SURVEY REPORT:

STYRENE EXPOSURES DURING CLOSED MOLDING OF SMALL PARTS FOR FIBERGLASS BOATS

at

Sea Ray Boats, Inc. Vonore, TN

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The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

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ABSTRACT

In August 2008, NIOSH researchers conducted an in-depth survey at Sea Ray Boats, Inc. in Vonore, Tennessee. Sea Ray Boats, Inc. is the largest manufacturer of recreational boats in the United States. This survey focused on evaluating occupational exposures to styrene during closed molding of small parts. NIOSH researchers did not evaluate occupational exposures from any processes that used open molding or gelcoating of large parts during this survey. Sampling results from this survey indicated that personal breathing zone and general area air samples were well below regulatory and recommended limits for occupational exposure to styrene for closed molding and gelcoating of small parts. The highest personal breathing zone concentration for styrene measured during this survey was 6.4 ppm from the gelcoater. The highest personal breathing zone sample for styrene collected for styrene was 1.6 ppm. The low exposures were likely attributed to a combination of good work practices and the effectiveness of the closed molding process at reducing exposures.

INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) is part of the Centers for Disease Control and Prevention (CDC) in the U.S. Department of Health and Human Services (DHHS). NIOSH was established in 1970 by the Occupational Safety and Health (OSH) Act, at the same time that the Occupational Safety and Health Administration (OSHA) was created in the U.S. Department of Labor (DOL). The OSH Act mandated NIOSH to conduct research and education programs separate from the standard-setting and enforcement functions conducted by OSHA. An important area of NIOSH research involves measures for controlling occupational exposures to potential chemical and physical hazards.

In the early 1980s, NIOSH researchers conducted an engineering control technology assessment of styrene exposures in the fiberglass reinforced plastic (FRP) boat manufacturing industry [NIOSH 1983]. The study focused mainly on ventilation systems and work practices used in the open molding production of large FRP boats and yachts. In 2004, NIOSH researchers from the Engineering and Physical Hazards Branch (EPHB) of the Division of Applied Research and Technology (DART) began a follow-up assessment to evaluate worker exposures from new processes that have been introduced since the previous NIOSH study. Several of the technologies include processes that use low styrene resins, non-atomizing spray equipment, pressure driven rollers, improved ventilation, and closed molding.

From 2004 to 2007, NIOSH researchers conducted walk-through surveys and in-depth evaluations at several boat manufacturing facilities. Personal breathing zone and area samples from all styrene emitting process at the facilities were evaluated. During the in-depth surveys, NIOSH researchers collected personal breathing zone and area samples from open mold lamination, gelcoating, and closed molding processes. However, many of the closed molding processes at the evaluated facilities were not physically separated from the open molding processes and usually shared the same ventilated space. In several cases the personal breathing zone styrene concentrations collected from the closed molding workers were in the same range as the area samples collected near the open molding lamination processes. At those facilities, the personal breathing zone samples of the closed-molding workers were more representative of an area sample of the well mixed plant air and not representative of the closed-molding processe.

Following the aforementioned surveys, NIOSH researchers began trying to identify more facilities with closed-molding processes that were physically separate from open molding or other styrene emitting processes. In October 2005, NIOSH researchers conducted a walk-through survey at the Sea Ray Tellico Plant in Vonore, Tennessee. During the survey, it was discovered that the Sea Ray Tellico Plant in Vonore, Tennessee, had a closed molding process that was in a separate building from open molding process. In August 2008, NIOSH researchers returned to the Tellico Plant, and evaluated the closed molding process and associated occupational exposures to styrene. The purpose of this report is to document the study methods, results, and conclusions of the evaluated closed

molding process at the Tellico Plant. Recommendations are provided to further reduce occupational exposures to styrene and provide a safer and healthier work environment.

<u>Styrene Usage</u>

Styrene is the major chemical component of concern in terms of occupational exposures in the FRP process. Styrene is a fugitive emission that evaporates from resins, gel coats, and putties used in the manufacturing process. The thermo-set polyester production resins used during the closed-molding processes at the Tellico Plant contain approximately 45% styrene by weight. Closed-molding processes are exempt from the U.S. Environmental Protection Agency (EPA) requirements for Maximum Achievable Control Technology (MACT) due to the low emission rating. Styrene is an essential reactive diluent for polyesters because it reduces the viscosity of the polyester mixture making it thinner and more capable of coating fiber reinforcements. This process allows the reactive sites on the molecules to interact. As an active diluent, styrene will react in the free-radical cross-linking reaction. Cross-linking is the attachment of two chains of polymer molecules by bridges composed of molecular, in this case styrene, and primary chemical bonds. This produces a solid resin material that is impervious to most solvents, petroleum, and other chemicals found in the marine environment. Since styrene is consumed as part of this reaction, there is no need for removal of the diluents after a part is formed from the polymer. However, if the process is not controlled properly, vapors from the application and curing process may pose an inhalation exposure hazard for workers near the process.

Exposure Hazards of Styrene

Humans exposed to styrene for short periods of time through inhalation may exhibit irritation of the eyes and mucous membranes, and gastrointestinal effects [40 CFR 63 (2000)]. Styrene inhalation over longer periods of time may cause central nervous system effects including headache, fatigue, weakness, and depression. Exposure may also damage peripheral nerves and cause changes to the kidneys and blood. Several studies have shown that styrene exposures were linked to central and peripheral neurologic [Mutti et al. 1984; Tsai et al. 1996; Fung et al. 1999], optic [Triebig et al. 2001; Gong et al. 2002], and irritant [Minamoto et al. 2002] effects when occupational exposures to styrene vapors in air were greater than 50 parts per million (ppm).

There is also evidence concerning the influence of occupational styrene exposure on sensory nerve conduction. Studies indicate that: (1) 5% to 10% reductions can occur after exposure at 100 ppm or more; (2) reduced peripheral nerve conduction velocity and sensory amplitude can occur after styrene exposure at 50 to 100 ppm; (3) slowed reaction time appears to begin after exposures as low as 50 ppm; and, (4) statistically significant loss of color discrimination (dyschromatopsia) may occur [ACGIH[®] 2001].

Evaluation Criteria

In evaluating the hazards posed by workplace exposures, NIOSH investigators use mandatory and recommended occupational exposure limits (OELs) for specific chemical, physical, and biological agents. Generally, OELs suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or hypersensitivity (allergy) to the specific hazardous substance. In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the exposure limit. Combined effects are often not considered in the OEL. Also, some substances can be absorbed by direct contact with the skin and mucous membranes in addition to being inhaled, thus contributing to the overall exposure. Finally, OELs may change over the years as new information on the toxic effects of an agent become available.

Most OELs are expressed as a time-weighted average (TWA) exposure. A TWA refers to the average exposure during a normal 8- to 10-hour workday. Some chemical substances and physical agents have recommended short-term exposure limits (STEL) or ceiling values where there are health effects from higher exposures over the short-term. Unless otherwise noted, the STEL is a 15-minute TWA exposure that should not be exceeded at any time during a workday, and the ceiling limit is an exposure that should not be exceeded at any time, even instantaneously.

In the U.S., OELs have been established by Federal agencies, professional organizations, state and local governments, and other entities. Some OELs are mandatory, legal limits; others are recommendations. The U.S. Department of Labor OSHA permissible exposure limits (PELs) [29 CFR 1910 (general industry); 29 CFR 1917 (maritime industry); and 29 CFR 1926 (construction industry)] are legal limits that are enforceable in workplaces covered under the OSH Act. NIOSH recommended exposure limits (RELs) are recommendations that are made based on a critical review of the scientific and technical information available on the prevalence of hazards, health effects data, and the adequacy of methods to identify and control the hazards. Recommendations made through 1992 are available in a single compendium [NIOSH 1992]; more recent recommendations are available on the NIOSH Web site (http://www.cdc.gov/niosh). NIOSH also recommends preventive measures (e.g., engineering controls, safe work practices, personal protective equipment (PPE), and environmental and medical monitoring) for reducing or eliminating the adverse health effects of these hazards. The NIOSH recommendations have been developed using a weight of evidence approach and formal peer review process. Other OELs that are commonly used and cited in the U.S. include the threshold limit values (TLVs[®]) recommended by the American Conference of Governmental Industrial Hygienists (ACGIH[®]), a professional organization [ACGIH[®] 2007]. ACGIH[®] TLVs[®] are considered voluntary guidelines for use by industrial hygienists and others trained in this discipline "to assist in the control of health hazards." Workplace environmental exposure levels (WEELs) are recommended OELs developed by American Industrial Hygiene Association (AIHA), another professional organization.

WEELs have been established for some chemicals "when no other legal or authoritative limits exist" [AIHA 2007].

Employers should understand that not all hazardous chemicals have specific OSHA PELs and for many agents, the legal and recommended limits mentioned above may not reflect the most current health-based information. However, an employer is still required by OSHA to protect their employees from hazards even in the absence of a specific OSHA PEL. In particular, OSHA requires an employer to furnish employees a place of employment that is free from recognized hazards that are causing or are likely to cause death or serious physical harm [Occupational Safety and Health Act of 1970, Public Law 91–596, sec. 5(a)(1)]. Thus, NIOSH investigators encourage employers to make use of other OELs when making risk assessment and risk management decisions to best protect the health of their employees. NIOSH investigators also encourage the use of the traditional hierarchy of controls approach to eliminating or minimizing identified workplace hazards. This includes, in preferential order, the use of: (1) substitution or elimination of the hazardous agent, (2) engineering controls (e.g., local exhaust ventilation, process enclosure, dilution ventilation), (3) administrative controls (e.g., limiting time of exposure, employee training, work practice changes, medical surveillance), and (4) PPE (e.g., respiratory protection, gloves, eye protection, hearing protection).

The NIOSH REL for styrene is 50 ppm as a 10-hour TWA, with a 15 minute STEL of 100 ppm [NIOSH 2004]. These recommendations are based upon reported central nervous system effects, eye irritation, and respiratory irritation effects. The NIOSH immediately dangerous to life or health (IDLH) value for styrene is 700 ppm, which is based on acute inhalation toxicity in humans. The OSHA PEL for styrene is 100 ppm TWA with a ceiling limit of 200 ppm. ACGIH[®] revised its TLV[®] in 1997, and recommends styrene be controlled to 20 ppm TWA with a 40 ppm STEL [ACGIH[®] 2004]. The TLV[®] is based on a number of health effects of low styrene exposure such as ototoxicity, central and peripheral neurologic, optic, and irritant actions in humans [ACGIH[®] 2001]. The ACGIH[®] also recommends Biological Exposure Indices (BEI[®]) for end of shift and prior to next shift values for worker exposure to styrene by measuring mandelic acid in urine, phenylglyoxylic acid in urine, and styrene in venous blood [ACGIH[®] 2001].

In February 1996, the Styrene Information and Research Center (SIRC) and three other styrene industry trade associations--American Composites Manufacturers Association, National Marine Manufacturers Association, and the International Cast Polymer Association--entered into a precedent-setting arrangement with OSHA to voluntarily adhere to the 50-ppm level set by the 1989 update of the OSHA PEL that was later vacated by court order. OSHA announced the voluntary agreement in a 1996 newsletter [OSHA 1996]. The SIRC encouraged its members to continue to comply with the 50-ppm standard as an appropriate exposure level for styrene, regardless of its regulatory status [SIRC, 1996].

Exhaust ventilation, low styrene-content resin, non-atomizing spray equipment, and PPE have been recommended to limit styrene vapor exposures to workers. Recent developments in specific closed molding technologies may also provide protection by reducing process emissions of styrene, and, in turn, the concentration of styrene in the workers' breathing zones.

Facility Description

Sea Ray Boats, Inc. is the largest manufacturer of recreational boats in the United States, producing more than forty models ranging in length from 18 to 68 feet. Four families of Sea Ray boat products include sport boats, sport cruisers, sport yachts, and yachts. In 1986, Sea Ray became a part of Brunswick Corporation making Brunswick Corporation the world's largest producer of marine engines and boats. At the time of the NIOSH survey, Brunswick had six Sea Ray Boats, Inc. manufacturing facilities in the United States: Knoxville Plant, Riverview Plant, Tellico Plant, Palm Coast Plant, Sykes Creek Plant, and Merritt Island Plant. The Sea Ray Boats, Inc.'s Product Development and Engineering facility is located in Florida. This report will focus solely on the closed molding of small parts at the Tellico Plant located in Vonore, Tennessee. The Tellico Plant produces 18 ½- to 24-foot sport boats. At the time of the NIOSH survey, the Tellico facility produced approximately 37 boats per day (148 per week). The facility size is roughly 274,000 square feet on 48 acres of property. There were approximately 600 hourly employees and 43 salaried employees working at the Tellico Plant. There were less than 10 workers in the small parts area evaluated during this survey.

The majority of the FRP parts produced at the Tellico Plant are manufactured using an open-molding process; however, approximately 50% of the small parts are manufactured using the closed-mold process. These parts include hatches, motor boxes, and similar pieces.

Process Description

Closed molding

Closed molding typically refers to a manufacturing process that uses two rigid half molds (male and female) or a solid mold (female) and a flexible film. Variations of closed molding include the use of two flexible molds, or a flexible mold and flexible film.

There are two core closed molding technologies that are used in manufacturing FRP: resin transfer molding (RTM) and vacuum infusion processing (VIP). RTM is a pressure-driven process, whereby resin is injected into a closed-mold cavity at higher than atmospheric pressure. VIP is a vacuum driven process where resin is pulled into the mold cavity that is lower than atmospheric pressure. There are a number of variations and combinations of these core technologies. For example, pressure injection RTM can be combined with vacuum assist in a process known as vacuum assisted resin transfer molding (VARTM). Likewise, the vacuum infusion process can use low pressure injection assist and is known as pressure assisted vacuum infusion processing.

The two types of closed molding technology used at the Sea Ray Tellico Plant are both variations of RTM. They are Multiple Insert Tooling (MIT) and VIP. The MIT process is used to fabricate small parts. This process is pressure-driven, whereby resin is injected into a closed-mold cavity at higher than atmospheric pressure. The MIT process, a derivative of RTM, involves three layers. A thick previously assembled glass matt is inserted into the two part molds. An assembly line is used to efficiently make the small parts. The small-part assembly line proceeds in the following order: gelcoating (in a booth), glass load, injection, and pull. The reaction which consumes styrene is completed before molds open thus very little styrene emission occurs. The specific job function of the RTM worker is to perform all of the above tasks of the closed molding MIT process. At the time of the NIOSH survey, Sea Ray was in the process of transferring processes from MIT to VIP due to the lower cost of tooling, extended tooling life, easier removal of parts, and overall cost effectiveness of VIP. Compared to open molding, closed molding technology should significantly reduce environmental emissions and worker exposure to styrene. However, the gelcoating portion of most closed molding processes is still performed in an open mold and represents a potential source of exposure [Hammond et al. 2007].

Gelcoating

Before applying the gelcoat, the mold is cleaned. Gelcoat is applied to the mold to provide a smooth outer finish to the part. All guns used for gelcoating are calibrated before each shift. Gelcoating for the small parts area is performed in a booth with a dedicated exhaust to the outdoors. The gelcoat booth is not fully enclosed. Make up air enters the open side of the spray booth and is exhausted to the outdoors. The exhaust flow rate of the booth was reported by the company to be approximately 480,000 dm³/s (17,000 cfm). The gelcoat operator wore a half mask respirator with organic vapor/P95 cartridges.

METHODS

Air Sampling for Styrene

Personal breathing zone and general area air samples for styrene were collected and analyzed in accordance with NIOSH Method 1501 [NIOSH 1994]. Samples were collected on SKC sorbent tubes (model number 226-01, Anasorb CSC, coconut charcoal, Lot #2000). The tubes were 7 centimeters (cm) long with a 6 millimeter (mm) outer diameter and a 4-mm inner diameter. The ends were flame-sealed, and contained two sections of activated coconut shell charcoal, 100 milligrams (mg) in front and 50 mg in back, separated by a 2-mm urethane foam plug. A glass wool plug precedes the front section, and a 3-mm urethane foam plug follows the back section. After breaking the sealed ends, each tube was connected to a Gilian low flow pump or an SKC Pocket Pump set at a nominal flow rate. The pumps' actual flow rates were calibrated before and after sampling. For personal breathing zone air samples, the air inlet of the sampling apparatus was secured in each worker's breathing zone with a lapel clip, and the battery-powered pump clipped to the worker's belt. In addition, field blank samples were created each

day to ensure that the sample media was not contaminated and to account for any variance in sample preparation.

The analyses of the charcoal tube samples for styrene were performed by Bureau Veritas North America, Inc., in Novi, Michigan. The samples were analyzed by removing the individual sections of the charcoal tube and placing them into separate vials. The glass wool and the foam plugs that divide the sections of charcoal were discarded. The individual sections were chemically desorbed by using 1 milliliter (mL) of carbon disulfide. The samples were placed on a mechanical shaker for a minimum of 30 minutes before being analyzed by gas chromatography with flame ionization detection (GC/FID) in accordance with NIOSH Method 1501 [NIOSH 1994]. The limit of detection (LOD) and limit of quantification (LOQ) for styrene for this sample set was 10 µg and 180 µg respectively. At a flow rate of 30 ml per minute for eight hours of sampling, the corresponding LOD and LOQ would calculate to 0.16 ppm and 2.93 ppm, respectively.

General area air samples were collected to better understand the effectiveness of the installed engineering controls using the same type of sampling apparatus as used for the personal air sampling. These samples were placed in stationary locations to determine how well the ventilation system was performing throughout the plant, and to assess the spread of the styrene vapor throughout the facility.

Once the sample results were received from the analytical laboratory, the styrene breathing zone concentrations and general area concentrations were calculated using Equation 1. The concentration in milligrams per meter cubed (mg/m^3) was converted to ppm.

$$C = \frac{m}{V \times 4.26} \tag{1}$$

.....

Where, C = styrene concentration, ppm m = mass of styrene per sample, µg V = volume of air sample in liters, L Note: 4.26 is the constant used for styrene to convert from µg/L (mg/m³) to ppm obtained from: NIOSH Manual of Analytical Methods (NMAM) [NIOSH 1994].

RESULTS

All personal breathing zone and general area air sampling results were well below all regulatory and recommended occupational exposure limits for styrene. The mean, maximum, and minimum styrene concentrations for the personal breathing zone and area samples are shown in Table 1 along with the sample size. Although two workers

identified themselves as crew leaders or group leaders, their exposures were included with the RTM workers since they were performing similar tasks. The highest personal breathing zone concentration for styrene measured from the RTM workers was 3.7 ppm. The highest personal breathing zone sample for styrene measured from the gelcoater was 6.4 ppm. Sample identification, job or area description, sample mass, sample time, and concentration in ppm for the styrene air samples collected during the three day survey are shown in Appendix I. All sampling results are only for gelcoating and closed molding of small parts. No samples were collected for open molding lamination or gelcoating of large parts since the current evaluation only focused on closed molding.

Job Description	Sample Type	Mean (ppm)	Maximum Concentration (ppm)	Minimum Concentration (ppm)	n
Gelcoater	Personal	4.6	6.4	3.7	3
RTM worker	Personal	1.7	3.7	0.9	12
Area	Area	0.9	1.6	0	10

 Table 1: Personal and area summary results for styrene vapor

CONCLUSIONS AND RECOMMENDATIONS

Sampling results from this survey indicated that personal breathing zone concentrations for styrene were well below applicable exposure criteria for the evaluated workers. However, the sampling that was conducted represented the average exposure over approximately 8 hours of the shift. Short term or peak exposures were not evaluated. For this reason, it is recommended that the gelcoating operator continue to use respiratory protection while gelcoating. Monitoring with a suitable real time monitor calibrated for styrene would be useful in order to evaluate peak exposures.

The low occupational exposures to styrene measured during this evaluation were likely a result of a combination of controls. Work practices, nozzle design, and spraying techniques combined with a well designed ventilated booth helped prevent high personal breathing zone concentrations for the gelcoater. The gelcoater consistently stood upwind of the part while gelcoating. Closed molding appeared to effectively control occupational exposures to styrene compared to traditional open molding methods for lamination of small parts. The closed molding process took place in a sealed environment and was not located near any open molding processes. Evaluations of closed molding at other boat manufacturing facilities have resulted in much higher exposures when the processes were located near open molding processes away from open molding in order to take advantage of the full potential of the control option.

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APPENDIX I

Sample ID	Job or Area Description	Personal or Area Sample	Sample Mass (µg/sample)	Sample Time (min)	Concentration (ppm)
1001	BLANK		0	0	0
1002	RTM worker	Personal	150	491	2.4
1003	Gelcoater	Personal	390	479	6.4
1004		area	91	464	1.6
1005	RTM worker	Personal	89	476	1.5
1006	RTM worker	Personal	110	484	1.9
1007	RTM worker	Personal	100	474	1.7
1008		Area	56	464	1.0
1009		Area	63	464	1.1
1010		area	88	473	1.5
1011	RTM worker	Personal	32	297	0.9
1012	RTM worker	Personal	230	485	3.7
1013	RTM worker	Personal	100	484	1.6
1014	RTM worker	Personal	100	468	1.7
1015	Gelcoater	Personal	220	485	3.7
1016		area	53	472	0.9
1017		area	66	471	1.1
1018	BLANK		0	0	0
1019	RTM worker	Personal	64	462	1.1
1020	RTM worker	Personal	80	463	1.4
1021		area	48	454	0.8
1022		area	71	0	0
1023		area	29	453	0.5
1024		area	32	452	0.5
1025	BLANK		0	0	0
1026	RTM worker	Personal	60	464	1.0
1027	Gelcoater	Personal	210	456	3.7
1028	RTM worker	Personal	67	456	1.2