than 10 ppm. The time-weighted

Figure 6-2.

average NO_x generation for a thermal oxidizer installed in an automotive application was 2.7 ppm (Gupta, 1996).

- Process Combustion Corporation published a paper that concluded, “Various NO_x combustion control techniques are available. With waste gases free of nitrogen-bound compounds, NO_x emissions from thermal oxidation can be reduced to less than 10 ppm.” (Nutcher and Lewandowski, 1994)
- The Institute of Clean Air Companies noted that operation of a thermal oxidizer should result in less than 10 ppm of NO_x (Wax, 1995).

Fewer data are available for NO_x emissions from catalytic oxidizers. RTI investigation of this subject yielded the following:

- Englehard Process Emission Systems (South Lyon, Michigan) published a paper that concluded that a catalytic oxidizer produces 0 to 2 ppm of NO_x contribution (Gibbon, 1996).
- The Institute of Clean Air Companies noted that catalytic oxidizers run at much lower temperatures than thermal oxidizers (and should therefore produce less NO_x).

Figure 6-3 shows normalized NO_x emission curves for various control technologies. There are actually three NO_x curves for thermal oxidation, based on three different assumptions for NO_x outlet concentration. The top curve represents an assumption of 15-ppm outlet NO_x, as assumed in the SPI/CI study. The middle thermal-oxidation curve represents an assumption of 8.8-ppm outlet NO_x, as quoted from Smith Engineering. The bottom thermal-oxidation curve represents an assumption of 2.7-ppm outlet NO_x, as measured in the May 1995 testing by Durr (Gupta, 1996).

6.2 Calculations for Specific Plant

Bar graphs depicting energy use and secondary pollutant emissions are presented for a specific plant: the Universal Rundle plant in Ottumwa, Iowa. This plant has calculated characteristics as shown in Table 6-1.

The Universal Rundle plant in Ottumwa, Iowa, has a calculated uncontrolled styrene exhaust concentration of 88 ppm, and a flow rate of 110,700 ft³/min. For each bar graph, there is one bar representing a concentration of 20 ppm and a flow rate of 487,080 ft³/min. This 487,080 ft³/min flow rate represents the flow rate that would occur if emissions were diluted from the actual value of 88 ppm to the hypothetical value of 20 ppm assumed in the SPI/CI study.

Figure 6-3.

Table 6-1. Characteristics for Specific Plant (Universal Rundle, in Ottumwa, Iowa)

| Characteristic | Value |
|------------------------------------|--|
| Uncontrolled styrene emissions | 328 ton/yr |
| Assumed control efficiency | 95 percent (i.e., 312 ton/yr of styrene removed, and resulting controlled emissions of 16 ton/yr). |
| Control device inlet concentration | 88 ppm |
| Air flow rate into control device | 110,700 ft ³ /min |
| Operational schedule | 4,160 h/yr |

6.2.1 Natural Gas Usage

Figure 6-4 compares natural gas usage for several control options and for sensible heating for the specific plant. The bar on the left side of the page represents the natural gas that would be used if the flow rate were raised to 487,080 ft³/min, producing the 20-ppm value assumed in the SPI/CI study. All other bars represent the actual plant flow rate of 110,700 ft³/min.

Figure 6-4 indicates that the natural gas used in annual heating for an exhaust flow of 110,700 ft³/min is approximately 3.6 million ft³/yr (based on heating requirements in Fort Wayne, Indiana). In contrast, the natural gas requirement for the preconcentrator/catalytic oxidizer option (which is based on the Polyad system), is approximately 1.5 million ft³/yr. It should be noted that the calculated value of 3.6 million ft³/yr for sensible heating of the exhaust stream does not reflect all the heating requirements for an FRP facility. Additional heating would be required to replace heat losses through the walls and ceiling of the facility. Natural gas might also be used for latent heating, if humidification is required during the winter.

The calculations for natural gas usage in Figure 6-4 can be compared with total natural gas usage in the United States in 1995. The total natural gas usage in the United States in 1995 was approximately 2.2×10^{13} ft³, which is approximately a factor of 100,000 times greater than the natural gas usage of the highest option shown in Figure 6-4.

6.2.2 Carbon Dioxide Emissions

Figure 6-5 presents carbon dioxide emissions for several control options for the specific plant. The bar on the left side of the page represents the carbon dioxide that would be produced if the flow rate were raised to 487,080 ft³/min, producing the 20-ppm value assumed in the SPI/CI study. All other bars represent the actual plant flow rate of 110,700 ft³/min.

Figure 6-4.

Figure 6-5.

Each bar in Figure 6-5 has three components: 1) the CO₂ produced by natural gas used in oxidation, 2) the CO₂ that would be produced by burning natural gas to heat the flow stream from the average outdoor temperature to 75 °F, and 3) the CO₂ produced from the stoichiometric degradation of styrene to CO₂ (and water).

The bar on the left side of the figure represents the CO₂ that would be produced assuming straight thermal oxidation of a 20 ppm flow stream. In order to reduce the concentration from the actual value of 88 ppm, it would be necessary to increase the exhaust flow from the actual value of 110,700 ft³/min to a hypothetical value of 487,080 ft³/min. The total CO₂ produced in this hypothetical situation would be over 14,000 tons/yr, of which approximately 12,000 tons/yr would be due to natural gas used for oxidation.

Other bars in Figure 6-5 reflect the actual exhaust conditions for the plant (110,700 ft³/min at 88 ppm). The bar on the far right presents the CO₂ emissions from a preconcentrator/catalytic oxidizer. A preconcentrator/oxidizer is the control that would be most likely to be selected for a flow stream of 110,700 ft³/min at 88 ppm, due to the fact that the preconcentrator/oxidizer has a lower total annualized cost than the other options. For a preconcentrator/oxidizer, the total CO₂ emissions are approximately 1,400 tons/yr. The vast majority of these emissions (over 1,100 tons/yr) are due to the stoichiometric degradation of styrene to CO₂. Only 90 tons/yr of CO₂ emissions are due to combustion of natural gas used in heating the air for desorption.

6.2.3 Nitrogen Oxide Emissions

Figure 6-6 presents NO_x emissions (as NO₂) for several control options for the specific plant. The bar on the left side of the page represents the NO_x emissions that would be produced if the flow rate were raised to 487,080 ft³/min, producing the 20-ppm value assumed in SPI/CI study. All other bars represent the actual plant flow rate of 110,700 ft³/min.

The bar on the right, which is barely visible, indicates NO_x emissions for a preconcentration/catalytic oxidation system. A preconcentration/oxidation system would be the most likely control choice for a flow rate of 110,700 ft³/min, containing 88 ppm styrene, due to lower total annualized cost. The NO_x emissions for this control option at this facility would be 0.09 tons/yr. This can be contrasted with the estimated styrene removal of 312 tons/yr.

6.2.4 Radon Emissions

Figure 6-7 presents radon emissions from natural gas combustion for several control options for the specific plant. The bar on the left side of the page represents the radon emissions that would be produced if the flow rate were raised to 487,080 ft³/min, producing the 20 ppm value assumed in the SPI/CI study. All other bars represent the actual plant flow rate of 110,700 ft³/min.

Figure 6-6.

Figure 6-7.

The radon emission calculations in Figure 6-7 are based on an average radon content of 20 pCi/L in natural gas as assumed in the SPI/CI study. This value was also used in a study of radionuclide emissions from natural-gas fired steam-electric generating plants (Nelson, 1995). According to the Institute for Clean Air Companies, the Institute for Gas Technology reports radon levels typically less than 1 pCi/L (Wax, 1996).

6.3 Conclusions

Calculations of noneconomic impacts in the SPI/CI study were based on an exhaust stream containing 20 ppm of styrene, directed to a thermal oxidizer. However, for economic reasons, it would be unlikely that a new plant would be designed with a 20-ppm exhaust stream directed to an end-of-pipe control device. And, if a new plant were designed with a 20-ppm exhaust stream directed to a control device, a preconcentration/oxidation system would probably be chosen over straight thermal oxidation, again for economic reasons.

Natural gas usage and secondary pollutant emissions were found to be considerably less for preconcentration/oxidation systems than for thermal oxidation, in the range from 0 to approximately 300 ppm of styrene. Since preconcentration/oxidation systems appear to have lower annualized costs than straight thermal oxidation in this range, the choice of preconcentration/oxidation systems in this range lowers both economic and noneconomic impacts.

References

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- Wax, M., Institute of Clean Air Companies, memorandum to Madeleine Strum, U.S. Environmental Protection Agency, August 11, 1995, Subject: Reinforced Plastic Composites.

Wax, M., Institute of Clean Air Companies, memorandum to Mark Bahner, Research Triangle Institute, October 15, 1996, Subject: Radon Concentration in Natural Gas.

Appendix A

Comments on Individual Statements in the SPI/CI Study

Appendix A

Comments on Individual Statements in the SPI/CI Study (Haberlein, 1996)

- 1) *The (catalytic oxidizer) bed temperature is maintained at about 600° C (1,100° F) during normal operation. (Page III-2).*

A more typical temperature range for catalytic oxidation of styrene is 600-700°F (Patkar et al., 1994).

- 2) *The problem (of catalyst poisoning in a catalytic oxidizer) is severe and unpredictable... (Page III-2).*

A July 19, 1996 memorandum from Michael Wax (Institute of Clean Air Companies) to Madeleine Strum (EPA-OAQPS) states that catalyst plugging, poisoning, and deactivation are well understood, and may be ameliorated through appropriate system design and operating practices. He refers to an article in the September 1994 issue of *Chemical Engineering*, "Extend the Life of Pollution Control Catalysts," that discusses in-situ catalyst rejuvenation as an alternative to catalyst replacement.

- 3) *A thermal regenerative incinerator was selected for the hypothetical plant (30,000 ft³/min, 20 ppm styrene, 8,760 h/yr, 43 tons uncontrolled styrene emissions) because this type of incinerator has been shown to be the most cost-effective type of control compared to the recuperative or catalytic (recuperative) types. (Page III-3).*

This analysis ignores the option of preconcentration/oxidation, which appears to have a lower total annualized cost than any of these options (including regenerative thermal oxidation), for the hypothetical inlet conditions.

- 4) *For the hypothetical incinerator discussed above...at an oxidation temperature of 1800° F... (Page III-5).*

A thermal oxidation temperature of 1,800 °F is compatible with Haberlein's assumed styrene destruction efficiency of 99 percent. A lower thermal oxidation temperature, such as 1,500 °F, would be compatible with a lower destruction efficiency, such as 95 percent.

- 5) *The supplemental fuel requirement for an incinerator (with 95 percent heat recovery) operating at an exhaust flow rate of 30,000 cfm at 20 ppm VOC (and 1,800 °F) is 3,310,000 Btu/h. (Page III-5).*

The RTI cost spreadsheet for a thermal oxidizer under these conditions produces a calculated supplemental fuel requirement of 2,984,000 Btu/h, or approximately 10 percent less. This represents fairly close agreement.

- 6) *Annual electrical consumption (for the hypothetical thermal oxidizer) is 1,230,000 kWh (over 8,760 hours). (Page III-6).*

This represents power usage of 140 kW/h. The RTI cost spreadsheet for a thermal oxidizer (with 95 percent heat recovery) under these conditions is 125 kW/h, or approximately 10 percent less. This represents fairly close agreement. RTI's calculation was based on quotations from Salem Englehard (Mack, 1996).

- 7) *Unfortunately, these compounds (catalyzed resin aerosols and polystyrene-forming agents) are indeed present in the exhaust streams at most plants, as evidenced by the solid plastic residue that coats the inner surface of the ductwork in many locations. Further, no effective means of removing all of these airborne compounds is presently known. (Page III-13).*

Catalyzed resin aerosols are present in many plants, due to spraying operations. These resin aerosols are actually quite large, and are therefore easily removed by even coarse filtration. For example, RTI mass-balance testing conducted in June 1995 indicated approximately 99 percent particle collection by a thin fiberglass veil. It could be expected that the fiberglass filter pads used at most plants would have an even higher collection efficiency. RTI has observed that casual fiberglass filter pad installation at many plants allows gaps or holes in the filter banks. This practice can dramatically lower collection efficiency, and would need to be avoided. Styrene gas (which can form polystyrene) is indeed present, and cannot be removed by physical filtration. However, Durr Industries reports having rotary concentrator systems in Japan that have been running for over 10 years without styrene polymerization.

- 8) *The report (on Polyad) shows an annual 10 % Bonopore (adsorbent) loss out of the system's cyclone separator. (Page III-14)*

Weatherly, Inc. (manufacturers of Polyad), in a July 18, 1996, memorandum to Madeleine Strum (EPA-OAQPS), indicated that they now guarantee annual Bonopore loss of 5 percent or less.

- 9) *The calculated energy requirements for a 30,000 scfm Polyad concentrator system are 130 kW, and 96,000 Btu/hr. (Page III-15).*

Weatherly, Inc. (manufacturers of Polyad), in a 1996 memorandum to Madeleine Strum (EPA-OAQPS), indicated that the electrical requirement would actually be 62 kW, but the natural gas usage value was correct.

References

Haberlein, R.A. 1996. The Non-Economic Impacts of Incineration Controls for the Reinforced Plastics Industry. Prepared for SPI/Composites Institute, Ann Arbor, MI.

Mack, S., Englehard Corporation, A facsimile on RCO Costs to Mark Bahner, Research Triangle Institute, February 8, 1996.

Patkar, A.N., J.M. Reinhold, and G. Henderson. 1994. "Demonstration of Capture and Control Efficiency for a Styrene Emission Source," Paper number 94-RA111.03, in *Proceedings for the Air and Waste Management Association 87th Annual Meeting and Exhibition*, Cincinnati, OH.

Appendix B

Revision of the Styrene Control Cost Spreadsheet Model and Cost Figures

44 45 46 47 48 4 5

Table 2-1. Continued