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#### IN-DEPTH SURVEY REPORT: STYRENE EXPOSURES DURING FIBER REINFORCED PLASTIC BOAT MANUFACTURING

at

#### U.S. MARINE INCORPORATED Arlington, Washington

REPORT WRITTEN BY: Rebecca V. Carlo Duane Hammond, P.E. H. Amy Feng, M.S.

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U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES Centers for Disease Control and Prevention National Institute for Occupational Safety and Health Division of Applied Research and Technology Engineering and Physical Hazards Branch 4676 Columbia Parkway, Mail Stop R-5 Cincinnati, Ohio 45226-1998 SITE SURVEYED:

SIC CODE:

NAICS CODE:

SURVEY DATE:

SURVEY CONDUCTED BY:

U.S. Marine, Inc. Arlington, Washington

3732 (Boat Manufacturing And Repair)

336612 (Boat Building)

August 28-31, 2006

Rebecca V. Carlo Ron Hall Duane Hammond Adam Paberzs Alberto Garcia Dan Farwick Srinivas Durgam

All mentioned above: NIOSH, Cincinnati, OH

EMPLOYER REPRESENTATIVES CONTACTED:

Dennis Pearson Safety/ Environmental Manager U.S. Marine

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# ACKNOWLEDGEMENT

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#### ABSTRACT

A one-week in-depth survey was performed to assess the occupational exposures of styrene vapors, and to evaluate the effectiveness of the engineering controls currently installed for reducing styrene exposures during two distinct fiberglass reinforced plastic (FRP) boat manufacturing processes. The primary objective of this study was to quantify the exposures occurring during both an open and closed mold process. The effectiveness of the styrene controls examined in this study was evaluated by measuring styrene concentrations in personal breathing-zone and general-area samples during typical work shifts. The highest geometric mean of personal breathing-zone air samples for gun operators was 52 ppm in an open-molding process in Building 3. The highest geometric mean of general-area air samples was approximately 17 ppm in the gelcoating booth for an open-molding process in Building 2. The geometric mean area air sample concentration for the closed-molding RTM injection area in Building 10 was 2.36 ppm. At the time of the evaluation, the majority of the measured styrene concentrations were below the OSHA PEL of 100 ppm and the NIOSH REL of 50 ppm for most jobs. However, many of the measurements for open-molding processes in all evaluated buildings indicated that concentrations were higher than recommended exposure limits such as the 20 ppm TLV recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) and European standards such as the 20 ppm occupational exposure level limit values (LLV) for styrene set by the Swedish Work Environment Authority and the 20 ppm limit for styrene concentrations set by the German Federal Institute for Occupational Safety and Health. Efforts should be made to keep styrene concentrations below the lowest applicable recommended occupational exposure criterion. Workers performing tasks in open-molding processes should continue to wear half-mask respirators that protect against inhalation of organic vapors (e.g., styrene vapors). When possible, implementation of the closed-molding processes should be continued since less styrene vapor is emitted in a sealed environment.

#### **INTRODUCTION**

According to the 2004 Statistics of U.S. Businesses, 51,409 workers were employed in the boat manufacturing industry (most involved in the fiber-reinforced plastic boat production), with 26,633 in firms of 500 employees or less.<sup>1</sup> In the early 1980s, the National Institute for Occupational Safety and Health (NIOSH) conducted a control technology assessment of the boat manufacturing industry, primarily focusing on large FRP boats using open molding techniques. Since then, many changes have occurred in this industry, including the development of closed molding processes and the promulgation of the Environmental Protection Agency's (EPA) Maximum Achievable Control Technology (MACT) standard for boat manufacturing in August of 2001.<sup>2</sup> Recent meetings with industry trade associations and individual companies have shown an interest in a study to assess and quantify the effectiveness of closed-mold operations and the MACT technologies for reducing occupational styrene exposures. In addition, trade-association representatives have also expressed interest in NIOSH developing costeffective ventilation controls for open-molding processes, recognizing that open-molding processes emit the most styrene vapors and are the processes most widely used in manufacturing facilities today.

On August 28-31, 2006, researchers from the Engineering and Physical Hazards Branch (EPHB) of the Division of Applied Research and Technology (DART) conducted an indepth survey at U.S. Marine, Inc. in Arlington, Washington. The primary purpose of this survey was to assess the occupational exposures to styrene vapors in the air and to evaluate the effectiveness of engineering exposure-control measures during FRP boat manufacturing operations. The specific aims of this field survey were to:

1) Assess the occupational exposures of styrene vapor in air during a resin transfer molding (RTM) process (a close-molding process) and the traditional open-molding process.

2) Evaluate the currently installed ventilation system and recommend costeffective ventilation controls for better reduction of styrene exposures during open molding processes.

The effectiveness of preventing styrene exposures was evaluated in terms of personal breathing-zone styrene exposures. Personal air sampling was the measurement of a particular employee's exposure to styrene. In addition, styrene air concentration measurements were taken at various fixed locations throughout the facility under study (area air samples). For this report, effective engineering controls are those that maintain styrene exposures below applicable occupational exposure criteria—the NIOSH Recommended Exposure Limit (REL), the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV<sup>®</sup>), or the OSHA Permissible Exposure Limit (PEL).

This report will focus on the documentation of styrene exposures measured during the closed- and open-molding manufacturing processes. In addition, engineering controls

and work practice recommendations will be offered where styrene exposures exceed the NIOSH or OSHA exposure criteria.

## **Styrene Usage and Background**

The major chemical component of concern in terms of occupational exposures in the FRP process is styrene. Styrene is a fugitive emission, which evaporates from resins, gel coats, solvents, and surface coatings used in the manufacturing process. The thermo-set polyester production and tooling resins, along with the gelcoats, used at this plant are compliant with the U.S. EPA requirements for MACT. All of the various products used at U.S. Marine which contain styrene are listed in Table 1 along with their application method, building usage, and percent styrene by weight. The concentrations of styrene in tooling and production resins vary depending on the color of the gelcoat and other manufacturing environmental factors (temperature, humidity, etc.).

			%
Buildings	Name	Application	Styrene
		Production	
2, 3, 16	Polyester Resin	Resin	< 31.75
2, 3, 16	Vinylester Resin	Skincoat Only	33-35
2	Filled Resin	Tooling	49.8
2	Black Gelcoat	Tooling	46.9
3, 16, 10	Arctic White	Gelcoat	30.6
3, 16, 10	Champange	Gelcoat	35.2
10	Polyester Resin	Filled Resin	31.7
10	Silver 2004 Maxum	Gelcoat	36
10	Seal Gray	Gelcoat	36.82

Table 1: List of all products used at U.S. Marine containing styrene

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 allowing the reactive sites on the molecules to interact. As an active diluent, styrene will react in a 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. The product is 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, due to the volatility of styrene, 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.<sup>2</sup> 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. Numerous studies have shown that styrene exposures were linked to central and peripheral neurologic, <sup>3,4,5</sup> optic, <sup>6,7</sup> and

irritant<sup>8</sup> effects when occupational exposures to styrene vapors in air were measured at concentrations greater than 50 parts per million (ppm). There is also evidence concerning the influence of occupational styrene exposure on sensory nerve conduction indicating 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.<sup>9</sup>

# **Occupational Exposure Criteria**

The primary sources of occupational evaluation criteria for the workplace are: (1) the OSHA Permissible Exposure Limits (PELs);<sup>10</sup> (2) The NIOSH Recommended Exposure Limits (RELs);<sup>11</sup> and (3) the American Conference of Governmental Industrial Hygienists (ACGIH<sup>®</sup>) Threshold Limit Values (TLVs<sup>®</sup>).<sup>12</sup> Employers are mandated by law to follow the OSHA limits; however, employers are encouraged to follow the most protective criterion.

The NIOSH REL for styrene vapor in air is 50 ppm for a 10-hour time-weighted average (TWA) (meaning the limit applies to the average exposure during a work day of up to 10 hours and a work week of up to 40 hours), with a 15-minute short-term exposure limit (STEL) of 100 ppm, limiting average exposures over any 15-minute period during the work day. <sup>11</sup> These recommendations are based upon reported central nervous system effects and eye and respiratory irritation. The OSHA PEL for styrene is 100 ppm for an 8-hour TWA exposure, with a ceiling limit of 200 ppm.<sup>10</sup> The ceiling limit restricts exposures for any portion of the work day. The American Conference of Governmental Industrial Hygienists (ACGIH) revised its Threshold Limit Value (TLV<sup>®</sup>) in 1997, and recommends styrene be controlled to 20 ppm for an 8-hour TWA exposure with a 40 ppm, 15-minute STEL.<sup>12</sup> The Swedish Work Environment Authority has an occupational exposure level limit value (LLV) for styrene of 20 ppm and a short term value (STV) of 50 ppm.<sup>13</sup> The German Federal Institute for Occupational Safety and Health has an occupational exposure limit value of 20 ppm for styrene.<sup>14</sup>

#### Maximum Achievable Control Technology

The EPA has identified the FRP boat manufacturing industry as a major source of Hazardous Air Pollutants (HAPs)—mainly styrene. The final MACT regulation was issued to reduce HAPs for new and existing boat manufacturing facilities. The MACT standard affects any boat manufacturing stationary facility that emits or can potentially emit 10 tons per year of a single HAP or 25 tons per year of combined HAP. The MACT covers: (1) open molding resin and gel coat operations; (2) resin and gel coat mixing operations; (3) resin and gel coat application equipment cleaning operations; (4) carpet and fabric adhesive operations. The MACT standard requires boat manufacturers using open molding to adopt stringent air pollution control technologies in order to reduce environmental releases of styrene vapor in the air. Closed molding is one method for demonstrating compliance with the Boat Manufacturing MACT. Under the rule, boat manufacturers wishing to continue using open-molding operations must use one of the following options: (1) purchase materials that meet the organic HAP content

requirement; (2) meet the HAP content requirements for resin and gel coat operations on a weighted average basis; (3) use emissions averaging among different resin and gel coat operations: or, (4) use an add-on control device.<sup>15</sup> Closed molding is exempt from the MACT standard.

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 (which was later vacated by the courts). 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.<sup>16</sup>

#### **General Facility and Production Information**

U.S. Marine Corporation has 2600 employees nationwide. The Arlington facility employs approximately 1050 people and consists of three different departments: manufacturing, research and development, and administration. This site focuses primarily on manufacturing and research and development (engineering and documentation for all boat lines sold by U.S. Marine). Plant production time is split into three shifts: shift one is from 6:00 am to 2:30 pm, shift two is from 2:30 pm to 10:00 pm, and shift three is from 10:00 pm to 6:00 am. Eight different boat models are manufactured at the Arlington facility, at a rate of approximately 1.5 to 3 boats per day (including production and assembly). The boats range in size from 34 to 58 feet.

The manufacturing plant includes 17 buildings dispersed on 32 acres of land as shown in Figure 1. These include: prototype assembly, lamination facilities, office administration buildings, warehouses, wood shop buildings, a milling machine building, welding facilities, loading, a plug shop, and windshield installation. The pertinent buildings and the operations performed in each will be described in the paragraphs that follow.

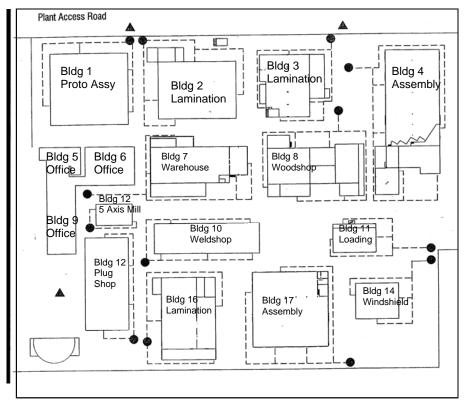


Figure 1: Plant layout (Provided by U.S. Marine)

# Buildings Involved with the Production of Tooling

U.S. Marine Corporation in Arlington, WA produces all of their tooling equipment for the Arlington facility. Tooling equipment refers to the molds used to make the boat parts during the production process. Various types of tooling parts are made for different phases of the boat building process. The production of tooling is very similar to the lamination production process; however, the materials used to make the tools are different. The percent styrene by weight in the resins used for tooling is higher than for production processes. The sections that follow explain the details involved with the production of tooling.

# 5-Axis Mill

Building 12A houses a 5-axis mill used to create a plug. A plug (also known as tooling or glass master molds) is an original mold used to make production molds. The plug is made from large blocks of high density Expanded Poly-styrene Foam (EPS). The EPS blocks are machined using a computer-controlled milling machine to approximately one-half an inch smaller than the desired thickness. The EPS blocks are coarse and roughly shaped, so a high density urethane spray is applied once the undersized plug has been machined. After the spray, the plug is re-machined to the proper dimensions to obtain a smooth finished surface. Upon completion, the plug is gelcoated and a Mold-A (a starting mold used to make a production mold) is made and later waxed in Building 2 (*See Gelcoat Application and Lamination*). In cases where small volume quantities (e.g., one to three boats) are going to be made, tooling or production molds are made directly

from the plug. However, in many cases a Mold-A and a glass master are made for high volume production. The glass master is identical to the plug.

#### Plug Shop

The plug shop is located in the southwest corner of Building 12 directly south of the 5axis mill. All of the small detailing that the 5-axis mill cannot complete is performed here. The air pockets from the foam are removed and a styrene based putty (Bondo) is applied. The final production and detail of the plugs occur in the south end of the plug shop. Two coatings of polyester surfacing primer (Duratec) containing styrene are applied to the plugs to give them a finished appearance. Any imperfections that may be present in the plug are fixed by sanding and applying a styrene based putty (Bondo) to the imperfection and sanding again.

## Gelcoat Application and Lamination

Two types of molds are made in Building 2—glass-master molds and Mold-A. Mold-A is used to make a tool known as the glass master which is the production mold. Before applying the gelcoat, the plug is cleaned. When needed, a wax is applied to the plug surface to ensure an easy part-plug separation. Once the plug is cleaned and waxed, it is placed in a ventilated spray booth. The tooling lamination process begins with the application of a black gelcoat (containing 46.9 percent styrene) to the plug-mold. When spraying hulls, the gel coater sprays one half of the mold, and then rotates the mold longitudinally on its stand to complete the other half. Small parts and large decks are gelcoated in the same spray booth. The small parts and deck molds are fastened to carts and moved through the plant manually. Gelcoat is sprayed by one gelcoater (specified in this report as the Gelcoater in Building 2) using an atomized spray gun (Magnum Venus, Pro Gun No. 58603-3 with Air Assist VPA-100; Kent, Washington) inside the spray booth.

Once the gelcoat is applied to the plug, it is moved to the non-shrink area. While in the non-shrink area, a special filler resin (49.8 percent styrene) along with eighty percent chopped fiberglass and twenty percent woven fiberglass mats are applied in layers to the plug. The filler resin is used to prevent shrinking of the part during the curing process. It is important to prevent distortion of the high gloss finish which is essential to the tooling parts. The filler resin is sprayed using a flow coater spray gun (model no. G03, Magnum-Venns Super Pearl Chopper Gun, Kent, Washington). The filler resin and chopped fiberglass are rolled together by hand to eliminate any air pockets that may be caught within the part. Depending on the part, there are three to six layers of filler resin and fiberglass added in the non-shrink area. Personal breathing-zone air samples were taken from the workers who spray and hand-roll the filler resin. They were categorized as filler resin personal air samples in this report. All parts except hulls were then transferred to the lamination bay (hulls were too large to fit in a lamination bay and were laminated in place). In the lamination bay, more fiberglass along with vinyl ester resin were added to obtain the final desired thickness. The personal samples from the rollers and gunoperators in contact with the vinyl ester resin are categorized as Roller (vinyl ester) and Gun-operator (vinyl ester) respectively.

## Buildings involved with Production of Boat Parts

The U.S. Marine plant in Arlington, Washington, manufactures Meridian Yachts mainly using the open mold process. The buildings involving the open molding production of boat parts are Buildings 3 and 16. The processes used to manufacture boat parts were similar in both buildings. The only difference between these two buildings was the type of parts made. Decks and medium-sized parts were produced in Building 3, while Building 16 was used for hull and large part laminations. The resin transfer molding (RTM), is a closed molding process, that was used only in Building 10 for building small hatch covers. The paragraphs that follow describe the open molding and closed-molding process used at this facility.

## **Open molding**

Fiberglass boats are built from glass fiber reinforcements laid in a mold and saturated with a polyester resin. The plastic resin hardens to form a rigid plastic part reinforced with the fiberglass. In open molding, fiberglass boat parts are built from the outside in according to a three step process.

- 1. The mold is sprayed with a layer of gel coat, which is pigmented polyester resin that hardens and becomes the smooth outside surface of the part.
- 2. The inside of the hardened gelcoat layer is coated with a "skin coat" of chopped glass fibers and polyester resin.
- 3. Additional layers of fiberglass cloth and chopped glass fibers saturated with resin are added until the part is the final desired thickness. These layers are compressed by rolling the surface by hand.

Styrene exposures potentially occur at all three steps of the open-molding process, as both the gelcoat and the polyester resin contain a significant percentage of styrene. Most of the employees exposed to styrene vapors during the open molding process in Buildings 3 and 16 were sampled during shifts 1 and 2. Gun-operators are those workers who operate the chopper gun. The resin is sprayed by a low flow MACT-compliant chopper gun. Gun-operators spend most of their time spraying the chopped glass and resin. Part of their job also includes helping the rollers eliminate any air bubbles that might get caught in the fiberglass. For data analysis purposes, the gun-operators were characterized according to the type of part they were working on. In Building 3, gun operators worked on decks, medium parts, and small parts. In Building 16, gun operators worked on hulls, decks, and small parts. Workers classified as rollers are those that work next to the gun operator and only press the fiberglass against the mold saturating the fiberglass with resin. For the purpose of data analysis, rollers in Building 3 and 16 were categorized according to the part they were rolling. In Building 3, rollers worked on hulls, decks, small parts, and medium parts. In Building 16, rollers worked on hulls and small parts.

Once the fiberglass mats and resin are applied and the desired thickness has been achieved in the hulls, a corefoam (a 2-part foam system that combines a spray-dried polymeric resin with a foaming catalyst to produce a "dry" foam) is installed in the boat for more support. The workers that were involved in a process known as stiffening were sampled and categorized as stiffening in this report. Stiffening is the addition of wood components and metal parts to add strength to the core of the boat, and enables other parts to be attached to the hull later in the assembly process.

#### Resin Transfer Molding (RTM)

RTM is a closed-mold technique which uses two rigid half molds that close before resin injection and curing to form the final part. RTM was only conducted in Building 10 and was used to produce small parts, mainly hatch covers. Prior to the injection of the resin to the closed mold, a gelcoat is applied to the interior surface of both molds to provide a smooth finish on all external surfaces after the cure. Following the gelcoat operation, dry fiber reinforcement mat is placed into the rigid mold before closing. After the mold is closed, resin and initiator are then transferred into the mold cavity by a pressure pump. The resin curing process takes place while the part is still in the closed-mold. Once the resin has cured, the composite part is demolded and trimmed. The RTM process has been implemented successfully for applications requiring a large volume of smaller parts where a smooth surface is desired on all exposed surfaces of the part. Although the RTM process does not control any styrene emissions during the gel coat application, it is expected that limited worker exposure would occur during the resin transfer and curing stages since these operations occur in a sealed environment. The greatest concern in this area is the styrene exposures during gelcoating. All of the gelcoating is done inside of a spray booth. One worker sprays the gelcoat inside the spray booth, and another applies the fiberglass inside the mold, closes the mold, and sets up the mold for resin injection. Both of the workers were sampled for styrene exposures. The gelcoater is denoted as gelcoat (RTM) and the closed mold workers is denoted as Resin Injector (RTM).

# <u>Safety</u>

#### Ventilation

Ventilation characterization was performed in four of the buildings at U.S. Marine. A hot wire anemometer (VelociCalc, TSI, Shoreview, MN) was used to measure the air flow at the supply units and the exhaust vents. Nine readings were taken from the face of each supply and exhaust vent. These readings were then averaged and recorded. The ventilation systems in Building 2 were push-pull ventilation systems. All of the gelcoating was performed in a gelcoating booth. Each lamination area had its own pushpull ventilation system. From observations using a smoke generator, it appeared that the ventilation system installed in Building 2 was effectively removing smoke away from the worker operations. However, Buildings 3 and 16 did not have a separate ventilation booth for the gelcoating processes. In Building 3, decks and medium parts were gelcoated and laminated in the same location (i.e. parts were not moved). Building 16 did have a gelcoating area; however, it was not enclosed. The much larger boats (54 foot) that were difficult to move around the plant were gelcoated and laminated in the same location. The building layout and ventilation system for Buildings 2, 3, 10, and 16 are shown below in Figures 2 through 5, respectively. During regular operations, a manometer was installed in all buildings adjacent to each cell to monitor the pressure differentials across the filters installed at the face of the exhaust hood. When the manometer read 0.20 inches of water, the filters were changed in an effort to maintain the designed air flow at each hood.

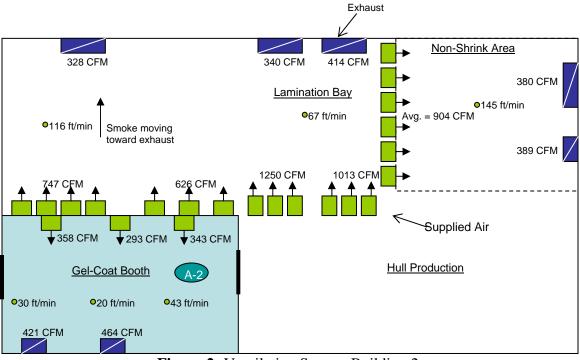


Figure 2: Ventilation System Building 2

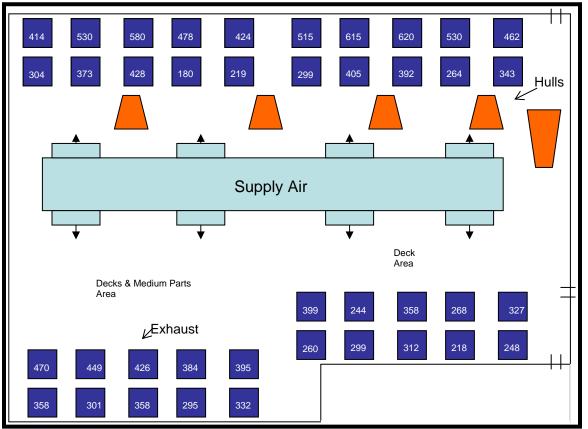


Figure 3: Ventilation System Building 3

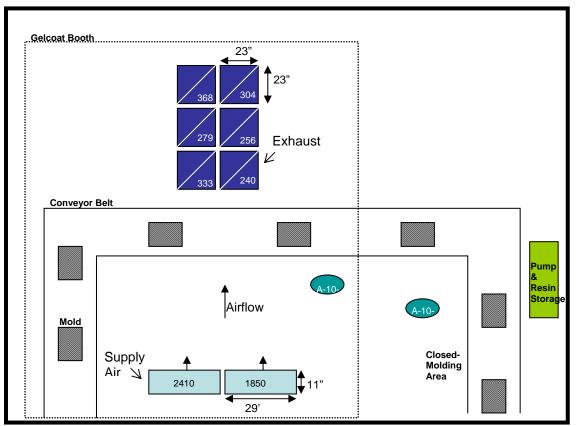
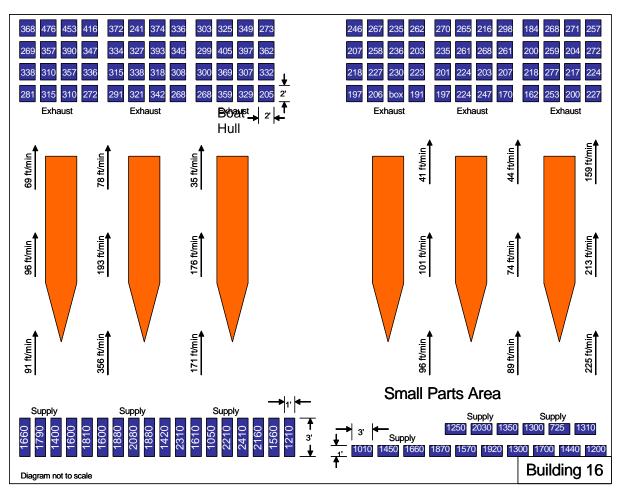


Figure 4: Ventilation System and Closed-Molding Process Building 10 (All values given above are in cubic feet per minute (cfm))



*Figure 5:* Ventilation System and Open-Molding Process Building 16 (All values given above are in feet per minute (ft/min))

# Personal Protection Equipment

Approved protective eyewear meeting the ANSI Z87 standard was required at all times on the plant site. All laminators, gun-operators, gelcoaters, and grinders were required to wear Tyvek® suiting. Hard hats were required whenever there was a risk of falling objects. Examples include shipping and receiving shelves, all overhead work such as cranes, warehouses, and loading and unloading dock areas. Safety shoes was required in the maintenance shop, warehouse, and for engine installers. Gloves were required according the work being performed. Welders required welding gloves, chemical handlers required impermeable nitrile gloves, and metal and wood handlers required leather or cotton gloves. Gloves are not required for laminators but are provided by the compliance manager. Some of the laminators who chose not to wear gloves had resin on their hands. Hearing protection was required in the wood shop, and any other location where the decibel level exceeds 82 decibels. Respiratory protection was not required for most of the workers; however, it was available for workers that want to wear them. Two stage respirators with organic vapor charcoal filters and a pre-filter for particulates were required for all lamination personnel working in Building 12.

#### **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 (Hydrocarbons, Aromatic) (NMAM, NIOSH Manual of Analytical Methods).<sup>17</sup> 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 flow rate of 0.3 liters per minute (L/min). 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. A calibration was performed on each pump before and after sampling. In addition, two field blank samples were taken 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 Clayton Group Services in Novi, MI. 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 then chemically desorbed by using 1 mL of carbon disulfide. The samples were placed on a mechanical shaker for a minimum of 30 minutes before analyzed by gas chromatography with flame ionization detection (GC/FID) in accordance with NIOSH Method 1501. The limit of detection and limit of quantification for styrene for this sample set was 0.33 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. Area samples were placed in eastern and western gelcoat spray booths, tooling area, closed-mold area, the small part lamination, and large part lamination area. See Figures 2-5 for area sample locations.

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 from milligrams per meter cubed was converted to parts per million.

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

Where,

C = styrene concentration, ppm

 $m = mass of styrene per sample, \mu g$ 

V = volume of air sample, L

**Note:** 4.26 is the constant used for styrene to convert from mg/m<sup>3</sup> to ppm obtained from: NMAM (NIOSH Manual of Analytical Methods) 1501(Hydrocarbons, Aromatic)

#### **Real-time Monitoring**

Direct reading instruments were used to determine how exposures varied with time and to identify specific job tasks that contributed most to the workers' exposures. Monitoring was performed using Pac III Drager Portable Gas Monitors (Drager Safety, Pittsburgh, PA). XS EC Organic Vapor Sensors programmed specifically for styrene were installed in the monitor to determine the concentration of styrene in the air. These sensors are electrochemical measuring transducers for measuring the partial pressure of gases under atmospheric conditions. They have an internal data memory (EEPROM) which includes storage of calibration data and default settings. The measuring range of these sensors is from 0 to 100 ppm with a relative sensitivity of 0 to 5 ppm. The monitors were configured to store a reading every five seconds, for approximately eight hours. The sensors were factory calibrated prior to this field survey. At the end of the sampling period, the data stored in monitors' memories were downloaded to a laptop computer. Work activity data were recorded with digital video camera and combined with the realtime exposure data by determining both the exposure and the activity at any given time. A time series analysis of the real-time exposure and work activity data resulted in a model to predict worker exposures. The data obtained were used to associate events with exposures and to promote more effective and focused recommendations for controlling the styrene vapor exposures in both open and closed-mold processes.

#### **Statistical Analysis and Results**

The distributions of all samples were checked for normality using the Shapiro-Wilk test. The results of this test suggested that the data were log-normally distributed; subsequently, all data were log-transformed for statistical analysis. Personal breathingzone and general-area air samples were analyzed separately. Geometric means, standard deviation, and 95% confidence limits are included in Table 2.

General-area and personal breathing-zone air samples were collected in Buildings 2, 3, 10, and 16. In each building, working areas were categorized based on the similarity of work occurring in each particular working area. Personal breathing-zone air samples were classified into fourteen job categories. Some job categories were unique to certain buildings while other job categories were seen in various buildings. Comparisons were only performed in the common jobs among buildings or among jobs in the same building

## General Area Air Samples

General-area samples were grouped based on the location and distance from the styrene sources. Most area air sample categories were unique to each building. Lamination area samples, however, were found in Buildings 3 and 16. Since lamination of production parts occurred in only two buildings (Buildings 3 and 16), a statistical test was performed on the area sample data of these two buildings to test the concentration differences, if any, around the lamination area. A one factor (building) Analysis of Variance procedure (ANOVA) was used at the 5% significance level. Statistically significant differences involving the lamination area in Building 3 (Gmean = 13.25, Gstd =1.39) has significantly higher exposure than the lamination area in Building 16 (Gmean=7.05 Gstd=1.67). The descriptive statistics for all the area samples are listed in Table 2.

Building 10 with the closed-molding process had low area air sampling concentrations of styrene. The geometric mean area air sample concentrations in Building 10 were 2.36 and 2.93 ppm for the RTM injection area and the gelcoating booth respectively.

## Personal Breathing-Zone Air Samples

The personal breathing-zone samples were divided into fourteen job categories. A twofactor (job and building) ANOVA model followed by Scheff's multiple comparison procedure was used to test for differences, if any, among five common job categories in Buildings 3 and 16. The following common jobs were compared: roller (hull), gunoperator (deck), gun-operator (small part), roller (smaller parts), and gelcoater. Statistically significant differences (p-value = 0.005) were found among the job categories tested. The Scheffe's test indicated that exposures of hull rollers (Gmean = 34.74; Gstd = 1.29) and deck gun-operators (Gmean = 34.48; Gstd = 1.33) were significantly higher than the exposure of the gelcoater (Gmean = 17.89; Gstd= 2.10). No other statistically significant differences were found between Buildings 3 and 16. For the same job, no day to day variation was found.

In Building 3, a one-factor (job) ANOVA procedure was used to test for differences among three similar job groups (gun-operator (med parts), roller (medium parts); roller (deck). No statistically significant difference was found among these three job groups (p value = 0.49). The calculated geometric means (measure of central tendency), standard deviations, lower and upper 95% confidence limits, and sample size are shown in Table 2. Each individual result sorted by job title or area location for all buildings are presented in Appendix 1. Appendix 1 lists sample type (either personal breathing-zone or general-area), job group (specific location for area samples or job title for PBZ samples), date, and sample ID.

Building 10 with the closed-molding process had low personal breathing-zone samples of styrene. The lowest personal breathing-zone sample measured in Building 10 was 3.22 ppm and the highest was 4.78 ppm.

Sample Type	Job Group	Building	n	Geometric Mean (ppm)	Geometric standard deviation	Upper 95% Confidence Interval	Lower 95% Confidence Interval
Area	Gelcoat Booth	2	3	16.93	1.37	36.79	7.79
Area	Lamination Area	3	12	13.25	1.39	16.36	10.73
Area	Gelcoat Booth (RTM)	10	3	2.93	1.4	6.75	1.28
Area	RTM Area	10	3	2.36	1.28	4.33	1.29
Area	Lamination Area	16	9	7.05	1.67	10.46	4.75
Personal	Filler Resin	2	10	17.47	1.34	21.59	14.14
Personal	Gelcoater	2	3	23.84	2.24	175.92	3.23
Personal	Gun operator (small parts)	2	2	20.02	1.37	334.13	1.2
Personal	Gelcoater	3	8	19.1	2.45	40.36	9.04
Personal	Gun operator (deck)	3	10	32.35	1.3	39.02	26.81
Personal	Gun operator (medium parts)	3	11	35.18	1.37	43.56	28.4
Personal	Gun operator (small parts)	3	2	52.01	1.05	79.78	33.9
Personal	Roller (Hull)	3	3	32.53	1.26	57.29	18.47
Personal	Roller (Deck)	3	14	37.91	1.26	43.39	33.12
Personal	Roller (Small Parts)	3	6	35.84	1.28	46.29	27.75
Personal	Roller (Medium Parts)	3	9	32.06	1.55	44.85	22.92
Personal	Pop and Prepping	3	2	9.03	1.09	19.78	4.12
Personal	Gelcoat (RTM)	10	3	4	1.22	6.59	2.43
Personal	Resin Injector (RTM)	10	2	2.65	1.31	29.42	0.24
Personal	Gelcoater	16	4	15.71	1.41	27.12	9.1
Personal	Gun operator (hull)	16	7	31.91	1.27	39.71	25.64
Personal	Gun operator (deck)	16	2	47.46	1.23	299.41	7.52
Personal	Gun operator (small parts)	16	3	22.78	1.53	65.32	7.95
Personal	Roller (Hull)	16	6	35.9	1.32	48.16	26.76
Personal	Roller (Small Parts)	16	3	19.1	1.14	26.49	13.78
Personal	Stiffening	16	25	23.14	2.09	31.35	17.09

Table 2: Statistical results of personal and area samples

#### DISCUSSION

Air sampling results in Building 10 indicate that the ventilation system installed in the gelcoating booth was removing styrene vapors and controlling exposures to concentrations below applicable occupational criteria. Louvers on the air supply unit in Building 10 were adjusted to keep the gelcoat from dispersing throughout the room. The airflow was high at knee level and near the floor and low at the working level and near the breathing-zone level. Quantitative smoke test indicated that the air in the gelcoat booth was turbulent, and moved quickly to the exhaust vent. Based on the records provided by U.S. Marine personnel, the supply vent (SV 2-8) supplies 11,500 cubic feet per minute to the gelcoat booth in Building 10.

Personal breathing-zone samples measured in the gelcoat booth of Building 2 were almost six times higher than the exposures measured in the gelcoat booth in Building 10. The measured geometric mean concentration of the gelcoat booth in Building 2 was 16.93 ppm. The gelcoating booth in Building 2 was five times bigger than the gelcoating booth in Building 10 in order to accommodate the larger parts and higher production rates. The supplied air (cubic feet per minute) in both gelcoating booths were mostly the same.

The open-molding lamination process for production of boat parts took place in Buildings 3 and 16. The processes were similar in both buildings with the primary difference being the type of part laminated. In Building 3, gun operators worked on decks, medium parts, and small parts. In Building 16, gun operators worked on hulls, decks, and small parts. The concentrations measured in Building 3 were statistically significantly higher than what was measured in Building 16. This was likely due to the layout of the plant and the fact that gelcoating and laminating were done in the same area throughout Building 3. The ventilation in Building 3 was also not operating as designed. Qualitative smoke tests indicated that in many areas inside Building 3 the air flow was not moving towards the exhaust vent. Although most of the styrene exposures measured in Buildings 3 and 16 were below the NIOSH REL of 50 ppm and the OSHA PEL of 100 ppm, higher airflow should be provided in the lamination areas specifically the hull and deck gun-operators in Building 3. The hull and deck gun-operators should always be positioned upwind of the airflow being careful not to spray resin into the wind. Among the jobs in Building 3, no statistically significant differences were found. The air in Building 3 was well mixed based on observations made during a quantitative smoke test.

The personal breathing-zone samples in Building 16 indicate that workers who spend a significant amount of time performing stiffening and other tasks in the hulls of large boats experienced some of the highest exposures to styrene. Due to the size of the hulls, the workers spend the majority of their day inside the hull with little ventilation reaching the lower portion of the hull. A higher airflow should be supplied to the workers who perform stiffening and other tasks in the hulls of large boats.

#### CONCLUSION AND RECOMMENDATIONS

At the time of this evaluation, nearly all of the measured personal breathing-zone and area air styrene concentrations were below the OSHA PEL of 100 ppm and NIOSH REL of 50 ppm. However, many of the measurements in all evaluated buildings indicated that concentrations were higher than recommended exposure limits such as the 20 ppm TLV recommended by ACGIH and European standards such as the 20 ppm occupational exposure level limit values set by the Swedish Work Environment Authority and the 20 ppm exposure limit set by the German Federal Institute for Occupational Safety and Health. Efforts should be made to keep styrene concentrations below applicable exposure criteria. The following recommendations are provided to further reduce styrene concentrations in an effort to help provide a safer and healthier environment.

- Workers should continue to wear half-mask respirators that protect against inhalation of organic vapors (i.e., styrene vapors). If additional inhalation hazards exist from potential exposures to particulates such as fiberglass dust, a respirator should be selected that is capable of removing both the particulate and the organic vapors. If a respirator is provided for an employee it should have the ability to remove organic vapors (i.e., styrene vapors). If particulates are of concern, the respirator should be able to remove both the particulate and the organic vapors. In accordance with 29 CFR 1910.134, if the employer determines that any voluntary respirator use is permissible, the employer shall provide the respirator users with the information contained in Appendix D of 29 CFR 1910.134.<sup>18</sup>
- When possible, workers performing rolling operations should be on the supply side of the ventilation system relative to the gun operator. This will help prevent air currents from directing styrene emissions from the gun directly into the breathing zone of the workers performing rolling tasks.
- Workers in several buildings did not consistently wear gloves and PPE when performing tasks that required routine contact with the resin. Since styrene is listed with a skin notation in the ACGIH TLV, and skin contact with styrene and other chemicals in the resin can cause dermatitis, proper gloves that protect workers against contact with styrene should be worn by all employees who have the potential to come into contact with the resin.
- Ventilation measurements and qualitative smoke testing indicated that the ventilation system in Building 16 performed as designed. However, several of the louvers in the supply vents were damaged and several exhaust vents near the ground were blocked by boxes. The damage to the vents were minor but should be repaired to allow for optimal airflow. Boxes should be moved away from exhaust vents.
- In Buildings 3 and 16, gelcoating processes were performed in the same location as lamination processes. It is recommended that the gelcoat operations be enclosed and properly ventilated to help reduce styrene concentrations in the rest of the building.
- Styrene exposures appear to be reduced by using enclosed processes such as the closed-molding RTM injection area in Building 10. It is recommended that manufacturers continue to explore the use of closed-molding processes where possible.

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# **APPENDIX 1**

		Sample	Result	Concentration	Noise Dosimeter
Job Title	Date	ID	(ug/Sample)		No.
Infusion	8/15/2006	101	(ug/Sample) 490	[ppm] 6.32	NO.
Infusion Small	6/15/2006	101	490	0.32	
Parts Supervisor	8/15/2006	102	380	6.06	1705
Area D	8/15/2006	102	330	4.46	1705
Small Parts	0/15/2000	103	330	4.40	
	9/15/2006	104	480	10.63	
Laminator Blank	8/15/2006 8/15/2006	104		0.00	
			0		
Blank	8/15/2006	106	0	0.00	
Small Parts	0/45/0000	407	700	0.00	4700
Laminator	8/15/2006	107	730	9.09	1706
Infusion Small					
Parts	0/40/0000	400		0.50	470.4
Supervisor	8/16/2006	109	320	8.52	1704
Hull Laminator	8/16/2006	110	730	11.84	
Hull Laminator	8/15/2006	111	830	11.11	
Small Tanks	8/15/2006	112	370	5.07	
Hull Laminator	8/15/2006	113	650	10.89	
Large Part					
Laminator	8/15/2006	114	1200	15.94	
Area F	8/15/2006	115	370	4.97	
Hull Laminator	8/15/2006	116	810	11.11	
Blank	8/15/2006	118	0	0.00	
Putty and					
Cutting	8/15/2006	119	410	7.11	17460
Blank	8/15/2006	120	0	0.00	
Area A	8/15/2006	121	390	4.89	
Gelcoat					
Supervisor	8/15/2006	122	580	10.50	
Tooling	8/15/2006	123	86	1.35	
Area E	8/15/2006	124	360	4.54	
Gelcoat	8/15/2006	125	920	12.88	
Tooling	8/15/2006	126	230	4.04	
Tooling	8/15/2006	127	210	3.12	1703
Gelcoat					
Assistant	8/15/2006	128	290	4.85	
Area C	8/15/2006	130	220	2.80	
Large Part			-		
Laminator	8/15/2006	131	710	12.61	
Grinding/Cutting	8/15/2006	132	410	6.56	1704
Large Part					
Laminator	8/15/2006	133	1100	19.83	
Area B	8/15/2006	135	520	6.69	
Large Part	3, 10, 2000				
Laminator	8/15/2006	136	750	12.52	
Area G	8/15/2006	137	420	5.52	
Large Part	5,15,2000	137	TLV	0.02	
Laminator	8/15/2006	138	640	8.52	

Large Part					
Laminator	8/15/2006	139	1000	14.10	
Large Part					
Laminator	8/15/2006	140	1200	19.81	
Area C	8/16/2006	141	120	1.44	
Gelcoat					
Assistant	8/16/2006	142	130	2.02	
Tooling	8/16/2006	143	56	1.00	
Tooling	8/16/2006	144	280	3.66	17460
Tooling	8/16/2006	145	500	6.58	
Infusion	8/16/2006	146	890	11.62	
Area E	8/16/2006	147	570	6.86	
Gelcoat	8/16/2006	148	1200	17.55	
Small Parts					
Laminator	8/16/2006	149	630	9.92	
Area A	8/16/2006	150	770	9.70	
Area D	8/16/2006	151	460	6.84	
Small Parts					
Laminator	8/16/2006	152	730	8.92	1706
Large Part					
Laminator	8/16/2006	153	1400	22.26	
Large Part					
Laminator	8/16/2006	154	1500	23.48	
Gelcoat					
Supervisor	8/16/2006	155	500	7.97	
Large Part					
Laminator	8/16/2006	156	1300	16.66	
Large Part					
Laminator	8/16/2006	157	1600	20.69	
Area B	8/16/2006	158	540	7.23	
Large Part					
Laminator	8/16/2006	159	1000	15.66	
Grinding/Cutting	8/16/2006	160	390	5.07	
Large Part					
Laminator	8/16/2006	161	350	5.18	
Area F	8/16/2006	162	510	6.44	
Area D	8/17/2006	163	420	5.45	
Area G	8/16/2006	164	720	9.18	
Hull Laminator	8/16/2006	165	790	9.89	
Small Tanks	8/16/2006	166	150	2.18	1705
Gelcoat	0/10/2000	100	100	2.10	1700
Supervisor	8/17/2006	167	740	11.37	
Putty and	0/11/2000	107	740	11.57	
Cutting	8/16/2006	168	400	5.87	
Large Part	0/10/2000	100	+00	5.07	
Laminator	8/16/2006	169	2000	26.12	
Grinding/Cutting	8/16/2006	170	470	7.26	1703
Tooling	8/17/2006	170	240	3.52	1703
<u> </u>					
Infusion	8/17/2006	172	600	7.37	
Area A	8/17/2006	173	770	10.04	
Blank	8/16/2006	174	0	0.00	
Area E	8/17/2006	175	580	7.90	

Small Parts					
Laminator	8/17/2006	176	1200	14.96	
Blank	8/16/2006	177	0	0.00	
Blank	8/16/2006	178	0	0.00	
Blank	8/16/2006	179	0	0.00	
Infusion Small			-		
Parts					
Supervisor	8/17/2006	180	550	8.62	1706
Large Part	0,, 2000			0.02	
Laminator	8/17/2006	181	860	11.58	
Large Part	0/11/2000		000		
Laminator	8/17/2006	182	780	12.33	
Large Part	0/11/2000	102	100	12.00	
Laminator	8/17/2006	183	720	9.37	
Grinding/Cutting	8/17/2006	184	220	4.07	17460
Large Part	0/17/2000	104	220	4.07	17400
Laminator	9/17/2006	105	800	44 75	
	8/17/2006 8/17/2006	185	890	11.75	
Grinding/Cutting	8/17/2006	186	250	4.11	
Large Part	0/47/0000	107			
Laminator	8/17/2006	187	790	9.90	
Hull Laminator	8/17/2006	188	1300	20.00	
Area F	8/17/2006	189	560	14.17	
Area B	8/17/2006	190	420	5.61	
Hull Laminator	8/17/2006	191	1200	16.08	
Tooling	8/17/2006	192	50	0.76	
Area G	8/17/2006	193	530	7.06	
Gelcoat					
Assistant	8/17/2006	194	340	5.11	
Grinding/Cutting	8/17/2006	195	350	4.57	1705
Small Parts					
Laminator	8/17/2006	196	1100	16.47	
Large Part					
Laminator	8/17/2006	197	590	7.73	
Hull Laminator	8/17/2006	198	1400	18.83	
Large Part	0,11,2000				
Laminator	8/17/2006	199	930	11.79	
Gelcoat	8/17/2006	200	730	10.92	
Area C	8/17/2006	200	120	1.59	
Small Parts	0/17/2000	201	120	1.55	
Laminator	8/18/2006	202	480	10.08	1705
Infusion Small	0/10/2000	202	400	10.00	1705
Parts					
Supervisor	9/19/2006	202	360	E	17460
	8/18/2006	203	<u> </u>	5.51 6.20	1/400
Area D	8/18/2006	204	400	0.20	
Small Parts	0/40/0000	205	000	44.07	
Laminator	8/18/2006	205	930	14.87	
Blank	8/17/2006	206	0	0.00	
Blank	8/17/2006	207	0	0.00	
Blank	8/17/2006	208	0	0.00	
Blank	8/17/2006	209	0	0.00	
Tooling	8/17/2006	210	180	2.30	1706
Gelcoat	8/18/2006	211	870	14.04	

Gelcoat					
Supervisor	8/18/2006	212	730	11.14	
Tooling	8/18/2006	213	320	4.26	
Area E	8/18/2006	214	580	7.09	
Tooling	8/18/2006	215	110	1.70	
Tooling	8/18/2006	216	370	4.83	1704
Gelcoat					
Assistant	8/18/2006	217	430	6.67	
Area C	8/18/2006	218	170	2.08	
Area A	8/18/2006	219	690	8.27	
Infusion	8/18/2006	220	430	5.37	
Grinding/Cutting	8/18/2006	221	370	4.67	1703
Hull Laminator	8/18/2006	222	920	11.75	
Hull Laminator	8/18/2006	223	1200	27.47	
Large Part					
Laminator	8/18/2006	224	1200	15.65	
Area G	8/18/2006	225	410	6.97	
Hull Laminator	8/18/2006	226	820	10.62	
Grinding/Cutting	8/18/2006	227	380	5.72	1705
Large Part					
Laminator	8/18/2006	228	1100	13.67	
Large Part					
Laminator	8/18/2006	229	900	11.66	
Large Part					
Laminator	8/18/2006	230	900	14.54	
Area B	8/18/2006	231	640	7.12	
Large Part					
Laminator	8/18/2006	232	950	12.28	
Blank	8/18/2006	233	0	0.00	
Large Part					
Laminator	8/18/2006	234	770	10.17	
Blank	8/18/2006	235	0	0.00	
Blank	8/18/2006	236	0	0.00	
Area F	8/18/2006	237	570	7.45	
Large Part					
Laminator	8/18/2006	238	1000	15.56	
Putty and					
Cutting	8/18/2006	239	410	7.10	
Blank	8/18/2006	240	0	0.00	

#### **APPENDIX 2**

