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EXTENT OF EXPOSURE TO STYRENE IN THE REINFORCED PLASTIC BOAT MAKING INDUSTRY

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ABSTRACT

Industrial hygiene surveys were conducted in seven fiberglass reinforced plastic boat fabrication plants. This study was designed to quantitate worker exposure patterns to styrene monomer. Exposure to acetone was also measured. There were 464 personal air samples collected in all (results of 96 of these are in excess of the OSHA eight-hour time weighted average standard of 100 parts per million). Statistical analyses were conducted to assess the comparability of certain job categories among the seven plants and within each plant.

Results show that there are differences in exposure among the job categories which may be indicative of resin use patterns. Also, plants with similar ventilation efficiency (as indicated by overall plant styrene levels) showed job category exposure similarities interplant. Dilution ventilation is indicated as being an adequate control measure in some plants. Control technology discussion proposes that in conjunction with general ventilation, the use of local ventilation, styrene-suppressed resins and work practice guidelines can be effective control methods in those plants with over-exposure problems.

POTENTIAL EXPOSURES

Exposure to styrene is directly related to the use of thermoset polyester resins. The polyester resin system used in the FRP boat industry is a mixture of styrene monomer, glycols (propylene glycol or diethylene glycol), saturated acid (phthalic anhydride or isophthalic anhydride), maleic anhydride and inhibitors. The handling of resins after manufacture does not involve exposure to these chemicals other than at trace levels, since they are substantially converted to polyester (1). The styrene content in the resin is approximately forty percent (by weight) (1, 2). It is both a reactant and a diluting solvent. During manual spray-up and lay-up operations, ten to fifteen percent of the styrene can evaporate into the work place air (1, 3). The remainder is consumed in the chemical reaction. The hardening system used may contain a cobalt salt (cobalt haphthenate) as an initiator and a hydroperoxide (methylethylketone peroxide (MEKO) or benzoyl peroxide) as a catalyst (1, 2). An attempt was made to determine exposure levels to MEKO. The analytical results were inconclusive, and the significance of exposure to this substance was not determined. Acetone is the only other compound likely to be present in large concentrations in the vapor phase. Its copious use as a solvent for cleaning laminating tools, spraying equipment and workers' hands warranted documentation of exposure levels. Its high vapor pressure (226.3 mm Hg @ 25°C) causes it to readily evaporate into ambient air from open containers. The presence of fiberglass dust was virtually nonexistant in the laminating areas and therefore was not quantitated.

CHEMICAL AND PHYSICAL PROPERTIES

Styrene (C6H5CH - CH_2) is a volatile liquid with an odor threshold reported to be less than one part per million (PPM) (4, 5). It is soluble in many organic solvents and its solubility in water is about 3.1 mg/ml. Some properties of styrene are given in Table I (7-10). Monomeric styrene production peaked at 7.2 billion pounds in 1979 (11). Approximately 500 million pounds of this were used in the production of polyester resins (12).

Acetone (CH3COCH3) is a colorless, highly volatile, flammable liquid with a burning taste and aromatic odor. It is the simplest but most commercially important ketone. Important properties of acetone are presented in Table II (13, 14).

TABLE I

PROPERTIES OF STYRENE

Synonymns	Cinnamene, cinnamol, cinnamenol, vinyl benzene, phenylethylene, phenethylene, stryol
Molecular formula	C6H 5CH=CH2
Formula Weight	104.1
Boiling Point (760 mm Hg)	145 C (292.4 F)
Melting point	-30.6 C (-23.1 F)
Vapor density	3.6 (air = 1)
Density	0.9021 g/cu cm (25 C)
Solubility	0.31 g/100 ml water at 25 C; soluble in ethyl ether, benzene, heptane, ethanol, acetone
Flammable (explosive) limits	1.5 to 6.7% by volume in air
Flash Point	24-98 F 31 C (88F) Tag closed cup 37 C (98F) Tag open cup
Fire Point	99F
Autoignition temperature	490 C (914 F)
Critical temperature	362 C (684 F)
Critical pressure	37.8 atm
Vapor pressure	see below

Vapor pressure:

Temp F	Temp C	mm Hg
50	10	2.34
68	20	4.50
86	30	8.21
104	40	14.30

Concentration in saturated air	5,700 ppm (15 C)
Conversion factors, (25 C, 760 mm Hg)	1 ppm = 4.26 mg/cu m 1 mg/cu m = .235 ppm

TABLE 2

PROPERTIES OF ACETONE

Synonyms	2-Propanone, dimethylketal, dimethyl ketone, beta-ketoacopane, methyl ketone, pyroacetic ether, pyroacetic spirit
Molecular formula	C3H60 CH_3 C=0 CH_3
Formula Weight	48.08
Boiling point	56.1 C (133 F)
Melting Point	-95.6 C (-140 F)
Density	0.7911 gm/cu m (20 C)
Flammable limits	2.15 to 13% by volume in air
Critical Temperature	188 C (370 F)
Critical pressure	57.1 atm
Vapor pressure	226.3 mm Hg at 25 C
Conversion factors (25C, 760 mm Hg)	1 ppm - 24.0 mg/cu m 1 mg/cu m - 0.417 ppm

PROCESS DESCRIPTION

The method used in manufacturing FRP boats is called contact molding and is a zero pressure molding method in which only one side contacts the mold surface. There are two principal techniques, hand lay-up and spray-up. Materials used in contact molding are polyester resin, gel coat (pigmented resin), split-strand glass fiber roving which is used for chopping in the spray-up operation, chopped-strand mat (made by chopping split-strand glass fibers, mixing with a binder and pressing into a mat) which is used in hand lay-up, and woven roving (a heavy cloth made from strand roving in a square weave pattern) whose greatest use is to provide a structural backbone in the hand lay-up operation.

Hand lay-up: Mat or mat-and-woven roving layers are wetted out with resin and manually laid-up on the gel coated mold. Resin is applied to the mold, using a brush on smaller pieces or an airless sprayer system on larger ones, and mat is laid on top of the resin. The preferred practice uses alternate layers of mat and woven roving.

Spray-up: A mechanism attached to the sprayer system used for wet out in hand-lay-up allows for chopping split-strand roving and "throwing" the chopped fibers onto the mold surface while at the same time spraying polyester resin. This tool is called a chopper-gun. In this manner a structure can be built up layer by layer in a mat-like style. Following deposition of fiber and resin, it is necessary to roll-out the structure (compacting the resin and glass) with a special rolling wheel. Spray-up is often used in combination with hand lay-up techniques.

The boat making process begins with polishing the surface of an FRP mold having the converse shape of the part being made, and the application of a releasing agent (usually a wax) in preparation for the initial layer of gel coat.

The pigments in gel coat are used for color, since this layer will appear as the outside surface of the boat, and for resistance to ultraviolet deterioration. The name gel coat stems from the fact that when the coat reaches a gel state, the remainder of the laminate is applied.

Methods of contact molding, or lamination, varied between companies. Plants 2, 5, and 6 used only hand lay-up techniques. That is, the parts were constructed of alternating layers of chopped strand mat and woven roving, with each layer being wetted with resin. Plant 4 used spray-up to manufacture some of the smaller pieces but the process was extensively hand lay-up. Plants 1, 3 and 7 used a combination of hand lay-up and spray-up. These parts were constructed of alternating layers of chopped fiberglass from a chopper gun and woven roving. The chopped glass layer is, of course simultaneously mixed with resin as it is applied. The woven roving layer requires wet-out which is done using only the spraying mode of the chopper-gun. The chopped layer requires roll-out to compact the fiberglass and resin. The other layers, whether chopped-strand mat or woven roving, are usually squeegeed to insure saturation and to remove excess resin. A reason given, aside from any economic considerations, for choosing chopped-strand mat over spray-up, was the layer uniformity that this technique offers, resulting in uniform strength and flexibility of the piece.

Following lamination, structural support is necessary on certain parts. Plywood and end grain balsa wood are two materials used for this support. The wood is positioned and then overlayed with fiberglass and resin to secure it in place. Chopped fiberglass, either from a gun or in mat form is generally used for this.

The following discussion addresses the factors affecting exposures in the lamination jobs.

Gel coat is applied in a ventilated booth using an airless sprayer system, except in the case of stationary molds which are coated in place. Generally only large hull and deck molds are stationary and at plants using this system the gel coating was performed on an off-shift so that exposure was experienced by the gel coater only. Plants 5 and 6 had this arrangement. In all plants surveyed, the gel coaters were the best protected from exposure. In addition to booth ventilation, protective clothing was commonplace on the gel coater. Coveralls, hoods and respirators were almost always worn during the gel coating operation.

The rest of the jobs are performed in a large area in the plant designated as the lamination area. Invisible boundaries usually segregate one section from the other (i.e., the hull lamination from deck lamination), with the entire environment being controlled by a central dilution ventilation system consisting of exhaust fans and tempered make-up air. The exception is Plant 6 which used natural ventilation exclusively. In some instances, the ventilation system was aided by the use of circular fans which developed directional air flow patterns. Aside from the effectiveness of the particular ventilation system, exposure potential is affected by the amount of resin used, the size and configuration of the part, and the protective equipment used.

The hull has the largest surface area over which catalyzed resin is applied resulting in greater exposure potential for these workers because of styrene evaporation. Since the hull has a somewhat concave shape its positioning affects exposure. On the mobile mold frame, the hull is turned on a longitudinal axis to access both halves for lamination. Laminating on this type mold is somewhat confining; however, if proper air movement is present styrene vapor does not accumulate. If a stationary hull mold is used, it is always in an upright position and the worker must perform his job inside this mold. Because styrene is more dense than air it will accumulate when the mold is in this position and exposure potential is greater.

Those working in deck and other large parts (flying bridges and aft decks) lamination also use a great deal of resin. Surface area of these parts is not as great but is proportional to the hull size. The frame generally holds these pieces flat or upright and there is no configuration type problem. Directional fans are used to limit accumulation of vapor.

In small parts lamination, the number of pieces being laid-up will affect exposure potential. The molds are laid on a table top instead of being mounted on a frame. There are no configuration problems with these pieces.

Acetone exposure in all instances will depend on the frequency of use as well as location of dispensing cans.

In the lamination jobs the protective equipment provided included half-face cartridge respirators and in some plants aprons and gloves. In plants 1, 3, 4, and 6, no formal policy existed governing respirator (or other protective equipment) use. The other plants had programs with varying enforcement policies.

i) local ventilation;

ii) styrene suppressed resins;

iii) work practice guidelines.

<u>Local Ventilation</u>

Localized ventilation in general has the advantage of being more effective in removal of contaminants from the workplace. In operations where pieces are fabricated at fixed stations local exhaust in the form of hoods or booths is practical. However, the shapes and sizes of the pieces needing this type of control (hull molds in particular) have not lended themselves practically to application. An added factor is the mobile nature of most processes. The mold is moved from preparation, to gelcoat, to lay-up and then to a removal station.

There is one source of over-exposure that may be fitted with local ventilation. That is the stationary hull mold, as used in Plants 2, 5 and 6. In fact, since the survey was conducted at Plant 5, they have been experimenting with a local system for this purpose. The design includes an exhaust hood over the aft portion with fixed fans at the bow. The effect is a push-pull system sweeping air from bow to stern, while workers proceed to laminate counter current to airflow.

The major drawback to local ventilation is the retro-fitting into existing operations. The unique problems from plant to plant and the variety of operations and sizes of parts creates the difficulties inherent in the non-general solution to the problem.

<u>Styrene-suppressed Resins</u>

Recently the introduction of environmental resins, called styrene-suppressed resins, has been cause for optimism. The manufacturers claim less styrene evolution from these than from their general purpose resins. The mechanism which produces this effect is an additive which migrates to the surface of the resin after catalyst is added and forms a barrier preventing the evaporation of styrene (1).

Schumacher et al conducted laboratory and in-plant testing of two styrene-suppressed resins. In the laboratory tests one resin showed a reduction of about 30 percent of styrene in the vapor phase. The plant test showed no difference in employee exposure to styrene using another type of styrene-suppressed resin (49). Plant 5 has also reported testing of these types of resins subsequent to the NIOSH survey (50). Some results of this in plant testing have indicated reductions in styrene exposure of nearly fifty percent.

As with many innovations there are problems to be solved in regard to the use of styrene-supressed resins. Primarily there may be differences in the mechanical properties of finished plastic, such as reduced interlaminar adhesion (1,50). Most agree that the development of a satisfactory resin of this type is a long way off.

Work Practice Guidelines

If properly conceived and implemented work practices can be very effective in exposure control, it is an opportunity for the workers to become directly involved. There are always choices to be made when performing job tasks, and education in the right choice at the right time can have an effect. Examples are things like spraying resin away from fellow workers and toward ventilation when possible; being certain that solvent containers are closed when appropriate; and minimizing overspray on to floors and walls. Other advantages to work practices are better housekeeping and more efficient operations.

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