Emis

## I. Introduction

The EPA's Air Management Technology Branch (AMTB), Research Triangle Park, North Carolina, is responsible for maintaining the document Compilation of Air Pollutant Emission Factors, AP-42. This document is supplemented or updated periodically to present the most up-to-date process emissions information. Subsequent to receiving inquiries about VOC emissions from processes using polyester resins in the fabrication of plastics products, AMTB became aware of the report of a study performed in California to develop VOC emission factors for these processes. Pacific Environmental Services, Inc. (PES) was contracted to review the available information on this industry and prepare a new AP-42 section reporting process emission factors (EPA Contract No. 68-02-3887, Assignment 58, February 1987, and Contract No. 68-02-4393, Assignment 10, October 1987). This report documents the source of the emission factors that are presented in Section 4.12, Polyester Resin Plastics Product Fabrication.

## II. Fiberglass Fabrication Processes and Emissions

Products made of fiber-reinforced plastics are becoming increasingly prevalent due to their favorable strength-to-weight characteristics, corrosion resistance, and ease of molding into a great variety of shapes and sizes. While generally referred to as "fiberglass," some of these plastics products do not contain fibers (but instead some sort of powdered or granulated fillers) and many contain fibers other than glass (carbon and aramid fibers are growing in use). The manufacture of all of these types of products, however, utilizes unsaturated polyester resin, which contains a vinyl-type monomer ingredient (almost always styrene), and so all of them can be considered under a single product category. For convenience, the term "fiberglass" can be used to refer to all types of polyester resin plastics products. When these liquid resins are mixed with a polymerization initiator, or catalyst (methyl ethyl ketone peroxide and benzoyl peroxide are common), a curing process begins which solidifies the resin/fiber composite. During mixing, application and curing, while the resin is in a liquid state, styrene evaporates from the surface and constitutes a source of volatile organic compound (VOC) emissions. The VOC emissions from some resins (vapor-suppressed resins) are reduced due to a lowered styrene content or through the addition of vapor suppressing additives. While many facilities rely completely on manual production steps, others are highly automated, assembly line type operations. The principal fabrication processes include hand layup, spray layup (or sprayup), continuous lamination, pultrusion, filament winding, and various closed molding operations. These processes are briefly described below.

Hand layup, as the term implies, is a process in which layers of glass cloth wetted with laminating resin are applied by hand to an open mold. Layers are smoothed out and compressed as the product thickness is built up. Often, the mold is first sprayed with gel coat, a clear or colored resin that forms the smooth outer surface of many parts.

Sprayup is a semi-manual process in which resin and fiber are applied to an open mold with a spray gun (the gun that cuts glass fiber, or roving, and applies it to the part is known as a "chopper gun"). As in hand layup, gel coat is often applied as one step in the fabrication process.

Continuous lamination is carried out using a conveyor system, where resin and cut fibers are applied onto a moving carrier film (usually to form flat or corrugated panels). Heated curing and cutting are performed automatically as the laminate progresses along the conveyor.

Pultrusion, "extrusion by pulling," is a process in which resin-saturated fibers are pulled through a heated machined steel die to form a constant cross-section, and then cut off as desired.

Filament winding is the process of applying a band of resin impregnated fibers to a rotating mandrel surface in a precise geometric pattern to form cylindrically shaped parts.

Closed molding operations utilize a completely enclosed mold to fully define the contours of a part. Synthetic marble for sinks, countertops, and the like is often produced by a "semi-closed" molding process, using a resin mix containing fillers, but no reinforcing fibers. A translucent gel coat is sprayed onto the mold or the cast product to produce a smooth, glossy surface that simulates natural marble.

## III. Sources of Process and Emission Information

Industry information was collected through a literature search and through telephone contacts with industry and control agency experts. The following subsections summarize the principal references and contacts consulted.

### A. Literature Survey

As mentioned in the Introduction, a study was performed in California in 1981, to survey the industry and develop VOC emission factors for the key fabrication operations. This study was sponsored by the California Air Resources Board (CARB), and carried out by Science Applications, Inc. (SAI). In this study, SAI utilized both previous emission measurement studies and its own test results from three fabrication plants. The final report on the study, Control Techniques for Organic Gas Emissions from Fiberglass Impregnation and Fabrication Processes,[1] provided useful process information and was the only significant source of emission factors in the literature survey. Section IV of this documentation report summarizes the origin of and rationale for the emission factors presented in the 1981 CARB/SAI report. It should be noted at this point that most of these factors were not used in AP-42 Section 4.12 because they were superceded by suggested factors received in industry comments on the draft section sent out for external review. (See Section VI for a discussion of these comments and the rationale for the emission factors selected for the AP-42 section).

Other good sources of process information were recent issues of Modern Plastics and the current edition of Modern Plastics Encyclopedia.[2] The process figures (of continuous lamination and filament winding) used in the AP-42 section were found in two books.[3,4]

A search through the microfiche subject index at EPA's library in Research Triangle Park (key words: Fiberglass, Plastic, Polystyrene and Styrene) showed that most reports were sponsored by the National Institute for Occupational Safety and Health (NIOSH), and dealt with the occupational health hazards of styrene emissions (generally only styrene concentrations in the workspaces were reported). Two of the reports located at the library provided some process information.[5,6]

An article in Modern Plastics dealt with styrene emissions from certain low-styrene-emission (LSE) resins, recently introduced by USS Chemicals.[7] These resins contain 36 percent styrene content, versus the approximately 44 percent styrene in conventional open-mold resins. The article stated that tests showed the LSE resins to manifest a 60 to 70 percent decrease in emission levels versus conventional resins. However, emission results were presented only in terms of personnel exposure concentrations (ppm styrene), and not in terms useful for emission factor development.

## B. Telephone Contacts

1. Joseph Pantalone, CARB, Sacramento, CA. Mr. Pantalone was the project officer on the 1981 CARB study conducted by SAI. He felt that the study and report were sound, and was unaware of any more recent emissions studies for this industry. He suggested that the South Coast and Bay Area Air Quality Managment Districts (SCAQMD and BAAQMD) in California be contacted for possible further information.

2. Joe Studenberg, Aristech Chemical Corporation, Polyester Unit (formerly USS Chemicals), Linden, NJ. Mr. Studenberg answered some basic questions about processes and LSE resins. He is active on behalf

of the Society of the Plastics Industry (SPI) in reviewing the proposed rule of the SCAQMD related to control of VOC emissions from polyester resin operations. He sent a summary of proposed Rule 1162 and industry background information assembled by the SCAQMD. This material did not contain any specific emission factor information, but contained useful information about processes and controls.

3. Moustafa Elsherif, SCAQMD, El Monte, CA. Mr. Elsherif is the Senior Air Quality Engineer on the development of Rule 1162 governing emissions from polyester resin operations. He commented that in general the factors presented in the 1981 CARB/SAI study are higher than those assumed by SCAQMD. While they do not have any recent test data to substantiate their assumptions, the District might do some testing soon. With regard to specific factors, he felt that the CARB/SAI report factors for sprayup are probably too low, and the gel coat factors are too high. He further pointed out that the filament winding process does not use gel coat.

## IV. Emission Factor Investigation in 1982 CARB Study

As mentioned in Section III, SAI, Inc. investigated several previous emission measurement efforts in its study for CARB, and also performed source tests at three fabrication facilities to supplement this information. This section summarizes the emission factor data collected in this study.

### A. Previous Emission Estimates

SAI identified five sponsors of previous investigations into styrene losses from polyester resins. As they point out in the CARB report (Section 5.1): "These results should be interpreted with great care. Experimental conditions, resin types, test procedures, collection methods, and analytical techniques were different in each case. Important data, such as the styrene content of the resin used, were often missing." This statement highlights the lack of uniformity in these studies and the hazard of applying the results uncritically to situations in which conditions may be quite different. The five test efforts previous to the CARB study were as follows.

1. Dade County, Florida. These studies, reported in 1968, involved a hand layup procedure performed in the lab (vapor-suppressed resin) and a set of tests at a fabrication plant. The resin styrene percentage in the lab tests was not reported, but could be inferred with only small uncertainty from the brand name of the resin. Only one field test, on a gel coat spray gun operation, was considered complete enough to use.

2. Bay Area AQMD, California. Reports on emission tests at six fabrication facilities between 1974 and 1978 were reviewed. As SAI points out, "the purpose of these tests was to verify compliance with hourly and daily emission standards, not to develop emission factors." For most tests, the styrene percentage in the resin had to be assumed. All operations in these tests involved spray gun and/or chopper gun application of resin and gel coat.

3. Ashland Chemical Company, Columbus, Ohio. Ashland Chemical performed lab tests (undated) to measure weight loss from various resin/glass formulations, including laminating, casting, and filament winding resins. Several of the resins tested contained vapor suppressants. The CARB report cautions, "As with the other experiments reported here, these data should be interpreted with care. Information on experimental conditions is inadequate to permit repetition, and the extent to which they simulate actual operations is unknown."

4. Shasta County, California. In these lab tests, performed in 1978, the weight loss due to organic vapor emissions was measured for glass plates covered with various layers of gel coat, resin, and glass fibers. The styrene percentage in the resins was assumed by SAI with a fairly high degree of confidence.

5. Kingston Polytechnic Studies, England. These were rather thorough lab tests in which the styrene losses from hand layup laminates were measured gravimetrically. The investigators controlled and noted the ambient temperature, wind speed, amount of hand rolling,

glass reinforcement type, and styrene and wax (suppressant) concentrations.

Table 1, adapted from CARB/SAI report Table 5.1-1, shows the emission factors calculated by SAI from these studies. Note that the studies cover only the hand layup and sprayup processes. Emission factor estimates for the remaining fabrication processes are derived from source tests performed by SAI during the course of the CARB/SAI study.

## B. SAI Source Tests

To complement previous studies, which covered only the manual hand layup and sprayup processes, SAI undertook a field sampling program at three fabrication facilities.

Facility 1 - Continuous lamination plant, 3/18-19/81. This plant makes fiberglass panels on a production assembly line consisting of an impregnation table, a gas-fired curing oven, and a product cutting zone. Emissions from the impregnation table are ducted to an incinerator control device, and an ESP removes particulate matter from air collected at several points in the production line. Several ventilation exhaust ducts were sampled, including the incinerator exhaust, to produce both uncontrolled and controlled emission factors. Tests were run during the use of two different resins, one containing 40 percent styrene and the other containing a mix of 35 percent styrene and 5 percent methyl methacrylate (MMA).

Styrene sampling was performed using a Foxboro Instruments Model 128 OVA organic vapor analyzer in combination with charcoal tube traps. An HP Model 5730A gas chromatograph was used to analyze the contents of the charcoal traps. Individual emission factors were added together to produce ranges for both uncontrolled and controlled situations. It should be noted that SAI considered results from both the straight styrene resin and the styrene/MMA blend resin when selecting the final emission factor range for this process. The uncontrolled emission

## TABLE 1. EMISSION FACTORS ESTIMATED BY SAI FROM PREVIOUS STYRENE LOSS STUDIES

| Test Source[a] | Process[b] | Resin Type[c] | Test Location[d] | Emission Factor, percent[e] |
|---|---|---|---|---|
| 3 | H | L | L | 8.5 - 10.5 |
| 5 | H | L | L | 15.6 - 35.4 |
| 4 | H | L | L | 8 |
| 1 | H | L* | L | 5.6 - 6.3 |
| 3 | H | L* | L | 1.9 - 2.6 |
| 5 | H | L* | L | 13.6 - 19.6 |
| 4 | H | G | L | 47 |
| 3 | H | FW | L | 71 - 82 |
| 3 | H | FW* | L | 16 |
| 4 | H | FR | L | 6.6 |
| 3 | H | C | L | 3.8 - 4.1 |
| 3 | H | C* | L | 1.0 - 1.4 |
| 2 | S | L | F | 8 - 18 |
| 2 | S | L | F | 16 - 25 |
| 2 | S | L | F | 13 |
| 2 | S | G | F | 26 - 28 |
| 2 | S | G | F | 7 - 12[f] |
| 2 | S | G | F | 24 - 38 |
| 2 | C | L | F | 27 |
| 2 | C | L | F | >12[g] |

[a] Test source: 1 = Dade County, 2 = Bay Area, 3 = Ashland Chemical, 4 = Shasta County, 5 = Kingston Polytechnic.

[b] Process: H = hand layup, S = sprayup, C = chopper gun.

[c] Resin type: L = laminating, G = gel coat, FW = filament winding, FR = fire retardant, C = casting. Asterisk indicates a vapor-suppressing type resin.

[d] Test location: L = laboratory, F = field.

[e] Emission factor = 100 x (styrene emissions/styrene input).

[f] These emission factors are for laminating resin and gel coat combined.

[g] Exhaust air in this test was diluted to an unknown extent, so this factor represents a lower bound.

factor is 0.059 to 0.13 (styrene emitted/ styrene input), while the controlled (incineration) emission factor is 0.0092 to 0.028.

Facility 2 - Tank manufacturing plant (sprayup), March 31 and April 15, 1981. At this plant, tanks are spray coated with a resin/ glass fiber mix in a steel shed. The ventilation exhaust air from this shed was collected and analyzed using the same type of test apparatus used for facility 1. This plant has no emission controls. The emission factor calculated for this process is 0.092 to 0.13.

Facility 3 - Synthetic marble plant, 7/7-8/81. This plant manufactures bathroom sinks and related products using partially closed molding and hand spraying of gel coat. The plant used both regular and vapor-suppressed casting resins during the testing. The same sampling and analytical methods were used to test potential emission points (all uncontrolled) as were used for the first two plants. Since emissions from casting resin and gel coat spraying were impossible to distinguish, the casting resin factors may include some emissions from gel coat and therefore may be somewhat too high.

Emission factors were determined for both nonvapor-suppressed (NVS) and vapor-suppressed (VS) casting resins. The NVS emission factor is 0.026 to 0.031, and the VS factor is 0.014 to 0.030.

## V. Description of CARB/SAI Emission Factors

Table 2 is a reproduction of CARB/SAI report Table 5.4-1, showing SAI's recommended VOC emission factors for both NVS and VS laminating (and casting) resin and gel coat. These factors are for the most part presented as ranges rather than single values. This is made necessary by the variability in the rather limited amount of data that was available in deriving the factors. The rationale for this selection of emission factors is presented in the CARB/SAI report (Section 5.4) and

### TABLE 2. RECOMMENDED MONOMER-BASED EMISSION FACTORS FOR POLYESTER RESIN/FIBERGLASS OPERATIONS[a] (EF = 100 x (Monomer emitted/Monomer input))

| Process | Resin | | Gel Coat | |
|---|---|---|---|---|
| | NVS | VS | NVS | VS |
| Hand layup only | 16 - 35 | 8 - 25 | 47 | 24 - 33 |
| Spray layup only | 9 - 13 | 5 - 9 | 26 - 35 | 13 - 25 |
| Hand and spray | 11 - 19 | 6 - 13 | 31 - 38 | 16 - 27 |
| Marble casting | 1 - 3 | 1 - 3 | 26 - 35 | 13 - 25 |
| Continuous lamination | 6 - 13[b] | | NA[c] | |
| Pultrusion | 6 - 13 | | NA[c] | |
| Filament winding | 6 - 13 | 3 - 9 | 26 - 35 | 13 - 25 |
| Closed molding | 1 - 3 | 1 - 3 | NA[c] | |

[a] Table 5.4-1 in CARB/SAI report, Reference 1. For use in AP-42, these factors have been modified based on review comments; see the next section of this report.

[b] Emission factor is 1 - 3 when incinerator is used.

[c] NA = Not applicable; gel coat normally not used for these processes.

NVS = nonvapor-suppressed (conventional) formula.

VS = vapor-suppressed formula.

summarized below. Note again that these factors from the CARB/SAI report have generally not been used unchanged in AP-42 Section 4.12 (see Section VI herein).

### Hand layup

The laboratory test data from the Kingston Polytechnic studies

are the best documented and most representative of actual process conditions, so they were used for the factors for laminating resins. For gel coat, the only available data were those from the Shasta County lab tests, so these were used to derive the factors for gel coat.

### Sprayup

SAI believed that its test measurements at Facility 2 yielded more reliable data than was previously reported. Thus, the range calculated for Facility 2 was used for laminating resin. For gel coat spraying, the tests at Facility 3 yielded an upper bound of 35 percent. This was combined with a lower limit derived from Bay Area AQMD field tests.

### Hand layup and sprayup combined

Since many plants use a combination of hand layup and sprayup operations, SAI calculated composite emission factors for resin and gel coat assuming 25 percent hand layup and 75 percent sprayup. Since this was an arbitrary calculation, and will be different for each situation, these composite factors have not been included in AP-42.

### Marble casting

For casting resin, the emission factor range from the tests at Facility 3 was used. The factors selected for gel coat application at marble plants are the same as for gel coat spraying in general (sprayup process).

### Continuous lamination and pultrusion

The emission factors calculated for Facility 1 were applied for continuous lamination. Since incineration is not widely used, and generally treats only part of the total emissions at a facility, the controlled emission factor referred to in the table footnote has not been included in AP-42. Since continuous lamination and pultrusion are somewhat similar processes, and specific test data for pultrusion were unavailable, SAI assigned the same emission factor ranges to pultrusion.

Emission factors for gel coat were not assigned because gel coat is not normally used in these two operations.

### Filament winding

While laboratory tests with filament winding resins have been performed (Ashland Chemical), no actual process data from this operation are available. Therefore, SAI assigned the emission factors for the most similar process, continuous lamination, to filament winding.

### Closed molding processes

As with filament winding, no specific emission test data were available for bag molding, matched metal molding, and other closed molding operations. Therefore, the emission factors for marble casting (a semi-closed process) were applied to closed molding. Emission factors for gel coat were not assigned because gel coat is not normally used in these operations.

## VI. Selection of Final Emission Factors

On August 13, 1987, a draft of the new AP-42 Section 4.12 was sent to several technical experts at State and local agencies, an environmental group, the ASTM, and a resin producer, for their comments on the draft emission factors. The draft factors reflected those presented in the 1981 CARB/SAI report discussed in Sectons IV and V of this documentation report. The resin producer (Aristech) circulated the draft to the Polyester Resin Technical Committee of the Society for the Plastics Industry (SPI), and as a result comments were collected from several other companies, including Ashland Chemicals, Freeman Chemicals, Interplastics, Koppers Company, Norac, Owens Corning Fiberglas, Reichhold Chemicals, and Silmar. The comments received addressed several areas of technical content in the descriptive text, as well as the emission factors themselves.

Specific comments on the factors were received from the SPI Committee and two other commenters.[8-10] In general, several factors were felt to be too high. Alternate emission factors were suggested in Aristech's letter incorporating comments of the SPI Committee. The following table was included in this comment letter.

TABLE FROM ARISTECH COMMENT LETTER

| | Emission Factors | | | |
|---|---|---|---|---|
| | SAI Resin NVS | Ashland Resin NVS | SAI Gel Coat NVS | Ashland Gel Coat NVS |
| Hand lay up | 16-35 | 5-10[1] | 47 | 26-35[5] |
| Spray lay up | 9-13 | 9-13 | 26-35 | 26-35 |
| Continuous lamination | 6-13 | 2-6[2] | | |
| Pultrusion | 6-13 | 2-6[3] | | |
| Filament Winding | 6-13 | 5-10[4] | | |
| Marble Casting | 1-3 | 1-3 | | |

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1. Hand lay up does not result in more emissions than spray lay up. This was shown to be a more accurate range in our testing (paper presented at the 34th Annual SPI Conference, 1979).
2. SAI number for continuous lamination based on a styrene/MMA blend. For most applications 2-6 would be more typical.
3. Pultrusion is a semi closed molding operation and emissions are lower than 6-13%.
4. Losses in filament winding are similar to hand lay up.
5. Gel coat emissions for hand lay up should be the same as for spray lay up. Emissions of 26-35% seem reasonable.

The principal change to the factors suggested in this letter involved the relationship of the hand layup and sprayup emission factors. Another commenter, Florida's Hillsborough County, also commented that the spray layup process results in more emissions than does hand layup. These comments, as well as others involving the remaining factors, were taken into account in developing a revised emission factor Table 4.12-2 for the AP-42 section. This revised table is presented below, along with notes describing the rationale for changes made in the table as a result of external review comments. (Only the factors for conventional, or nonvapor-suppressed (NVS), resins are shown.)

TABLE 3. REVISED EMISSION FACTORS FOR AP-42 TABLE 4.12-2

| Process | Resin (NVS) | Gel Coat |
|---|---|---|
| Hand layup | 5-10[a] | 26-35[b] |
| Spray layup | 9-13 | 26-35 |
| Continuous lamination | 4-7[c] | |
| Pultrusion | 4-7[d] | |
| Filament winding | 5-10[e] | |
| Marble casting | 1-3 | |
| Closed molding | 1-3 | |

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[a] The range suggested in the Aristech letter was accepted. It is recognized, however, that data are sparse and a fairly low level of confidence is associated with this range.

[b] The argument that emissions from gel coat spraying should be similar for both hand and spray layup processes was accepted as reasonable. Since the range for spray layup is based on production measurements, this range is applied to both of these processes.

[c] For a straight styrene resin, the CARB/SAI range for continuous lamination is approximately 6-8 (Table 5.2-04 in Ref. 1). The range suggested in the Aristech letter is 2-6. Taking the center of each range range as the bounds of the final range, a final range of 4-7 was selected.

[d] The range for continuous lamination is assumed to apply to pultrusion.
[e] The suggestion in the Aristech letter that filament winding emissions are similar to emissions from hand layup was accepted.

## VII. References*

1. M.B. Rogozen, Control Techniques for Organic Gas Emissions from Fiberglass Impregnation and Fabrication Processes, Science Applications, Inc., Los Angeles, CA. Prepared for California Air Resources Board (CARB), Sacramento, CA, June 1982.
   NTIS - PB 82-251109

2. Modern Plastics Encyclopedia, 1986-1987, Vol. 63, No. 10A, October 1986.

3. R.N. Shreve and J.A. Brink, Jr., Chemical Process Industries, Fourth Ed., McGraw-Hill, 1977.

4. C.A. Brighton, G. Pritchard and G.A. Skinner, Styrene Polymers: Technology and Environmental Aspects, Applied Science Publishers, Ltd., London, 1979.

5. M.S. Crandall, Extent of Exposure to Styrene in the Reinforced Plastic Boat Making Industry, National Institute for Occupational Safety and Health (NIOSH), Publication No. 82-110, Cincinnati, OH, March 1982.

6. Criteria for a Recommended Standard ... Occupational Exposure to Styrene, National Institute for Occupational Safety and Health (NIOSH), Publication No. 83-119, September 1983.

7. L. Walewski and S. Stockton, "Low-Styrene-Emission Laminating Resins Prove It in the Workplace," Modern Plastics, Vol. 62, No. 8, p. 78-80, August 1985.

8. Written communication with enclosure from R.C. Lepple, Aristech Chemical Corporation, Linden, NJ, to A.A. MacQueen, U.S. Environmental Protection Agency, Research Triangle Park, NC, September 16, 1987. (Cover letter from J.E. Studenberg, Aristech, to A.A. MacQueen, September 16, 1987.)

9. Written communication with attachment from E.G. McCune, North Carolina Department of Natural Resources and Community Development, Raleigh, NC, to A.A. MacQueen, U.S. Environmental Protection Agency, Research Triangle Park, NC, September 1, 1987.

10. Written communication from H.R. Lue, Hillsborough County (Florida) Environmental Protection Commission, Tampa, FL, to A.A. MacQueen, U.S. Environmental Protection Agency, Research Triangle Park, NC, September 16, 1987.

*Note: All of these references have been placed in the Section 4.12, AP-42 files of AMTB, U.S. EPA, Research Triangle Park, NC.

# APPENDIX A

## AP-42 SECTION 4.12: POLYESTER RESIN PLASTICS PRODUCT FABRICATION

## 4.12 POLYESTER RESIN PLASTICS PRODUCT FABRICATION

### 4.12.1 General Description[1-2]

A growing number of products are fabricated from liquid polyester resin reinforced with glass fibers and extended with various inorganic filler materials such as calcium carbonate, talc, mica or small glass spheres. These composite materials are often referred to as fiberglass reinforced plastic (FRP), or simply "fiberglass". The Society Of The Plastics Industry designates these materials as "reinforced plastics/composites" (RP/C). Also, advanced reinforced plastics products are now formulated with fibers other than glass, such as carbon, aramid and aramid/carbon hybrids. In some processes, resin products are fabricated without fibers. One major product using resins with fillers but no reinforcing fibers is the synthetic marble used in manufacturing bathroom countertops, sinks and related items. Other applications of nonreinforced resin plastics include automobile body filler, bowling balls and coatings.

Fiber reinforced plastics products have a wide range of application in industry, transportation, home and recreation. Industrial uses include storage tanks, skylights, electrical equipment, ducting, pipes, machine components, and corrosion resistant structural and process equipment. In transportation, automobile and aircraft applications are increasing rapidly. Home and recreational items include bathroom tubs and showers, boats (building and repair), surfboards and skis, helmets, swimming pools and hot tubs, and a variety of sporting goods.

The thermosetting polyester resins considered here are complex polymers resulting from the cross-linking reaction of a liquid unsaturated polyester with a vinyl type monomer, most often styrene. The unsaturated polyester is formed from the condensation reaction of an unsaturated dibasic acid or anhydride, a saturated dibasic acid or anhydride, and a polyfunctional alcohol. Table 4.12-1 lists the most common compounds used for each component of the polyester "backbone", as well as the principal cross-linking monomers. The chemical reactions that form both the unsaturated polyester and the cross-linked polyester resin are shown in Figure 4.12-1. The emission factors presented here apply to fabrication processes that use the finished liquid resins (as received by fabricators from chemical manufacturers), and not to the chemical processes used to produce these resins. (See Chapter 5, Chemical Process Industry.)

In order to be used in the fabrication of products, the liquid resin must be mixed with a catalyst to initiate polymerization into a solid thermoset. Catalyst concentrations generally range from 1 to 2 percent by original weight of resin; within certain limits, the higher the catalyst concentration, the faster the cross-linking reaction proceeds. Common catalysts are organic peroxides, typically methyl ethyl ketone peroxide or benzoyl peroxide. Resins may contain inhibitors, to avoid self curing during resin storage, and promoters, to allow polymerization to occur at lower temperatures.

TABLE 4.12-1. TYPICAL COMPONENTS OF RESINS

| To Form the Unsaturated Polyester | | |
|---|---|---|
| Unsaturated Acids | Saturated Acids | Polyfunctional Alcohols |
| Maleic anhydride | Phthalic anhydride | Propylene glycol |
| Fumaric acid | Isophthalic acid | Ethylene glycol |
| | Adipic acid | Diethylene glycol |
| | | Dipropylene glycol |
| | | Neopentyl glycol |
| | | Pentaerythritol |

| Cross-linking Agents (Monomers) |
|---|
| Styrene |
| Methyl methacrylate |
| Vinyl toluene |
| Vinyl acetate |
| Diallyl phthalate |
| Acrylamide |
| 2-ethyl hexylacrylate |

The polyester resin/fiberglass industry consists of many small facilities (such as boat repair and small contract firms) and relatively few large firms that consume the major fraction of the total resin. Resin usage at these operations ranges from less than 5,000 kilograms per year to over 3 million kilograms per year.

Reinforced plastics products are fabricated using any of several processes, depending on their size, shape and other desired physical characteristics. The principal processes include hand layup, spray layup (sprayup), continuous lamination, pultrusion, filament winding and various closed molding operations.

Hand layup, using primarily manual techniques combined with open molds, is the simplest of the fabrication processes. Here, the reinforcement is manually fitted to a mold wetted with catalyzed resin mix, after which it is saturated with more resin. The reinforcement is in the form of either a chopped strand mat, a woven fabric or often both. Layers of reinforcement and resin are added to build the desired laminate thickness. Squeegees, brushes and rollers are used to smooth and compact each layer as it is applied. A release agent is usually first applied to the mold to facilitate removal of the composite. This is often a wax, which can be treated with a water soluble barrier coat such as polyvinyl alcohol to promote paint adhesion on parts that are to be painted. In many operations,

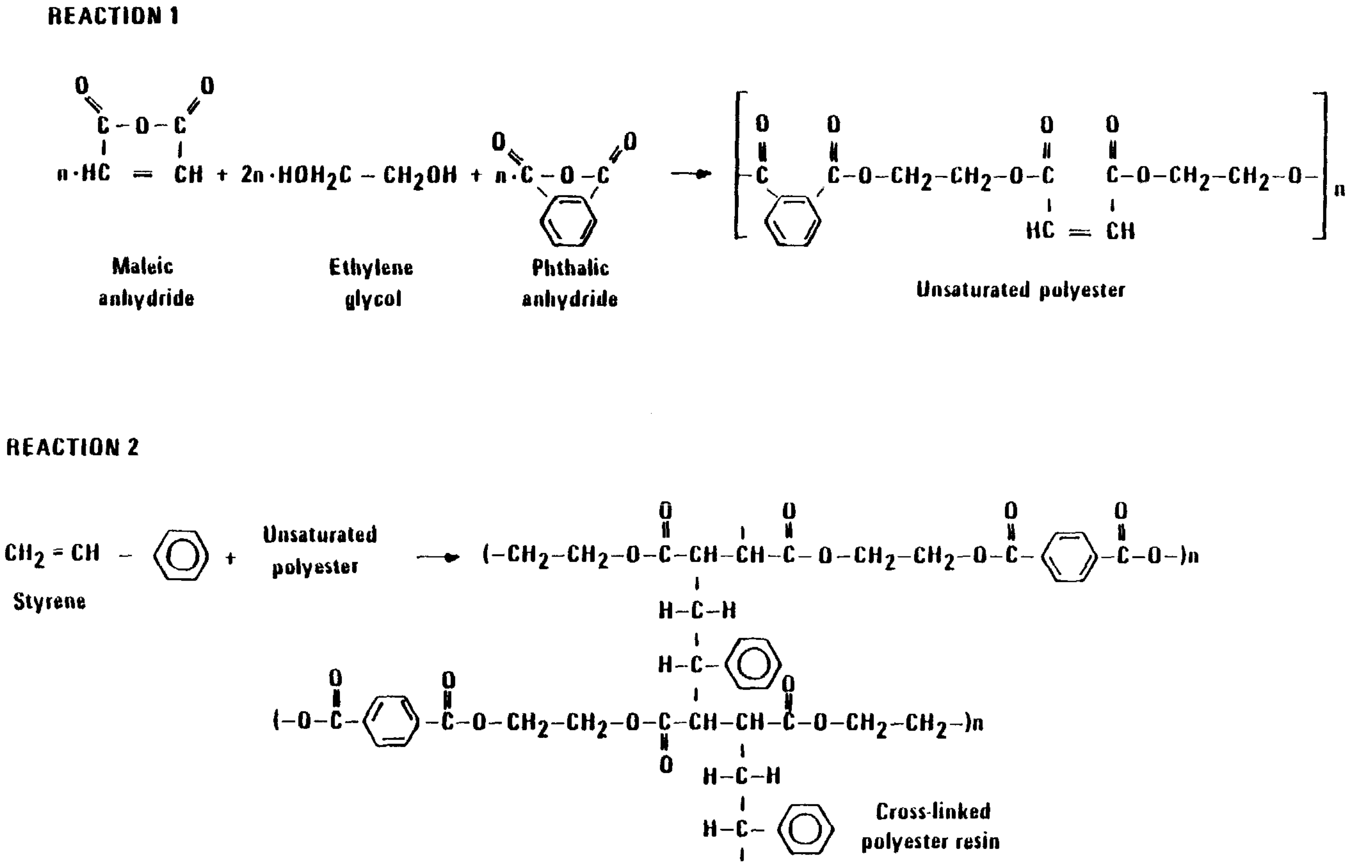


Figure 4.12-1. Typical reactions for unsaturated polyester and polyester resin formation.

the mold is first sprayed with gel coat, a clear or pigmented resin mix that forms the smooth outer surface of many products. Gel coat spray systems consist of separate sources of resin and catalyst, with an airless hand spray gun that mixes them together into an atomized resin/catalyst stream. Typical products are boat hulls and decks, swimming pools, bathtubs and showers, electrical consoles and automobile components.

Spray layup, or "sprayup", is another open mold process, differing from hand layup in that it uses mechanical spraying and chopping equipment for depositing the resin and glass reinforcement. This process allows a greater production rate and more uniform parts than does hand layup, and often uses more complex molds. As in hand layup, gel coat is frequently applied to the mold before fabrication to produce the desired surface qualities. It is common practice to combine hand layup and sprayup operations.

For the reinforced layers, a device is attached to the sprayer system to chop glass fiber "roving" (uncut fiber) into predetermined lengths and project it to merge with the resin mix stream. The stream precoats the chop, and both are deposited simultaneously to the desired layer thickness on the mold surface (or on the gel coat that was applied to the mold). Layers are built up and rolled out on the mold as necessary to form the part. Products manufactured by sprayup are similar to those made by hand layup, except that more uniform and complex parts can generally be produced more efficiently with sprayup techniques. However, compared to hand layup, more resin generally is used to produce similar parts by spray layup because of the inevitable overspray of resin during application.

Continuous lamination of reinforced plastics materials involves impregnating various reinforcements with resins on an in-line conveyor. The resulting laminate is cured and trimmed as it passes through the various conveyor zones. In this process, the resin mix is metered onto a bottom carrier film, using a blade to control thickness. This film, which defines the panel's surface, is generally polyester, cellophane or nylon, and may have a smooth, embossed or matte surface. Methyl methacrylate is sometimes used as the cross-linking agent, either alone or in combination with styrene, to increase strength and weather resistance. Chopped glass fibers free-fall into the resin mix and are allowed to saturate with resin, or "wet out". A second carrier film is applied on top of the panel before subsequent forming and curing. The cured panel is then stripped of its films, trimmed and cut to the desired length. Principal products include translucent industrial skylights and greenhouse panels, wall and ceiling liners for food areas, garage doors and cooling tower louvers. Figure 4.12-2 shows the basic elements of a continuous laminating production line.

Pultrusion, which can be thought of as extrusion by pulling, is used to produce continuous cross-sectional lineals similar to those made by extruding metals such as aluminum. Reinforcing fibers are pulled through a liquid resin mix bath and into a long machined steel die, where heat initiates an exothermic reaction to polymerize the thermosetting resin matrix. The composite profile emerges from the die as a hot, constant cross-sectional that cools sufficiently to be fed into a clamping and pulling mechanism. The product can then be cut to desired lengths. Example products include electrical insulation materials, ladders, walkway gratings, structural supports, and rods and antennas.

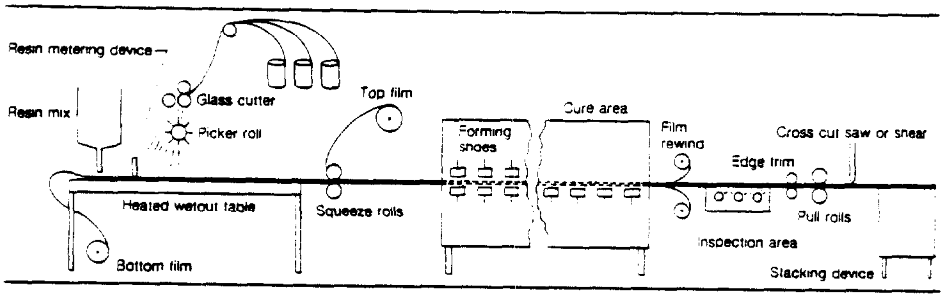
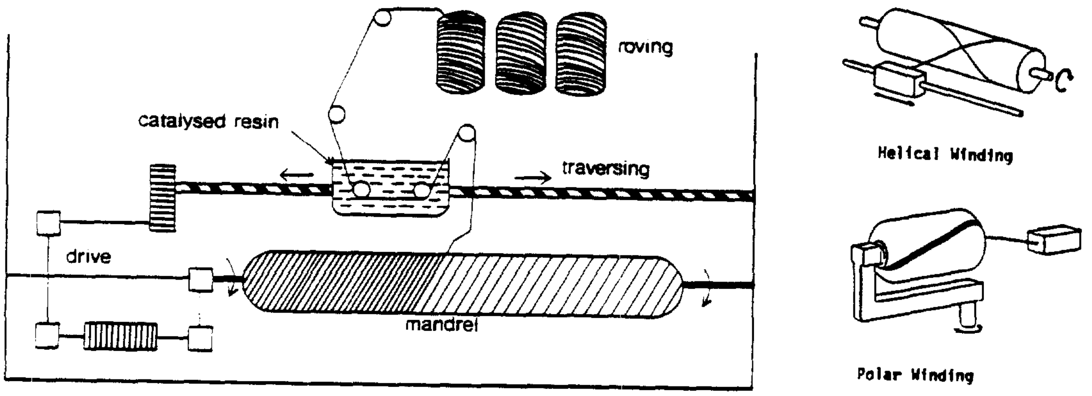


Figure 4.12-2. Typical continuous lamination production process.[2]

Filament winding is the process of laying a band of resin impregnated fibers onto a rotating mandrel surface in a precise geometric pattern, and curing them to form the product. This is an efficient method of producing cylindrical parts with optimum strength characteristics suited to the specific design and application. Glass fiber is most often used for the filament, but aramid, graphite, and sometimes boron and various metal wires may be used. The filament can be wetted during fabrication, or previously impregnated filament ("prepreg") can be used. Figure 4.12-3 shows the filament winding process, and indicates the three most common winding patterns. The process illustration depicts circumferential winding, while the two smaller pictures show helical and polar winding. The various winding patterns can be used alone or in combination to achieve the desired strength and shape characteristics. Mandrels are made of a wide variety of materials and, in some applications, remain inside the finished product as a liner or core. Example products are storage tanks, fuselages, wind turbine and helicopter blades, and tubing and pipe.



Helical Winding

Polar Winding

Figure 4.12-3. Typical filament winding process.[3]

Closed, such as compression or injection, molding operations involve the use of two matched dies to define the entire outer surface of the part. When closed and filled with a resin mix, the matched die mold is subjected to heat and pressure to cure the plastic. For the most durable production configuration, hardened metal dies are used (matched metal molding). Another closed molding process is vacuum or pressure bag molding. In bag molding, a hand layup or sprayup is covered with a plastic film, and vacuum or pressure is applied to rigidly define the part and improve surface quality. The range of closed molded parts includes tool and appliance housings, cookware, brackets and other small parts, and automobile body and electrical components.

Synthetic marble casting, a large segment of the resin products industry, involves production of bathroom sinks, vanity tops, bathtubs and accessories using filled resins that have the look of natural marble. No reinforcing fibers are used in these products. Pigmented or clear gel coat can either be applied to the mold itself or sprayed onto the product after casting to simulate the look of natural polished marble. Marble casting can be an open mold process, or it may be considered a semiclosed process if cast parts are removed from a closed mold for subsequent gel coat spraying.

## 4.12.2 Emissions And Controls

Organic vapors consisting of volatile organic compounds (VOC) are emitted from fresh resin surfaces during the fabrication process and from the use of solvents (usually acetone) for cleanup of hands, tools, molds and spraying equipment. Cleaning solvent emissions can account for over 36 percent of the total plant VOC emissions.[4] There also may be some release of particulate emissions from automatic fiber chopping equipment, but these emissions have not been quantified.

Organic vapor emissions from polyester resin/fiberglass fabrication processes occur when the cross-linking agent (monomer) contained in the liquid resin evaporates into the air during resin application and curing. Styrene, methyl methacrylate and vinyl toluene are three of the principal monomers used as cross-linking agents. Styrene is by far the most common. Other chemical components of resins are emitted only at trace levels, because they not only have low vapor pressures but also are substantially converted to polymers.[5-6]

Since emissions result from evaporation of monomer from the uncured resin, they depend upon the amount of resin surface exposed to the air and the time of exposure. Thus, the potential for emissions varies with the manner in which the resin is mixed, applied, handled and cured. These factors vary among the different fabrication processes. For example, the spray layup process has the highest potential for VOC emissions because the atomization of resin into a spray creates an extremely large surface area from which volatile monomer can evaporate. By contrast, the emission potential in synthetic marble casting and closed molding operations is considerably lower, because of the lower monomer content in the casting resins (30 to 38 percent, versus about 43 percent) and of the enclosed nature of these molding operations. It has been found that styrene evaporation increases with increasing gel time, wind speed and ambient temperature, and that increasing the hand rolling time on a hand layup or sprayup results in significantly higher styrene losses.[1] Thus, production changes that lessen the exposure of fresh resin surfaces to the air should be effective in reducing these evaporation losses.

In addition to production changes, resin formulation can be varied to affect the VOC emission potential. In general, a resin with lower monomer content should produce lower emissions. Evaluation tests with low-styrene-emission laminating resins having a 36 percent styrene content found a 60 to 70 percent decrease in emission levels, compared to conventional resins (42 percent styrene), with no sacrifice in the physical properties of the laminate.[7] Vapor suppressing agents also are sometimes added to resins to reduce VOC emissions. Most vapor suppressants are paraffin waxes, stearates or polymers of proprietary composition, constituting up to several weight percent of the mix. Limited laboratory and field data indicate that vapor suppressing resins reduce styrene losses by 30 to 70 percent.[7-8]

Emission factors for several fabrication processes using styrene content resins have been developed from the results of facility source tests (B Rating) and laboratory tests (C Rating), and through technology transfer estimations (D Rating).[1] Industry experts also provided additional information that was used to arrive at the final factors presented in Table 4.12-2.[6] Since the styrene content varies over a range of approximately 30 to 50 weight percent, these factors are based on the quantity of styrene monomer used in the process, rather than on the total amount of resin used. The factors for vapor-suppressed resins are typically 30 to 70 percent of those for regular resins. The factors are expressed as ranges, because of the observed variability in source and laboratory test results and of the apparent sensitivity of emissions to process parameters.

Emissions should be calculated using actual resin monomer contents. When specific information about the percentage of styrene is unavailable, the representative average values in Table 4.12-3 should be used. The sample calculation illustrates the application of the emission factors.

Sample Calculation - A fiberglass boat building facility consumes an average of 250 kg per day of styrene-containing resins using a combination of hand layup (75%) and spray layup (25%) techniques. The laminating resins for hand and spray layup contain 41.0 and 42.5 weight percent, respectively, of styrene. The resin used for hand layup contains a vapor-suppressing agent.

From Table 4.12-2, the factor for hand layup using a vapor-suppresed resin is 2 - 7 (0.02 to 0.07 fraction of total styrene emitted); the factor for spray layup is 9 - 13 (0.09 to 0.13 fraction emitted). Assume the midpoints of these emission factor ranges.

Total VOC emissions are:

$$(250 \text{ kg/day}) \; [(0.41)(0.045)(0.75) + (0.425)(0.11)(0.25)]$$

$$= 6.4 \text{ kg/day.}$$

## TABLE 4.12-2. EMISSION FACTORS FOR UNCONTROLLED POLYESTER RESIN PRODUCT FABRICATION PROCESSES[a]

(100 x mass of VOC emitted/mass of monomer input)

| Process | Resin | | Emission Factor Rating | Gel Coat | | Emission Factor Rating |
|---|---|---|---|---|---|---|
| | NVS | VS[b] | | NVS | VS[b] | |
| Hand layup | 5 - 10 | 2 - 7 | C | 26 - 35 | 8 - 25 | D |
| Spray layup | 9 - 13 | 3 - 9 | B | 26 - 35 | 8 - 25 | B |
| Continuous lamination | 4 - 7 | 1 - 5 | B | c | c | — |
| Pultrusion[d] | 4 - 7 | 1 - 5 | D | c | c | — |
| Filament winding[e] | 5 - 10 | 2 - 7 | D | c | c | — |
| Marble casting | 1 - 3 | 1 - 2 | B | f | f | — |
| Closed molding[g] | 1 - 3 | 1 - 2 | D | c | c | — |

[a] Reference 9. Ranges represent the variability of processes and sensitivity of emissions to process parameters. Single value factors should be selected with caution. NVS = nonvapor-suppressed resin. VS = vapor-suppressed resin.

[b] Factors are 30-70% of those for nonvapor-suppressed resins.

[c] Gel coat is not normally used in this process.

[d] Resin factors for the continuous lamination process are assumed to apply.

[e] Resin factors for the hand layup process are assumed to apply.

[f] Factors unavailable. However, when cast parts are subsequently sprayed with gel coat, hand and spray layup gel coat factors are assumed to apply.

[g] Resin factors for marble casting, a semiclosed process, are assumed to apply.

## TABLE 4.12-3. TYPICAL RESIN STYRENE PERCENTAGES

| Resin Application | Resin Styrene Content[a] (wgt. %) |
|---|---|
| Hand layup | 43 |
| Spray layup | 43 |
| Continuous lamination | 40 |
| Filament winding | 40 |
| Marble casting | 32 |
| Closed molding | 35 |
| Gel coat | 35 |

[a] May vary by at least ±5 percentage points.

Emissions from use of gel coat would be calculated in the same manner. If the monomer content of the resins were unknown, a representative value of 43 percent could be selected from Table 4.12-3 for this process combination. It should be noted that these emissions represent evaporation of styrene monomer only, and not of acetone or other solvents used for cleanup.

In addition to process changes and materials substitution, add-on control equipment can be used to reduce vapor emissions from styrene resins. However, control equipment is infrequently used at RP/C fabrication facilities, due to low exhaust VOC concentrations and the potential for contamination of adsorbent materials. Most plants use forced ventilation techniques to reduce worker exposure to styrene vapors, but vent the vapors directly to the atmosphere with no attempt at collection. At one continuous lamination facility where incineration was applied to vapors vented from the impregnation table, a 98.6 percent control efficiency was measured.[1] Carbon adsorption, absorption and condensation also have been considered for recovering styrene and other organic vapors, but these techniques have not been applied to any significant extent in this industry.

Emissions from cleanup solvents can be controlled through good housekeeping and use practices, reclamation of spent solvent, and substitution with water based solvent substitutes.

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