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CONTROL TECHNIQUES FOR ORGANIC GAS EMISSIONS FROM FIBERGLASS IMPREGNATION AND FABRICATION PROCESSES

FINAL REPORT

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A statewide inventory of air polluting styrene emissions from manufacturing plants processing or fabricating polyester resin-impregnated, glass fiber-reinforced products has been conducted for California. A total of 305 users of unsaturated polyester resin have been identified, who use approximately 50,000 tons of resin and emit approximately 2170 tons of styrene per year (1980-81). Styrene, and to a much smaller extent, methyl methacrylate are monomeric systems used primarily as cross linking and viscosity control agents for the polyester resins. In processing the impregnated systems and before polymerization occurs, various amounts of the monomer, depending upon method of application and manufacture, are released to the ambient air. The monomers are photochemically reactive and are smog precursors. The authors discuss methods of manufacture and assign emission factors to application and processing procedures. The authors also discuss emission control mechanisms including incineration. Inter-ply bond strengths are evaluated for those control techniques involving the use of vapor supressing waxes.

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This report was submitted in fulfillment of ARB Contract No. A9-120-30, "Control Techniques for Organic Gas Emissions from Fiberglass Impregnation and Fabrication Processes." Work was completed as of 21 October 1981.

ABSTRACT

The objectives of this study were (1) to locate and characterize as many sources of polyester resin/fiberglass process emissions in California as possible; (2) to establish an emission inventory based upon realistic emission factors for the pollutants of interest; and (3) to review the technology for controlling organic vapor emissions from this industry.

We conducted a survey by telephone and by written questionnaire, identifying thereby 305 unsaturated polyester resin users. Between August 1980 and May 1981, the industry used 44.4 to 45.5 million kilograms per year (97.9 to 100.4 million pounds per year) of resin and gel coat; to our knowledge this is the only California-specific estimate based upon an actual survey. The industry was in a recession during this period.

The California polyester resin/fiberglass industry consists of a large number of small firms and a few very large firms. The median firm size is 27,500 kg/yr (60,200 lb/yr) and the range is 99.8 kg/yr (220 lb/yr) to 8.8 million kg/yr (19.3 million lb/yr). The largest 10 percent of the users consume 72 percent of the unsaturated polyester resin. The industry is centered in Los Angeles, Orange and San Diego Counties, which in combination account for 81 percent of the state's resin consumption.

Fabrication processes used in California include hand and spray layup, marble casting, filament winding, bag molding, pultrusion, continuous lamination and matched metal molding. Almost three quarters of the firms in the state use hand layup, spray layup or a combination of the two. Continuous lamination and pultrusion use the most resin per plant. Styrene monomer is used as the cross-linking agent (to polymerize the unsaturated polyester resin) in all but three plants, which use methyl methacrylate. The most common catalysts are methyl ethyl ketone peroxide and benzoyl peroxide.

To develop improved emission factors, we first reviewed published and unpublished data from previous field and laboratory tests. We then conducted source tests at a large continuous lamination plant, a medium-sized spray layup facility, and a large synthetic marble casting plant. The last of these used normal and vapor-suppressed resins on successive days. Total emissions during each test run were determined by integrating the recorder trace of the output of a portable flame ionization detector. The detector was

calibrated by simultaneously collecting organic vapor samples on charcoal traps and analyzing them by gas chromatography. The emission factors developed from the literature review and our tests were based upon styrene or methyl methacrylate monomer input, rather than total amount of resin and/or gel coat.

NOTE

Organic vapor emissions from the industry statewide were estimated to be 1.41 to 2.55 million kg/yr (1549 to 2805 tons/yr). Only 4 percent of the firms account for half of the total emissions. The South Coast Air Basin accounts for 1152 to 2042 tons/yr, or about 73 percent of the statewide total. Emissions from Los Angeles, Orange and San Diego Counties are 262 to 512, 856 to 1478 and 143 to 272 tons/yr, respectively.

Estimated emissions from polyester resin/fiberglass fabrication constitute 0.054 to 0.098 percent of the total organic gas (TOG) emissions, and 0.075 to 0.13 percent of stationary source organic gas emissions, as reported in the 1979 statewide emission inventory. It is difficult, if not impossible, to compare our estimates with those reported in various emission inventories by manufacturing category, since polyester resin/fiberglass operations are often ambiguously or erroneously categorized.

Incineration (at two plants) and use of resins with vapor suppressant additives are the only means of organic vapor emission control in this industry. We reviewed the literature on vapor suppressants and performed laboratory tests on emissions from resin coatings placed in a wind tunnel. Under our test conditions, vapor suppressants indeed reduced weight loss; furthermore, long-term weight loss increased with increasing gel time. To determine whether use of vapor suppressant affected material properties, we performed interlaminar shear strength and bending tests on laminates made of normal and vapor-suppressed resin and glass mat and cloth. Use of vapor suppressant did not degrade the properties measured.

Incineration, activated carbon adsorption, and condensation were found to be applicable in principle to controlling emissions from polyester resin/fiberglass fabrication, although each has some drawbacks. Absorption was not found to be practical. Costs of controlling emissions from hypothetical small and large hand- and spray-layup plants were estimated to be $10.3 to $15 per pound of styrene removed for incineration (assuming no heat recuperation), $4.3 to $4.6 per pound for carbon adsorption (assuming no credit for recovered styrene) and $7.3 to $15 per pound for condensation (assuming a credit of 60 cents/pound for recovered styrene). These costs are for new installations.

Any control strategy developed for this industry should take into account the heavy concentration of emissions among a relatively small number of firms. Strategies examined included setting maximum emission levels, requiring a minimum percentage removal of organic vapors, and requiring specific control technology.

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1.1.1 Statewide Polyester Resin Use

(1) Our survey obtained detailed information on 291 polyester resin/fiberglass fabricators and partial information on another 14.

(2) It is likely that many small firms were not identified; however, their contribution to statewide resin use is believed to be miniscule.

(3) We estimate that 44.4 to 45.5 million kg/yr (97.9 to 100.4 million lb/yr) of unsaturated polyester resin is used in California. To our knowledge, this is the only California-specific estimate based upon an actual survey.

(4) During the survey period (August 1980 to May 1981), many firms were operating below their normal capacities. About 15 percent of the firms we contacted had gone out of business. These findings are consistent with the depressed state of this industry nationwide in 1980.

1.1.2 Distribution of Resin Users by Size and Location

(1) The California polyester resin/fiberglass industry consists of a relatively large number of small firms which, in combination, account for only a small fraction of the state's unsaturated polyester resin consumption; and a few very large firms, which use the great majority of the total resin.

(2) Resin use per firm ranges from 99.8 kg/yr to 8.8 million kg/yr (220 lb/yr to 19.3 million lb/yr). The median firm size is 27,500 kg/yr (60,200 lb/yr).

(3) The largest 10 percent of the users in California consume 72 percent of the unsaturated polyester resin.

(4) At least one polyester resin/fiberglass fabricator was identified in 32 of California's 58 counties.

(5) The industry is centered in Los Angeles, Orange and San Diego Counties, which in combination account for 63 percent of the number of firms and 81 percent of the state's resin consumption.

(6) The next-largest resin-using counties are Santa Clara, Sacramento and Alameda, whose 43 firms account for another 4 percent of the state's resin use.

(7) Most of the large firms are in Southern California, although the average resin use per firm in Sacramento, San Joaquin and Yolo Counties is actually higher than in Los Angeles and Orange Counties.

(8) The great majority of the firms and the resin use are centered in the South Coast Air Basin (federal Air Quality Control Region 24).

1.1.3 Use by Product and Production Process

(1) Our survey identified 17 major types of products made with polyester resin/fiberglass processes in California.

(2) The 16 firms which manufacture panels and bathroom fixtures use almost 25 million kg/yr (55 million lb/yr) of resin and gel coat, or about 55 percent of the state total.

(3) While plants which manufacture boats, synthetic marble, and laminates in general comprise over half of the user population, they account for only about one quarter of the total unsaturated polyester resin use.

(4) Panel and bathroom fixture plants average 2.5 million kg/yr (5.6 million lb/yr) and 550,000 kg/yr (1.2 million lb/yr) per plant, respectively. The smallest operations are the surfboard manufacturers, who average only 6,900 kg/yr (15,000 lb/yr) per firm.

(5) Fabrication processes used in California include hand and spray layup, marble casting, filament winding, bag molding, pultrusion, continuous lamination and matched metal molding.

(6) Almost three quarters of the firms in California use hand layup, spray layup or a combination of the two.

(7) Continuous lamination and pultrusion processes use the most resin per firm.

1.1.4 Cross-Linking Agents and Catalysts

(1) All but three plants reported that they used styrenated resin or did not know the cross-linking agent.

(2) The three exceptions all use methyl methacrylate. Since two of these are among the largest in the state, methyl methacrylate accounts for about 12 percent of the monomer use.

(3) All but eight percent of the firms in the state use methyl ethyl ketone peroxide (MEKP) as a catalyst. The second most commonly-used catalyst is benzoyl peroxide (BP).

(4) There did not appear to be any clear pattern of catalyst use among processes or products, except that firms using BP tend to be quite large.

1.2 DEVELOPMENT OF EMISSION FACTORS

1.2.1 Definition

[illegible]

Given the varying emission potential of different polyester resin/fiberglass manufacturing processes and the wide range of monomer content, uniform emission factors based upon resin mass may lead to inaccurate emissions estimates. We chose to develop emission factors for each process and to define them as (mass VOC emitted)/(mass VOC input).

1.2.2 Literature Review

(1) Data from Dade County (Florida) Department of Environmental Resources Management field tests, Bay Area Air Quality Management District source tests, Ashland Chemical Company laboratory tests, Shasta County Air Pollution Control District laboratory tests, and extensive laboratory tests by the Kingston Polytechnic Institute (England) were reviewed.

(2) Emission factors based upon the above definition were calculated from the data obtained through the literature review.

(3) Calculated emission factors varied widely with process and with experimental conditions.

1.2.3 SAI Source Tests

SAI conducted source tests at three representative polyester resin/fiberglass fabrication plants. In each case, grab samples were collected on charcoal adsorbent and later analyzed by gas chromatography. In two cases (Plants B and C), instantaneous concentrations measured with a portable flame ionization detector and recorded on a strip chart were integrated and then correlated with concentrations determined from charcoal trap samples taken concurrently. The average exposure during the test period could then be calculated by integrating the strip chart trace.

Source Tests at Facility A

Facility A is a large (3.6 million lb/yr) continuous lamination plant. An incinerator is used to control emissions from the impregnation table. Our findings were as follows:

(1) Styrene concentrations at the plant's 7 emission points ranged from 2 to 1100 ppm.

(2) Annual emissions are estimated to be 7 to 9 tons.

(3) The monomer-based emission factor for continuous lamination without emission controls was 0.059 to 0.13. With the afterburner in use, the emission factor for this plant was 0.0092 to 0.028.

FACTOR

Source Tests at Facility B

Facility B is a medium size (125,000 lb/yr of resin and gel coat) tank coating plant having no emission controls. All workplace air exits the plant through a single stack equipped with a fan. Resin and gel coat are applied to the tanks with spray guns and chopper guns. Our findings were as follows:

(1) Styrene concentrations in the 1.5-m^3/s (3200 cfm) plant exhaust varied from 82 ppm (during a time of no spraying) to 405 ppm.

(2) Given the large moment-to-moment fluctuation in the exhaust styrene concentration, it was necessary to use our integrated sampling method over a typical spraying cycle.

(3) Styrene mass emission rates during the spraying cycle ranged from 11 to 14 lb/hr.

(4) Emission factors for the spraying operation ranged from 0.092 to 0.13.

FACTOR

Source Tests at Facility C

Facility C is a large (420,000 lb/yr of resin and gel coat) synthetic marble plant. Gel coat is sprayed in a booth equipped with an exhaust fan. No exhaust gas treatment equipment is installed. Our tests covered production runs using normal resin and resin containing a vapor suppressant additive. Our findings were as follows:

(1) Styrene concentrations in the exhaust air ranged from 10 to 22 ppm. It was not possible to determine the relative contributions of the casting resin and the gel coat.

(2) As with Facility B, it was necessary to use our integrated sampling method to determine an average emission rate.

(3) Styrene mass emission rates were 2.2 to 2.6 lb/hr when the normal resin was used and 1.2 to 2.6 lb/hr when the vapor-suppressed resin was used.

(4) The monomer-based emission factors for the normal and vapor-suppressed cases were 0.026 to 0.31 and 0.014 to 0.030, respectively.

VAPOR SUPPRESSED

(5) The fact that the lower bound of the emission factor estimate is lower for the vapor-suppressed resin than for the conventional casting resin is probably due more to the uncertainty in the correlation between charcoal trap styrene concentrations and flame ionization detector readings than to a real difference in emissions.

1.2.4 SAI Laboratory Tests

(1) Under our test conditions, styrene emissions from the vapor-suppressed resins we tested were lower than those for most of the non-suppressed resins.

(2) Long-term cumulative weight loss from the test samples was inversely related to the percentage of catalyst used.

1.2.5 Recommended Emission Factors

The following recommendations are for cases in which vapor suppressant is not used. After reviewing the literature and discussing the effectiveness of vapor suppressants with other researchers, we concluded that emission factors for vapor-suppressed resins would be 50 to 70 percent of the values reported here.

Emission Factors

(1) For hand layup, the monomer-based emission factors are 0.16 to 0.35 for laminating resin and 0.47 for gel coat.

(2) For spray layup, the emission factors are 0.09 to 0.13 for laminating resin and 0.~~1~~26 to 0.35 for gel coat.

(3) For marble casting and other closed molding operations, the emission factors are 0.01 to 0.03 for casting resin and 0.26 to 0.35 for gel coat.

(4) For continuous lamination, pultrusion and filament winding, the emission factors are 0.06 to 0.13 for resin and 0.26 to 0.35 for gel coat. (Note that gel coat is rarely used in the first two processes.)

(5) Whenever possible, emission factor ranges should be used to estimate ranges of emissions, so that uncertainty may be explicit. Single values (such as the midpoints of the stated ranges) should be used with caution.

Note

1.3 ESTIMATED ORGANIC VAPOR EMISSIONS IN CALIFORNIA

1.3.1 Emissions by Geographic Unit

(1) Organic vapor emissions from polyester resin/fiberglass fabrication were estimated to be 1.41 to 2.55 million kg/yr (1549 to 2805 tons/yr) for the whole state.

(2) Los Angeles, Orange and San Diego Counties are responsible for 81 percent of the statewide emissions. Emissions for these counties are 262 to 512, 856 to 1478 and 143 to 272 tons/yr, respectively.

(3) The South Coast Air Basin accounts for 1152 to 2042 tons/yr, or about 73 percent of the statewide total.

1.3.2 Distribution of Emissions by Firm Size

(1) About three quarters of the firms in California account for only about 12 percent of the emissions.

(2) On the other hand, only 4 percent of the firms account for 50 percent of the total.

1.3.3 Distribution of Emissions by Product and Production Process

(1) Operations in which resin spraying is used alone or in combination with other processes are responsible for about 47 percent of the state's total emissions.

(2) Hand layup and continuous lamination processes are also significant emission sources, the former because they have high emission factors, and the latter because they are used in some of the state's largest plants.

1.3.4 Perspective

(1) Estimated emissions from polyester resin/fiberglass fabrication in California constitute 0.054 to 0.098 percent of the total organic gas (TOG) emissions, and 0.075 to 0.13 percent of stationary source TOG emissions, as reported in the 1979 Statewide Emission Inventory.

(2) Polyester resin/fiberglass emissions comprise about 0.66 to 1.2 percent of stationary source TOG emissions within the South Coast Air Basin, and constitute 2.8 to 4.9 percent of the total for Orange County.

(3) It is difficult, if not impossible, to compare our estimates with those reported in various emission inventories by manufacturing category, since polyester resin/fiberglass operations have heretofore been placed under several unrelated and often incorrect categories.

1.4 REVIEW OF EMISSION CONTROL TECHNOLOGY

1.4.1 California Survey Results

(1) Except for two continuous lamination plants which are equipped with incinerators, organic vapor removal equipment is not used in this industry.

(2) Vapor-suppressed resins are used by 54 companies, representing 25 percent of the statewide polyester resin and gel coat use.

(3) There was no statistically significant relationship between production type and vapor suppressant use.

(4) Only 38 firms, representing less than 5 percent of statewide resin use, use natural ventilation to control indoor exposures; the remainder have some form of forced air ventilation.

1.4.2 Changes in Existing Processes

(1) Emissions can be reduced significantly by using resins with lower monomer content, changing from open to closed molding, reducing rollout time, and improving housekeeping practices.

(2) The costs of such process and material changes could range from negligible to major, depending upon the amount of retooling required.

(3) Care must be taken that product quality is not degraded by the changes.

1.4.3 Vapor Suppressants

(1) The trend in vapor suppressants is away from aliphatic waxes and towards combinations of new resin formulations and polymeric additives.

(2) Laboratory and field tests of the effectiveness of vapor suppressants give widely varying results; we have assumed in our emission calculations that these additives reduce styrene emissions by 30 to 50 percent.

(4) An informal survey of California users of vapor-suppressed resin identified potential delamination as the most feared drawback of using these additives. Some manufacturers encountered serious problems, while others did not.

(5) Studies in Sweden have shown the effectiveness of installing a peelable material in the resin as it cures; peeling away the material permits secondary bonding without the need for sanding.

1.4.4 Incineration

(1) At facility A, a direct flame afterburner removed 98.4 to 98.8 percent of the styrene and methyl methacrylate in that portion of the plant exhaust which was treated.

(2) Unless recuperated heat can be used in a plant, incineration results in a large waste of energy. Polyester resin/fiberglass fabrication processes which could use recovered heat include heat curing in general, continuous lamination, pressure bag

molding, and some forms of filament winding.

(3) The use of catalytic incinerators could lower energy requirements. Poisoning of the catalyst by metallic salts in resin promoters may present a problem.

(4) Costs for using incineration in hypothetical small and large facilities used in our cost analyses range from $10.3 to $15.9 per lb styrene removed if no credit for heat recovery is assumed. With 50 percent heat recovery (which is unlikely for all but a few large plants) the cost could be as low as $7.8/lb.

(5) There is no economy of scale in using this control technique. Rising natural gas prices could increase costs significantly, since variable operating costs are a high percentage of the total.

1.4.5 Carbon Adsorption

(1) Carbon adsorption has been used, with apparent success, to control styrene emissions from a fiberglass pipe collar plant in Washington State.

(2) Potential problems with activated carbon adsorption include overheating of the adsorbent, polymerization of styrene, and clogging by particulate matter. Also, unless styrene can be efficiently recovered from the steam condensate after desorption, a liquid waste problem must be dealt with.

(3) Of the three techniques subjected to our cost analysis, carbon adsorption had the lowest cost, $4.3 to $4.6/lb styrene removed, assuming no credit for recovered styrene. At today's styrene prices, credits for recovered monomer would not offset the treatment cost significantly.

1.4.6 Absorption

(1) To our knowledge, absorption has never been used to control emissions from polyester resin/fiberglass fabrication.

(2) Absorption equipment manufacturers expressed doubts about the applicability of this technique, since styrene is relatively insoluble in water and use of organic absorbent solutions would create air pollution and liquid waste disposal problems of their own.

(3) An Oklahoma company built a pilot plant to assess the feasilibity of using dibutyl phthalate as the absorbent medium. High capital costs have delayed construction of a full-scale scrubber.

1.4.7 Condensation

(1) The only practical way to condense styrene vapors from plant exhaust would be to use surface condensers with a refrigerated coolant.

(2) Condensation is generally best applicable to waste gas streams having higher organic vapor concentrations than are normally encountered in the polyester resin/fiberglass industry.

(3) According to our analysis, the costs of removing styrene by condensation would be about $7.3 to $15/lb styrene removed, provided that no credit was obtained for recuperated styrene. Credits for styrene would reduce total costs to $6.7 to $14.4/lb.

1.5 MATERIAL TESTING

(1) Standard ASTM procedures were used to perform interlaminar shear strength and bending tests on five resin and glass laminates.

(2) There was no significant difference in mean interlaminar shear strength between the groups of laminates made with vapor-suppressed and non-vapor-suppressed resins. However, in the one "head-to-head" comparison of suppressed and non-suppressed resins, the laminate made with the suppressed resin had a 9-percent higher shear strength.

(3) The use of a vapor-suppressed resin for secondary bonding after a 24-hour wait resulted in a slightly greater interlaminar shear strength than when the laminate was made in one stage with the same vapor-suppressed resin.

(4) Correlation between bending modulus and interlaminar shear strength was rather low.

(5) The use of vapor suppressant evidently did not affect the flexibility of the laminates.

(6) An appreciable fraction (9 of 30) of the test specimens failed in tension, rather than in shear. Mixed mode failures are common in composites of this type.

1.6 CONTROL STRATEGY FORMULATION

(1) Only two local air pollution control districts have regulations specifically applicable to polyester resin/fiberglass fabrication. Because styrene is sometimes used as a diluent as well as a cross-linking agent, many districts place this type of fabrication under their solvent regulations.

(2) Any control strategy, whether it be at the state or the local air pollution control district level, should take into account the heavy concentration of emissions among a relatively small number of large firms.

(3) A strategy based upon setting maximum levels of emissions would affect only the largest firms in the state. Compliance would be expensive for these firms, since extensive retrofitting would be necessary in some cases.

(4) An approach based upon requiring a certain percentage of removal of organic vapors from all firms (or all firms whose emissions would otherwise exceed a minimum level) would place a heavy burden on smaller firms, while net emission reductions from the industry would be lower than if absolute emission standards were used.

(5) Industry-wide technology-based standards are inadvisable, since the requirements for, and applicability of, different types of equipment vary with fabrication process.

2.0

RECOMMENDATIONS

On the basis of our findings in this study, we make the following recommendations.

(1) The information obtained through our survey of the California polyester resin/fiberglass industry (and provided to the Air Resources Board as a separate document) should be incorporated into local emission inventories and the statewide Emission Data System (EDS). Furthermore, the ARB should establish category of emission source (CES) numbers for the several polyester resin/ fiberglass fabrication processes, so that speciated emissions from these sources can be identified unambiguously in the EDS.

= SCC ←

Note

Important

(2) Emission factors for the processes used in this industry should be (a) process-specific and (b) based upon the amount of cross-linking agent (e.g. styrene or methyl methacrylate) used in the process, rather than upon the total amount of polyester resin and/or gel coat. This approach will give a more accurate estimate of the uncontrolled emission potential.

(3) Any emission regulations covering this industry should recognize that styrene, methyl methacrylate and other cross-linking agents are not used primarily as solvents.

(4) Since only 4 percent of the polyester resin/fiberglass fabricators in California account for half the emissions from this type of source, any regulatory strategy should focus upon these plants.

(5) Changes in production process, use of low monomer resin, implementation of better housekeeping, and other relatively inexpensive but often highly effective measures should be encouraged wherever feasible.

(6) Resins containing vapor suppressant additives may be used as part of an overall emission control strategy, with the caveat that the potential user conduct thorough tests of material properties specific to the product to be manufactured.

(7) Carbon adsorption should be evaluated further as a means of controlling styrene emissions, especially from large sources.

3.0
INTRODUCTION AND BACKGROUND

3.1 INTRODUCTION

3.1.1 Purpose and Objectives of the Study

It has long been recognized that production of reinforced plastic materials through the combination of polyester resin/styrene mixtures and glass fibers results in the release of significant quantities of styrene vapors into the workplace air. In order to reduce workplace concentrations, fabricators commonly vent the styrene and other organic emissions to the outside air. Because styrene and the most common catalyst used in these processes, methyl ethyl ketone peroxide, are both photochemically reactive substances, there is concern that their release to the atmosphere may contribute to photochemical smog formation. There are at present no federal or state emissions standards for styrene for the reinforced plastics source category. Local air pollution control districts' control strategies vary considerably.

The objectives of the study were (1) to locate and characterize as many sources of polyester resin/fiberglass process emissions in California as possible; (2) to establish an emission inventory based upon realistic emission factors for the pollutants of interest; and (3) to review the technology for controlling organic vapor emissions from this industry.

3.1.2 Outline of the Research

Research under this contract was conducted between June 1980 and October 1981. The major elements of the study were as follows.

Emission Inventory Survey

Before this project, no comprehensive, detailed inventory of polyester resin/fiberglass fabricators existed. We therefore attempted to identify and obtain information from several hundred firms which were initially believed to be polyester resin users. The result of our survey, which was conducted through written questionnaires and telephone interviews, is a data base covering more than 300 California polyester resin/fiberglass fabricators. This portion of the research is described in Chapter 4.

Derivation of Emission Factors

Organic vapor emissions from polyester resin/fiberglass processes have traditionally been estimated by multiplying polyester resin use rates by "rule-of-thumb" emission factors. Because the potential for emissions varies with resin composition and production process type, using one or two emission factors for all cases can lead to serious errors. In order to develop more accurate and useful emission factors, we:

- Used data from previous field and laboratory work;
- Measured exhaust emissions from California plants which used three different production processes; and
- Performed laboratory tests of organic vapor emissions from resins containing vapor suppressant additives.

Our discussion of the derivation of emission factors is presented in Chapter 5. In Chapter 6, these factors are used in conjunction with industry survey data to estimate organic vapor emissions in California.

Review of Control Technology

Organic vapor emissions from polyester resin/fiberglass fabrication processes may be reduced by process changes, use of vapor-suppressed resin, or exhaust gas cleanup technology. With only a handful of exceptions, the first two approaches are the only ones currently taken by California plants. In this portion of the study we reviewed the applicability and costs of process changes, vapor suppressants, incineration, adsorption, absorption and condensation techniques. Because concern over the effect of vapor suppressant use on product quality had been expressed, we also conducted material tests on laminates made from various resin formulations. Our review of control technology is presented in Chapter 7. Chapter 8 contains our estimates of the costs of various control strategies, and Chapter 9 describes our materials testing. Control recommendations are presented in Chapter 10.

3.2 POLYESTER RESIN COMPOSITION, PROPERTIES AND USE TRENDS

Definition

Given the complex nature of the reinforced plastics industry, it is important to define carefully the scope of this study. As used here, the term "polyester resin/fiberglass" will mean a material composed of a cured, cross-linked polyester resin, a reinforcing agent and/or inorganic fillers. Figure 3.2-1 shows how various chemicals are combined to form the types of reinforced

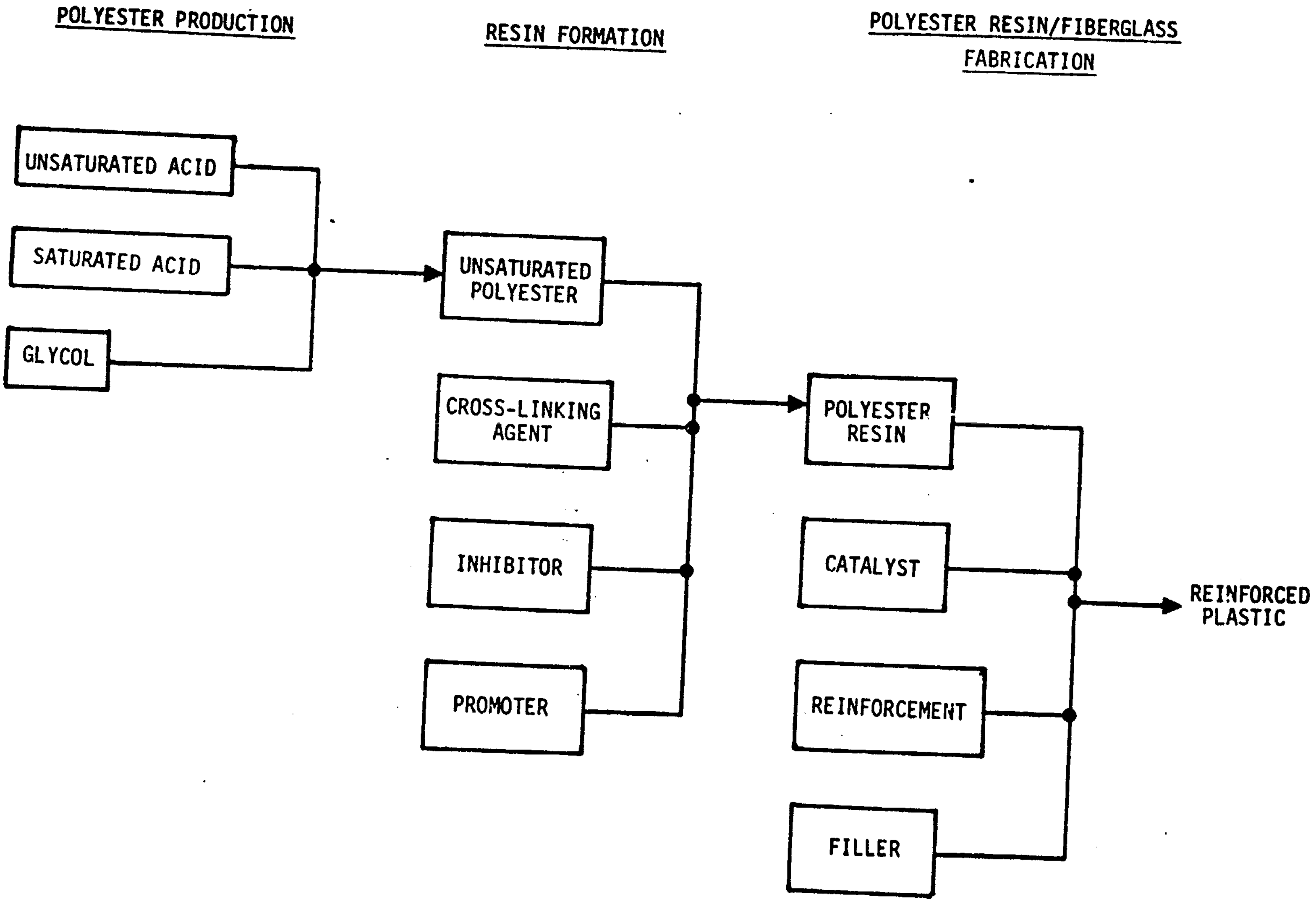


Figure 3.2-1 Composition of Unsaturated Polyester, Polyester Resin and Reinforced Plastics of Interests

plastics of interest. Although we are concerned only with organic vapor emissions from the third column of the flow chart, polyester resin/fiberglass fabrication, an understanding of unsaturated polyester and polyester resin formulation is essential.

3.2.1 Polyester Resin Composition and Chemistry

We further restrict the scope of this study to what are known in the plastics industry as thermosetting, unsaturated polyester resins. Polyester resins are complex polymers consisting of a liquid unsaturated polyester and a vinyl-type monomer. That they are thermosetting means that they cannot be softened by heat after they are cured (Shreve and Brink, 1977); indeed application of high temperatures to cured thermosetting re~~e~~sins tends to degrade the material. The polyester resins polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) are formed without cross-linking monomers and are therefore excluded from consideration, although they are discussed briefly at the end of this section.

Unsaturated Polyester

Note: This is the type of reaction to form the liquid polyester

Unsaturated polyester is formed from the condensation of an unsaturated dibasic acid or anhydride, a saturated dibasic acid or anhydride, and a polyfunctional alcohol. Table 3.2-1 lists the most common chemicals used for each component of the polyester "backbone." Structures of some of these compounds are shown in Figures 3.2-2 through 3.2-4.

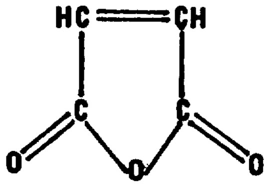
The purpose of the unsaturated acids is to provide double bond sites for reaction with cross-linking agents. Maleic anhydride is a common choice for the unsaturated acid because it will not homopolymerize, even at high temperatures, but will rapidly react with vinyl monomers, such as styrene. Especially important is the fact that maleic anhydride reacts more quickly with styrene than styrene does with itself (Kent, 1974).

Saturated acids are added to impart various desired properties to the final product. Phthalic anhydride increases flexibility and, because it is relatively inexpensive, lowers the overall costs of the resin. Isophthalic anhydride imparts good tensile strength and resistance to weathering and corrosion; it is frequently used in the manufacture of chemical storage tanks, ducts, and cooling tower louvers. Isophthalic resins are also used to make the molds on or in which other polyester resin/fiberglass products are fabri-

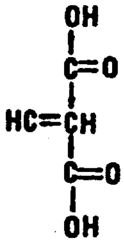
Table 3.2-1

COMPONENTS OF UNSATURATED POLYESTER

Unsaturated Acids	Saturated Acids	Alcohols
Maleic anhydride	Phthalic anhydride	Propylene glycol
Fumaric acid	Isophthalic anhydride	Ethylene glycol
	Adipic acid	Diethylene glycol
		Dipropylene glycol
		Pentaerythritol



Maleic anhydride

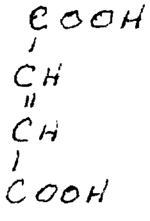


$C_4H_4O_4$

Fumaric acid

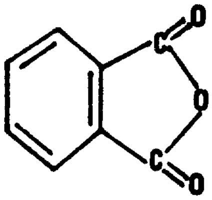
is trans

[illegible]

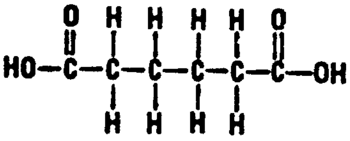


Trans

Figure 3.2-2 Structures of Some Common Unsaturated Acids

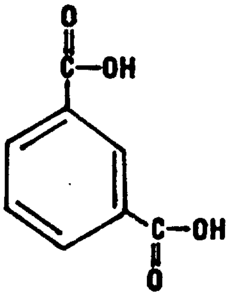


Phthalic anhydride



$$\mathrm{HO{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH}$$

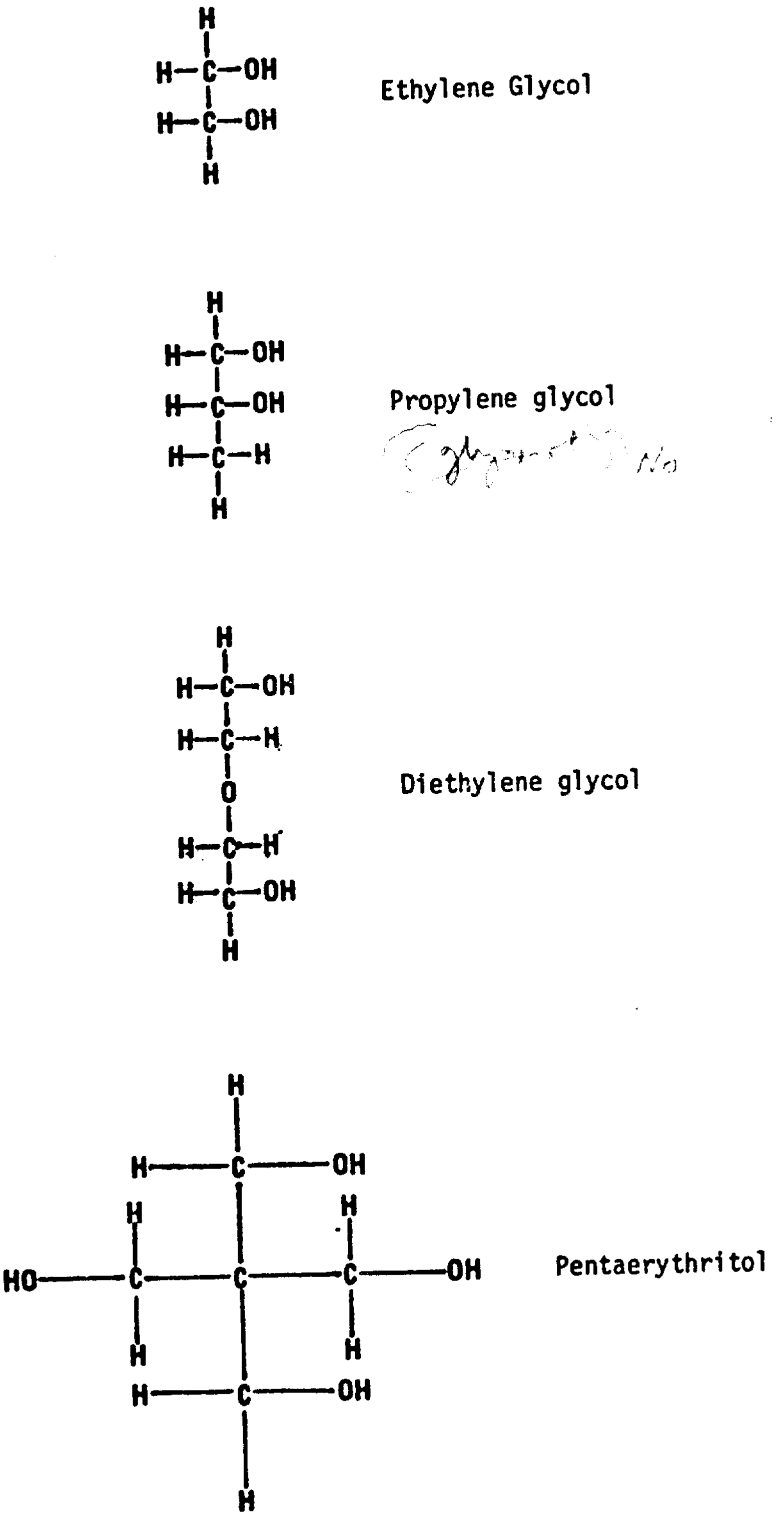
Adipic acid



Isophthalic acid

Figure 3.2-3 Structures of Some Common Saturated Acids

POLYFUNCTIONAL ALCOHOLS



(glycerol) No

[illegible]

Figure 3.2-4 Structures of Some Common Polyfunctional Alcohols cated, and are a component of 95 percent of the gel coats used in the marine industry (Edwards, 1979). Adipic acid, because of its long flexible aliphatic carbon chain, is used when a high degree of flexibility is desired. By lowering the concentration of double bonds, the saturated acids also alter the reactivity of the polyester (Czarnomski, 1979). The molar ratio of the saturated to unsaturated acid varies but is commonly between 1:1 and 1:1.5 (Kent, 1974).

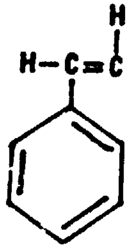
The third constituent of the unsaturated polyester backbone is the polyfunctional alcohol. Ethylene glycol is commonly used. It is frequently supplemented with propylene glycol, diethylene glycol, or dipropylene glycol to decrease the tendency for the liquid resin to crystallize and to increase the flexibility of the cured resin (Kent, 1974). According to Edwards (1979), gel coats composed of neopentyl glycol in combination with isophthalic acids have the best weatherability.

Cross-linking Agents

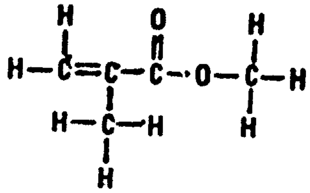
Unsaturated polyesters generally do not undergo homogeneous polymerization, even at high temperatures. In order to form a resin, therefore, it is necessary to add a cross-linking agent. Figure 3.2-5 shows the structures of several monomers used for this purpose, while Table 3.2-2 summarizes their properties. The most common cross-linking agent by far is styrene. According to our survey, the next-most frequently used monomer in California is methyl methacrylate. Vinyl toluene ranks a distant third. These compounds are discussed further in Section 3.2.2.

Figure 3.2-6 depicts a typical cross-linking reaction. Cross-linking requires the formation of three types of radicals: those of the unsaturated acid, the cross-linking monomer, and a catalyst. If temperature is applied to the resin mixture, then the catalyst decomposes thermally and initiates the reaction. At room temperature, however, it is necessary to add a "promoter" or "initiator." These components are discussed below.

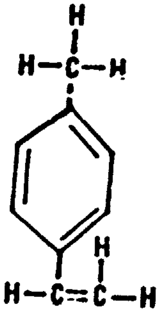
In a typical resin, about 95 percent of the unsaturation sites are reacted with the cross-linking agent (Boenig, 1964). It should be noted that both monomer-unsaturated acid and monomer-monomer reactions occur. In the case of styrene, an average of two monomers link up to form a bridge between two segments of polyester backbone.



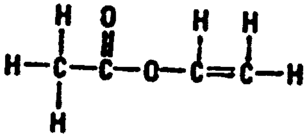
Styrene



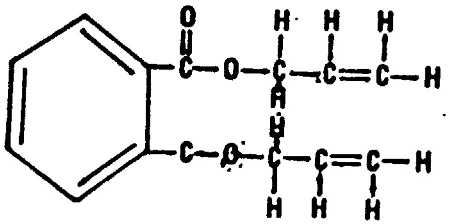
Methyl Methacrylate



Vinyl Toluene



Vinyl Acetate



Diallyl Phthalate

Acrylamide

Figure 3.2-5 Structures of Some Common Cross-Linking Agents in Polyester Resin

Table 3.2-2

PROPERTIES OF CROSS-LINKING AGENTS IN POLYESTER RESIN

Compound	Molecular Weight	Boiling Point, °C	Characteristics
Styrene	104.14	145.2	Good reactivity, low cost, wide availabilty
Methyl methacrylate	100.11	145.2	Reduced resin viscosity, improved optical qualities, improved weather resistance
Vinyl toluene	118.18	172	Short cure time, higher resin viscosity, higher cost
Vinyl acetate	86.1	72	Highly volatile. Poor weather and water resistance
Diallyl phthalate	246.25		Requires high-temperature cure; higher resin viscosity, high cost; lower volatility during cure
Acrylamide	71.08	(solid)	Water soluble, requires pressure, not a solvent
2-ethyl hexylacrylate	184.3	215	Mild irritant, flexibilizes resin, high cost

Source: Brighton et al., 1979; Verschueren, 1977

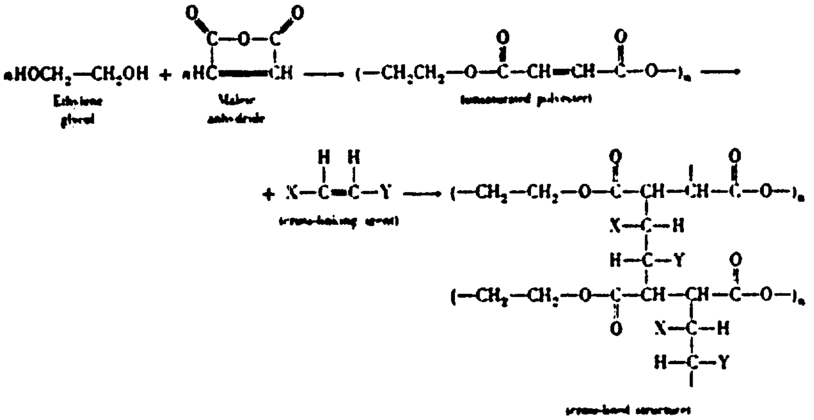


Figure 3.2-6. Typical Cross-Linking Reaction for Polyester Resin Formation.

Catalysts, Inhibitors and Promoters

Although methyl ethyl ketone peroxide (MEKP) and other such reagents are commonly called "catalysts" in the industry, they are more correctly termed polymerization initiators, since the free radicals generated become chemically bonded to the crosslinked resin (Lucidol, 1980). Our industrial survey (see Chapter 4) found that about 92 percent of the firms in California use MEKP, and that these firms account for about three quarters of the state's polyester resin use. The only other catalyst used to any appreciable extent is benzoyl peroxide (BP), which is commonly associated with high-temperature cures. Catalysts used in a few places include cumene hydroperoxide; peroxydicarbonate; and 2,4-pentanedione peroxide. Catalyst concentrations generally range from 1.0 to 2.0 percent by original weight of resin, depending upon desired gel time; the higher the catalyst concentration, the faster the cross-linking reaction proceeds.

Although the reaction rate is slow, polyester resins will self-cure without a catalyst if given enough time. The exothermic nature of the reaction could lead to explosion and/or fire if the resins are not stored properly. To avoid these problems, resin manufacturers add inhibitors such as para-tertiary-butyl-catechol and hydroquinone. Other inhibitors include phenolic resins, aromatic amines, pyrogallol, chloranil, and picric acid (Anon., 1970). It should be noted that oxygen is a powerful inhibitor.

The function of promoters is to activate decomposition of the peroxide catalyst. Common catalyst/promoter combinations include MEKP/cobalt naphthenate, MEKP/cobalt octoate, and BP/diethyl aniline, (Czarnomski, 1979). The reaction between the catalyst and the cobalt initiator is:

$$\text{R-O-O-H} + \text{Co}^{2+} \longrightarrow \text{R-O}\cdot + \text{OH}^{-} + \text{Co}^{3+}$$

The cobaltic ion generated by this reaction is reduced to its original form by reaction with more undissociated peroxide:

$$\text{R-O-O-H} + \text{Co}^{3+} \longrightarrow \text{R-O-O}\cdot + \text{H}^{+} + \text{Co}^{2+}$$

Promoters reduce the temperature at which the catalyst normally thermally decomposes and thus initiate the cross-linking reaction at lower temperatures (Gallagher and Kamath, 1978). Since mixing cobalt salts and catalyst directly is dangerous, most resin manufacturers now add promoters to the resin before sale; such resins are called "promoted."

Other Additives

A wide variety of organic and inorganic compounds are added by resin manufacturers and users to obtain desired product properties. The following discussion is, except where otherwise noted, based upon a review by Czarnomski (1979). Thixotropic agents such as pyrogenic silica are added to permit the fabricator to apply resin to vertical mold surfaces without the problem of dripping. Resin extenders, which are usually added by the polyester resin/fiberglass fabricator, reduce cost, modify physical properties, reduce shrinkage during cure and provide or increase flame retardance. The most common extenders, which are used heavily in the artificial marble industry, include alumina trihydrate (ATH), calcium carbonate, and various clays and talcs. Antimony oxide is also used. Aluminum alkoxid compounds may be used to eliminate the clouding that sometimes results from impurities in phthalic anhydride (Anon., 1978a). One chemical manufacturer claims that addition of dicyclopentadiene (DPCD) to polyester resin lowers the resin density (allowing lower resin use) while conserving mechanical properties (Nelson, 1978).

Polyester-Based Materials Not Considered

As polyester is a component of several important reinforced plastics not considered in this study, it is worthwhile to described them briefly and explain why they were excluded. Foamed polyester, which is not yet used to an important extent in California but which could be a styrene-saving substitute for many conventional liquid unsaturated polyester formulations, is discussed in Section 3.3.8.

Sheet Molding Compound (SMC). Sheet molding compound is a one-component molding system consisting of polyester resin, extenders, catalysts, release agents, pigments and glass fibers (Czarnomski, 1979). It is formed by impregnating the glass fiber with a "paste" composed of the other ingredients and compressing the mixture between polyethylene sheets (Lichtenberg, 1979). A typical use of SMC in fabrication is to compress it in matched-die molds. Up to now, the principal products made with SMC have been automobile parts, including front end panels, head lamp housings, spoilers, window frames, air deflectors and wheel covers. The auto industry is considering SMC formulations having 60 percent glass fibers (as opposed to the more typical 20 to 30 percent) for structural parts such as transmission and radiator supports (Czarnomski, 1979). Many new uses are reported in the trade journals; these include laundry tubs, machine housings, bathtubs, house sidings and shutters, welding helmets, and a variety of other products. SMC was excluded from the study because both the means of formulation and application appear to have a low potential for organic vapor emissions.

Bulk Molding Compound (BMC). Bulk molding compound is prepared by blending short (0.3 to 1.3-cm) glass fibers with polyester resin, fillers, and other additives into a putty- or dough-like consistency. BMC can be blended by the fabricator or bought in bulk to be used in compression and injection molding, or used as solid pellets or extruded preforms in compression or transfer molding (Lichtenberg, 1979). Typical products made with BMC include automobile distributor caps, circuit breaker housings, and other electrical parts. BMC was excluded because it is a thermoplastic material and has a low potential for organic vapor emissions.

Other Thermoplastic Polyesters. A material of increasing popularity is polyethylene terephthalate (PET), a thermoplastic polyester (Kirshenbaum and Rhodes, 1979). Most of the growth in use of PET in recent years has been in the beverage container industry, although it has been used for quite some time in food packaging film, clothing, carpeting and tire cord. No cross-linking agent is used in formulation or fabrication.

Polybutylene terephthalate (PBT) is another thermoplastic polyester. It is formed from the polycondensation of 1,4-butanediol and dimethyl terephthalate (Avery, 1979). Since it is a solid at room temperature and is used in injection molding, the potential for organic vapor emissions is quite low.

Copolyesters. Copolyesters are synthesized from more than one glycol and/or more than one dibasic acid (Rich, 1979). An example is a polyester copolymer based on terephthalic acid (PCTA), which is composed of cyclohexanedimethanol, terephthalic acid, and another acid, and is used for making packaging film. Copolyesters are solids at room temperature and have either a crystalline or an amorphous structure, depending upon their ingredients. They do not contain low-molecular-weight cross-linking agents and therefore have a low organic vapor emission potential.

3.2.2 Compounds of Potential Air Pollution Concern

The most important component of unsaturated polyester resin systems is styrene, since it is volatile, heavily used, and photoreactive. The following discussion, except where otherwise noted, is based upon a review of styrene and other alkyl benzenes by Santodonato et al. (1980). The chief properties of concern are styrene's odor threshold and its photoreactivity. One of the chief problems with styrene emissions, especially from facilities in or near residential areas, is that the compound can be detected at very low ambient concentrations. Estimates of odor threshold vary from 0.036 mg/m^3 (Verschueren, 1977) to 0.34 mg/m^3 (Smith and Hochstettler, 1969). (At 25 °C, these concentrations correspond to 8.4 and 80 ppb.) The higher of these two values has been reported by May (1966).

On the few occasions when they have been measured in ambient urban air, styrene concentrations have generally been below 10 ppb. Table 3.2-3 lists the concentrations measured by Neligan et al. (1965) in Southern California air. Concentrations in Los Angeles were below the 0.5-ppb limit of detection of the flame ionization gas chromatography method used. By reacting styrene with bromine and analyzing the resulting styrene dibromide with an electron capture detection system, Hoshika (1977) was able to detect styrene concentrations as low as 0.1 ppb. Concentrations of 0.2 ppb were measured in urban air in Japan by this technique.

Styrene does not absorb ultraviolet radiation with wavelengths greater than about 300 nm. It is therefore not likely to be photochemically decomposed by direct absorption of sunlight near the earth's surface. However, according to Santodonato et al., styrenes and ethylbenzenes "are among the most active generators of photochemical smog." The most important reaction is electrophilic addition (by atomic oxygen, ozone and other oxidants) to the olefinic double bonds. Santodonato et al. predict, in the absence of actual data, that the final reaction products would be peroxides, formaldehyde and benzaldehyde. The rate of reaction of styrene with hydroxyl radical has been estimated to be 7390 ppm^{-1} min^{-1} (Atkinson et al., 1981). This rate is considerably lower than those for alkanes (generally 10000 to 20000 ppm^{-1} min^{-1}), aldehydes (14000 to 46000 ppm^{-1} min^{-1}), and other alkylbenzenes (20000 to 60000 ppm^{-1} min^{-1}).

No data on methyl methacrylate or other cross-linking agents were available. From their structures, however, these compounds would be expected to be photoreactive also. Methyl methacrylate's odor threshold (210 ppb) is higher than that for styrene (May, 1966).

Table 3.2-3
STYRENE CONCENTRATIONS IN SOUTHERN CALIFORNIA AMBIENT AIR SAMPLES

Location	Time	Concentration (ppb)
Azusa		
	0900	4
	1000	5
Burbank		
	0600	2
	0900	3
Inglewood		
	0700	8
	0730	15
Long Beach		
	0700	2
	0730	1
Los Angeles		
	0600	a
	0700	a

Source: Neligan et al., 1965 (cited in Santodonato et al., 1980).

[a] Below detection limit of 0.5 ppb.

3.2.3 Trends in Use of Polyester Resin

The industry survey conducted under this project and described in Chapter 4 determined with a fair degree of accuracy how much unsaturated polyester resin was used in California in 1980-1981. The polyester resin/fiberglass industry was clearly in a slump during that period. About 15 percent of the firms believed to have been polyester resin users had gone out of business or had moved from California. Many survey respondents reported that production was less than half of normal and that their plants were operating fewer hours per day or days per week. Especially hard-hit was the marine industry, a major user of polyester resin in California. Boat sales suffered from the poor state of the economy in general, high fuel costs, and a lack of mooring spaces in Southern California, while manufacturers found land and labor costs to be lower in Florida (Byron, 1980). For the country as a whole, marine use of reinforced plastics fell by 28.6 percent from 1979 to 1980, and by 36 percent from 1978 to 1980 (Anon., 1981a).

Figure 3.2-7 shows U.S. production of unsaturated polyester resin for every year between 1970 and 1981. Between 1970 and 1973, production almost doubled; there then followed a two-year slump. Production reached a peak of 1.2 billion pounds in 1978 and declined during the next two years. The decrease between 1979 and 1980 was 17.4 percent. Another trend which can be discerned from data compiled by the Society for the Plastics Industry, Inc. (Anon., 1981b) is that unsaturated polyester resin's share of the plastics market (thermosetting plus thermoplastic resins) has declined rather steadily over the past ten years. In 1980, the resin accounted for 3.07 percent of U.S. production, compared with a high of 4.31 percent in 1973.

Industry experts have expressed optimism about a modest recovery of reinforced plastics sales during 1981-1982 (Anon., 1981a). Whether this optimism proves to be realistic will depend upon the ability of the industry to overcome the dampening effect of continued high interest rates upon purchases of products which account for a high percentage of polyester resin use, including boats, cars, houses and appliances. Among the factors which may stimulate recovery in California's boatbuilding industry--despite the high interest rates--are consistent growth in sailboat and canoe sales (even as yacht sales decline), increases in the prime boat-buying population, use of expensive yachts as investments and tax shelters, and increased use of

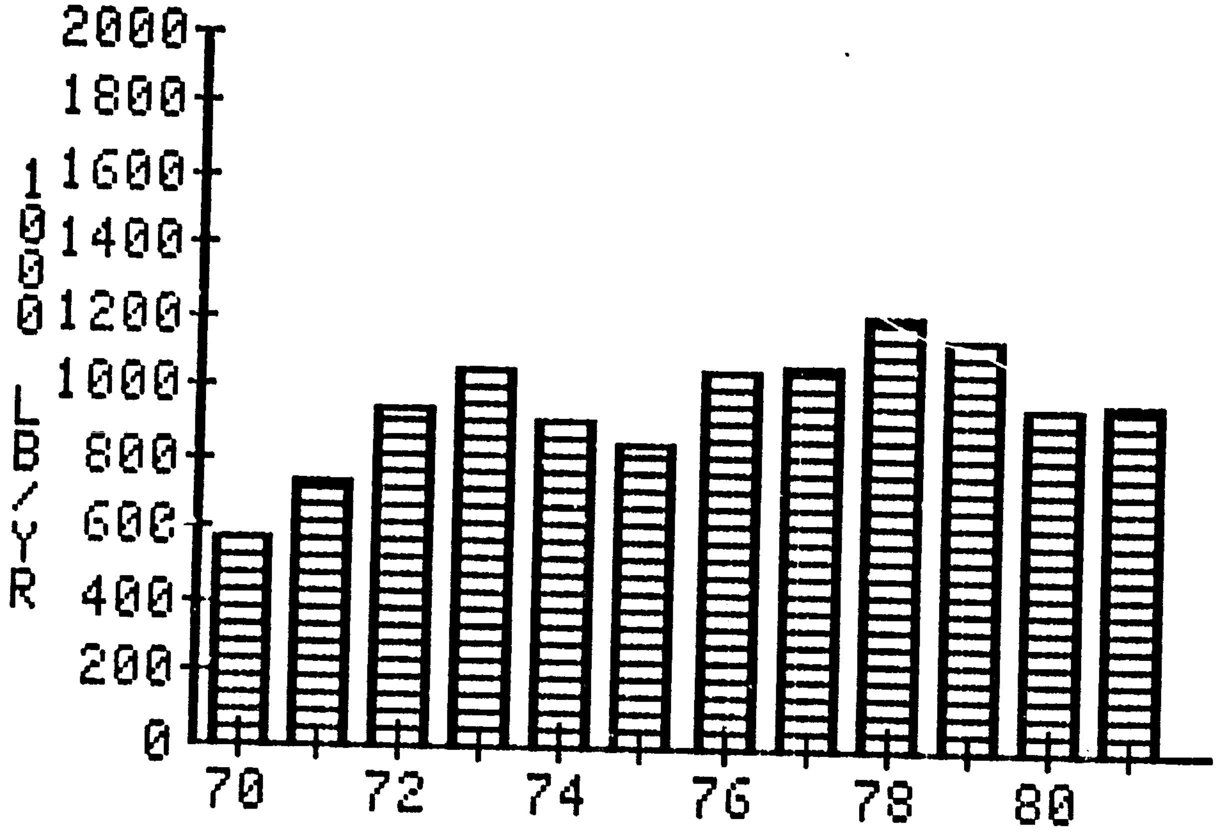


Figure 3.2-7. U.S. Production of Unsaturated Polyester Resin, 1970 - 1981 (Anon., 1981b)

fuel-efficient diesel engines in watercraft (Sing, 1981). In addition, according to one synthetic marble manufacturer we interviewed, the current slump in the home construction market is being offset by growth in sales of artificial marble for home remodeling. Increased use of thermosets in the auto industry is also expected (Anon., 1981c). Polyester resin sales declined through the first half of 1981, although the rate of decline steadily decreased; in fact, by July 1981 sales were increasing at an equivalent annual rate of about three percent (Anon., 1981d). As seen in Figure 3.2-7, this recovery continued for the rest of 1981.

Meanwhile, the trend in general-purpose polyester resin prices has been upward. The average resin price rose from 54 cents per pound in 1979 to 58 cents per pound in 1980, and is currently at 61 cents per pound (Anon., 1981d). Deregulation of the price of natural gas, from which about half of the weight of a typical polyester resin is derived, could lead to further price increases.

3.3 PRODUCTION PROCESSES

The potential for emission of organic vapors from polyester resin/fiberglass fabrication varies with the manner in which the resin is mixed, poured, manipulated and cured. In order to gain at least a qualitative understanding of the emission potential of various fabrication processes, project staff held numerous discussions with plant operators and toured seven facilities. As will be discussed in Section 4.3, our survey of polyester resin users determined that eight processes, singly or in combination, account for the vast majority of resin use in California. These are, in descending order of resin use:

- Spray layup
- Hand layup
- Continuous lamination
- Marble casting
- Pultrusion
- Filament winding
- Bag molding
- Matched metal molding

These processes, along with others which may see increasing use during the next decade, are described in the following subsections. Along with each description, judgments of the relative potential for organic vapor emissions are presented.

3.3.1 Hand Layup

Hand layup, which is the oldest method of polyester resin/fiberglass fabrication, is used by over two-thirds of the polyester resin users in California. Figure 3.3-1 shows a typical hand layup process. The mold, which defines the shape of the outermost surface of the finished product, is itself generally made of reinforced plastic; isophthalic polyester resins are frequently used. The first step in production consists of coating the mold with a releasing agent, such as wax, to ensure that the finished product may be removed after cure. Then, in most cases, a layer of "gel coat," which consists of unsaturated polyester resin, catalyst and (optionally) colorants, is applied. Since the gel coat layer is closest to the mold, it forms the outermost surface of the finished piece. It should be noted that some products, notably surfboards, generally do not include a gel coat layer.

The next step in hand layup is the application of alternate layers of polyester resin and reinforcement material. A wide variety of reinforcements are used, but the most common are glass cloth, woven glass mat, chopped glass strand mat and preimpregnated glass cloth ("prepreg"). The ratio of resin to glass varies with the desired product properties, but is generally in the neighborhood of 60 to 40 by weight. After a reinforcement layer is placed on the mold, it is "wetted out" with resin. The new surface is then "rolled out" by hand with small rollers or squeegees to remove air pockets and other imperfections, and to assure complete contact between resin and reinforcement. The process is continued until the desired thickness is achieved. Because the cross-linking reaction is exothermic, hand layup processes do not need an external heat source to facilitate curing; room temperature cure is the most common.

The potential for organic vapor emissions from hand layup is rather high. A relatively large surface of resin and/or resin-impregnated glass is exposed to the atmosphere for most of the production cycle. Field and laboratory studies of emissions from hand layup processes are discussed in Chapter 5.

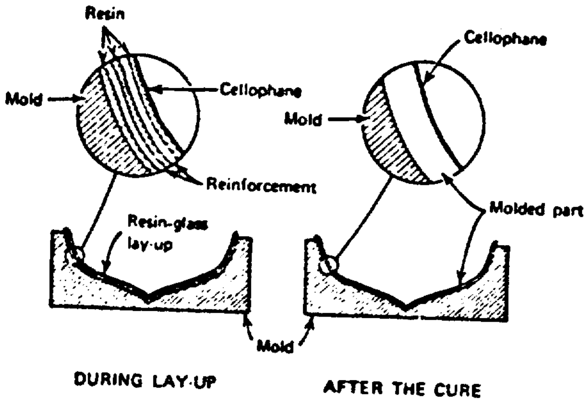


Figure 3.3-1. Typical Mold Arrangement for Hand Layup (Anon., 1970).

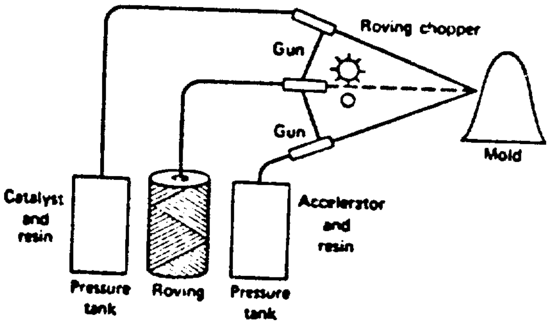


Figure 3.3-2. Schematic of Chopper Gun Molding Process (Anon., 1970).

3.3.2 Spray Layup

Our industry survey showed that about half of the polyester resin/fiberglass fabricators in California use some form of spray application of resin to a mold. In many operations, one of the first steps is to spray the mold with gel coat. Gel coat spray systems consist of separate resin and catalyst sources and an airless spray gun similar to the type used in paint spraying. The two chemical ingredients are mixed as they exit from the gun.

The other principal type of spray apparatus is the "chopper gun" system, which is depicted in Figure 3.3-2. The chopper gun contains a mechanism for cutting glass roving into pieces about one inch long; the chopped glass then mixes with the resin and catalyst streams as all materials leave the gun.

Both types of spraying are done by hand. In each case, the amount of spraying depends upon the desired thickness of the layer being applied. Since the gel coat is usually the first of several coats of resin to be applied to a mold, it is normally not allowed to cure significantly before the next step; the gel coat surface should remain "tacky," so that subsequent layers can readily adhere. Sprayed-on layers of resin and glass are often rolled out by hand, as in hand layup, to remove imperfections.

Of all the production processes reviewed here, spray layup probably has the highest potential for emission of organic vapors. Atomization of resin creates an enormous surface area for evaporation of cross-linking agent. Given the ease of operation, large amounts of resin can be applied rapidly to the mold; our survey found that plants using only spray layup use ten times more resin per plant than do those using only hand layup. Field and laboratory test data on emissions from spray layup processes are presented in Chapter 5.

3.3.3 Continuous Lamination

Continuous lamination is a substantially automated process for mass producing laminates. The following discussion is based upon descriptions by White (1979) and our own inspection of two plants which use this process. Figure 3.3-3 shows a schematic of continuous lamination. Resin and chopped glass are sandwiched between two carrier films and passed through a curing oven.

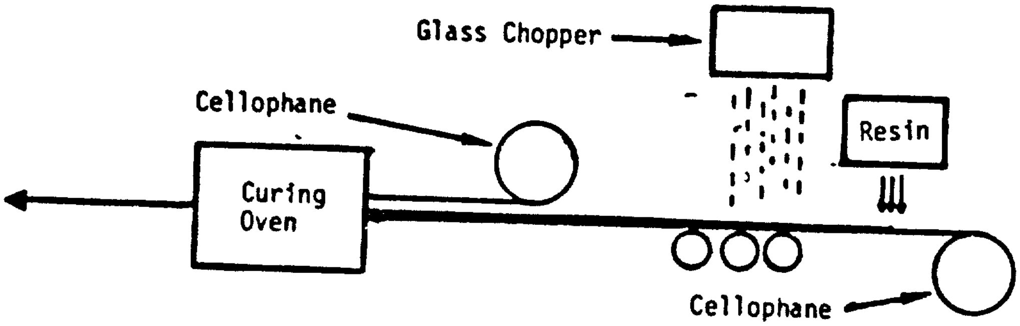


Figure 3.3-3. Schematic of the Continuous Lamination Process

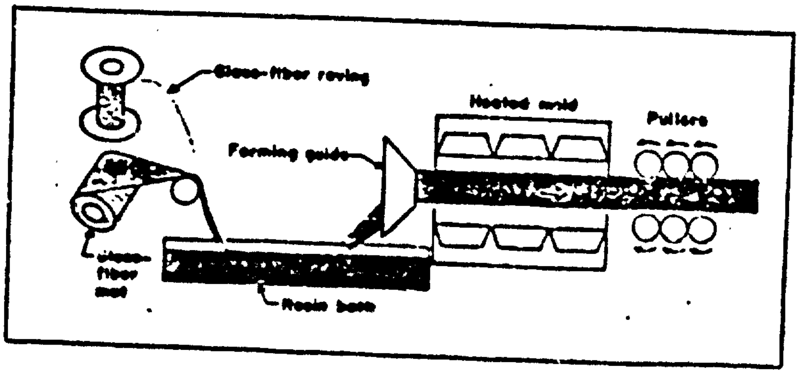


Figure 3.3-4. Schematic of the Pultrusion Process (Martin, 1989)

At the start of the process, resin is metered onto the lower carrier film, which is carried on a conveyor belt. The film, which creates the panel's outer surface, usually consists of polyester, cellophane or nylon, and can be smooth, embossed, or matte-finished. For extra weather resistance, a polyvinyl fluoride film, which permanently bonds to the polyester resin, is used. The polyester resin used in this process usually contains various additives to increase weather resistance and decrease flammability. Common fillers are calcium carbonate and aluminum trihydrate. Methyl methacrylate is sometimes used as the cross-linking agent, either alone or in combination with styrene, to increase strength and weather resistance. After the resin is spread evenly across the carrier film, chopped glass roving is made to fall over the wetted surface.

Shortly before the conveyor belt enters the curing oven, a top layer of carrier film is added. The resulting "sandwich" is pulled through a set of squeeze rollers to eliminate entrapped air and set the sheet thickness. When the laminate enters the oven, it is still very pliable. It is therefore possible to achieve various cross-sectional patterns, such as corrugation, by passing the laminate over a wooden or metal pattern, call a "shoe." Ovens are heated by electricity or gas and operate at temperatures as high as 200 ^{o}C (400 ^{o}F). When the fully-cured laminate leaves the oven, it is trimmed to its final width and cut into desired lengths by saws. The carrier films are then stripped off.

[illegible]

The largest use of continuous lamination is for manufacture of patio covers, awnings, fences and skylights. Depending upon the amount of filler used in the resin, the panel's light transmission can vary from none to 95 percent. Thus another large use is for greenhouse panels. Weather- and chemical-resistant panels are used as louvers in cooling towers. Uses which are increasing in popularity include covers for solar collectors, garage doors and truck/trailer liners.

[illegible] 25 [illegible]

In one of our field tests (see Section 5.2.3), we determined that the most important source of organic vapor emissions from this process was the impregnation table, where a thin layer of polyester resin is exposed for up to a few minutes to the atmosphere. The emission potential increases when the impregnation table is heated, as it was at one of the facilities we visited. Other emission sources are the ovens and the final sawing operations; the latter release some uncured resin, which includes volatile organics, to the atmosphere.

3.3.4 Synthetic Marble Casting

Manufacture of synthetic marble from polyester resin is becoming increasingly popular in California. Resins used for marble production have higher viscosities and lower monomer contents than do laminating resins or gel coats. Fillers such as calcium carbonate and aluminum trihydrate are used to increase product strength and flame resistance. These fillers, along with coloring agents, are added to the resin in large rotating kettles or buckets. In some versions of casting, the mixture is poured into a female mold and stirred by hand to achieve the swirling patterns characteristic of real marble. In other cases, the resin is applied by a trowel to a male mold which has been previously covered with gel coat. A cover is then placed on the mold, and additional resin is poured between the two surfaces.

The potential for organic vapor emissions from marble manufacture is considerably lower than for other production processes, if only because the cross-linking agent content of the resin is lower (30 to 38 percent versus 40 to 48 percent for most laminating resins). Emission rates will also depend Note upon the extent of exposure of the curing material to the atmosphere.

3.3.5 Pultrusion

The following discussion is based upon papers by Wood (1978a), Martin (1979), and Ewald (1979). Pultrusion is a relatively new technique for making substitutes for products which are normally made by thermoplastic processes or by extruding metals such as aluminum. While equipment design varies widely, the basic process is the same: reinforcement materials are pulled continuously through first a resin bath and then a closed mold having the desired cross-sectional shape. The process is thus suitable for long products requiring a uniform cross section, although numerous short products are also manufactured.

Figure 3.3-4 is a schematic of the pultrusion process. Reinforcing material, which is usually glass roving or continuous strand glass mat, is pulled from a creel. If the product is to have high strength only along its longitudinal axis, then the reinforcement material is pulled directly through the system. For greater transverse strength, additional reinforcement may be wrapped around the moving part. This filament wrap may be applied by a stationary creel as the part moves past, or by "overwinding wheels," which orbit around the part and apply the wrap at an angle to the direction of motion. A California firm has developed special equipment to combine winding with pultrusion (Wood, 1978a).

Resin impregnation is accomplished by passing the fibers through a resin tank bath. Polyester resin is used in at least 85 percent, by weight, of pultruded products. The composite is often preheated by application of radio frequency energy before it reaches the heated die. Occasionally, the glass fibers are heated before the resin immersion step. Dies, which are made of metal, are heated electrically with exterior surface contact strips. In some cases, the heat source is internal. The pulling device consists of a set of clamps or a caterpillar tractor. After the pultruded composite emerges from the die, it is trimmed to the desired product length with a crosscut saw; since the process is continuous, the saw must move with the product.

The main advantages of pultruded products are their high strength-to-weight ratios and good electrical insulation, thermal insulation, and corrosion resistance characteristics. Products used in the electrical industry include antennas, suspension and strain insulators, booms for electrical maintenance trucks, fuse tubes and contact rail safety covers. Pultrusion is also used to make building panel insulating strips, chemical plant grating, snowmobile track stiffeners, floor slats for livestock confinement, rail car lading bars, solar collector frames, auto steering control arms, and a variety of other products. On the negative side, pultrusion throughput rates are slower than those for thermoplastic processes. Also, the stiffness of a roving-reinforced plastic bar is low compared to that of the same shape in aluminum, even when the glass content reaches 80 percent, and pultruded products are more expensive per unit weight than those made of extruded aluminum.

The main source of organic vapor emissions in pultrusion would be the resin impregnation bath, since curing takes place in the enclosed mold. The bath configuration could have a significant effect upon the potential for emissions. Long, narrow, deep baths would present the minimum surface area to atmospheric contact. Resin use can be minimized by pumping resin into the tank in carefully controlled amounts as the reinforcement fibers pass through.

If only longitudinal reinforcement is required, then the tank could be substantially enclosed; however, it would be difficult to enclose a system which included an overwinding apparatus. In addition, as one pultruder firm pointed out to us, covering the resin bath would make it very difficult to monitor the wetting of the reinforcement.

3.3.6 Filament Winding

Except where otherwise noted, this section is based upon a description by Como (1979). Filament winding is an increasingly popular method of manufacturing cylindrical products requiring high strength. In this process, continuous strands of reinforcement are impregnated with resin, wrapped around a rotating mandrel, and cured. Because of their high specific strength and relatively low cost, continuous glass fibers are most often used for the filaments; other fiber materials include graphite and aramid. The most common resins are epoxy, polyester, and vinyl ester. Low-viscosity resins are needed to allow resin to flow around each filament (Kober, 1981).

Figure 3.3-5 shows the three most common winding patterns. Note that in each case the mandrel spins but does not move longitudinally or laterally. Circumferential, or hoop, winding is used most often in conjunction with other winding patterns to increase hoop strength. Filaments are applied at right angles to the mandrel's axis of rotation. Helical winding is performed at winding angles of 15 to 85 degrees to the longitudinal axis of the mandrel; the angle determines the ratio of hoop to longitudinal strength. In polar winding, the angle to the longitudinal is from 0 to 15 degrees, and the reinforcing fibers are wrapped over the ends of the mandrel to prevent slippage. The different winding patterns may be used in combination to achieve desired strengths and shapes.

Mandrels are made of a wide variety of materials. To accelerate curing, hollow metal tubes are often used, permitting injection of steam through the center of the product. Mandrels which are to be removed are made in collapsible segments or of materials which can be dissolved or melted after the product is cured. In some cases, the mandrel remains inside the part as a liner or core.

Machinery which combines filament winding with chopper spraying was recently described (Anon., 1978b). First, catalyzed resin is sprayed onto a

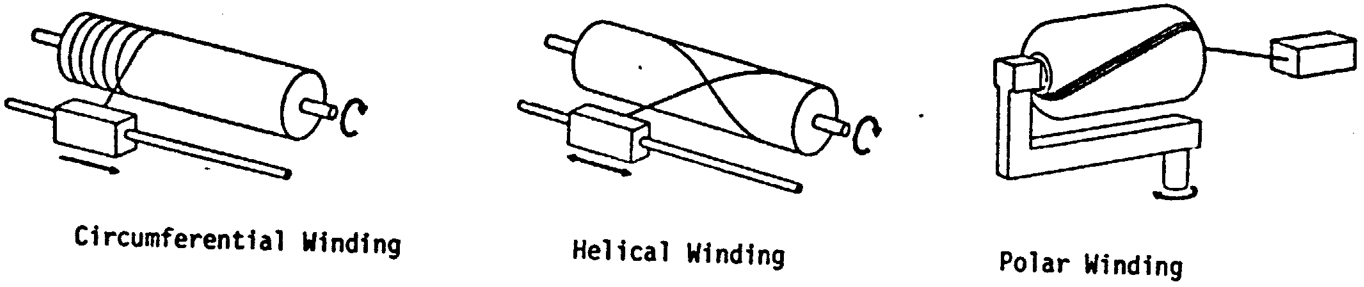


Figure 3.3-5. Three Major Types of Filament Winding (Como, 1979).

mandrel which has been pre-coated with a release agent. A layer of chopped-strand roving and catalyzed resin is then applied. Filaments are wound onto the resin- and glass-coated surface until the desired thickness is achieved. A final surface coating of resin is then applied.

As noted above, filament winding is most suitable for products of relatively uniform cylindrical cross-section. Concave areas, which cause bridging of the filaments, and changes in curvature, which cause filament slippage, cannot be wound conveniently. The process is used mainly for the construction of tanks, pipes, and special pressure vessels. Recent applications include radio towers, radomes, helicopter blades, lift truck booms, automotive drive shafts, and flywheels for energy storage. A prototype railroad hopper car having a filament-wound polyester resin/fiberglass body shell was recently introduced (Anon., 1981e). The car, called a "Glass-hopper," has a greater payload per unit weight than does a conventional steel hopper car, and may be able to absorb and dissipate shock more readily.

The potential for organic vapor emissions from filament winding appears to be moderate. The requirement for low resin viscosity often implies the use of higher ~~resin~~ monomer concentrations than with conventional laminating resins. Furthermore, catalysts are added to the resin in low enough concentrations that cure is delayed until after winding is completed (RCI, 1981); this delay could increase the availability of styrene for emission.

3.3.7 Closed Molding Processes

Bag Molding

In both vacuum bag and pressure molding, the part to be manufactured is first layed up by hand and/or spray techniques. In vacuum bag molding, the layup is covered with a film such as cellophane, polyvinyl alcohol, polyethylene or nylon. A vacuum is then drawn on the "bag" formed by the film and the layup. Atmospheric pressure on the film forces out entrapped air, improves resin distribution and glazes the surface. In pressure bag molding, the layup (which must be on a female mold) is covered with a rubber sheet, to which about 500 psi of pressure is applied. This process results in uniform physical characteristics and eliminates voids. In some cases either type of bagged assembly is placed in an autoclave and heated under pressure. This variant gives the product a higher density and allows use of a higher percentage of reinforcement materials. The emission potential of bag molding depends on the length of time the resin is exposed to the air before the bag is applied, since emissions after bagging would be negligible.

Resin Transfer Molding

Resin transfer molding (RTM) was virtually unknown 10 years ago and is used mainly in Europe (Anon., 1979a). In this process, continuous- or chopped-strand glass fiber mats are placed between the halves of a mold. After the mold is closed, catalyzed resin is injected and allowed to cure exothermically. The mold is then opened, and the finished part is removed. Sandwiches of polyurethane foam and polyester resin may also by made this way. A variation on the technique is to inject the resin at several points and to apply a strong vacuum at one end of the mold; resin flows more evenly through the mold, and voids are eliminated (Anon., 1979b). Vacuum-assisted resin transfer molding has been used in England to make racing yachts having foam cores. Since this process is entirely enclosed its emission potential is low.

3.3.8 New Processes

Application of Foamed Polyester

Foam systems for applying polyester resin to molds have been around for many years, but their use has been negligible. As will be discussed below, the chief problem has been the need--until recently--to store foaming agents at subzero temperatures. Now, however, "with the availability of new technology...and the climate of business increasingly receptive to the economies and other benefits feasible with foam, the stage appears set for a period of real growth" (Anon., 1980a). The process has been used since 1979 in a large bathtub/shower unit facility in Texas (Naitove, 1980).

Apparatus normally used for applying foamed plastics such as polyurethane can be modified for polyester foam use. The unsaturated polyester and the foaming agents are contained in separate canisters; when combined in a spray gun they react and evolve a gas which creates the foam.

The key ingredient in a polyester foam system is the foaming agent. Because of their potential threat to stratospheric ozone, fluorocarbons are not used. The first generation of polyester foaming agents were a family of azo compounds such as 2-tert-butylazo-5-methyl-2-hexanol, developed by Lucidol (a division of Pennwalt Corporation). These compounds decompose in the presence of acidic groups in the polyester resin to form nitrogen gas (Wood, 1978b). Early versions of the agents were highly volatile and had to be stored at -18 °C. Lucidol removed the product from the market in November 1980, after workers allegedly suffered nerve damage (Anon., 1981f). The latest Lucidol product is "Lucel-135," a methoxy azo compound which may be stored at room temperature and which has a pot life of a few days (Anon., 1980b). For room temperature molding the binary system consists of (1) polyester resin and Lucel 135 and (2) polyester resin and a two- to three-percent solution of phosphoric acid.

Another foaming agent has been developed by Whitney and Company of Stratham, New Hampshire. Their EMC-10 and EMC-20 compounds are bisphenylmethyl formulations which react with MEKP to form CO_2 gas. The EMC-10 has a 40-hour pot life and can be pigmented. Standard spray equipment can be used (Wood, 1980).

A second polyester foam system is one developed by Tanner Chemical Company and the Polyceramic Development Center, both in Greenville, South Carolina. The "A" side consists of a one-to-one mixture of low-styrene polyester resin and calcium carbonate, plus a promoter (phenylethyl ethanolamine). The "B" side is a one-to-one mixture of aluminum trihydrate and "Cerfoam," a water-based inorganic polymer of proprietary formulation, plus benzoyl peroxide catalyst. Two parts of A are combined with one part of B via a conventional spray gun fitted with a glass chopper. Acids in the Cerfoam react with the $CaCO_3$, releasing CO_2 gas, which produces the foam. During the exothermic reaction, a "ceramic cure" takes place, locking the water within the Cerfoam matrix (Anon., 1980c; Sels, 1981).

Light Curing of Resins

This relatively new technique uses visible light to convert a catalyst, which is added to polyester resin by the manufacturer, to a free radical. According to the developers of the technique (Dixon et al., 1977), resins gel and cure from the outside in. Since the outer layer cures within 10 to 15 seconds, styrene is trapped within the resin and emissions are reduced. Resins used in this process contain about 50 percent styrene, and cannot be pigmented (Lane, 1981). Xenon lamps designed to emit a specific wavelength to which the catalyst system is sensitive have been developed. The process has been used so far in conjunction with filament winding of pipes.

3.4 REGULATORY FRAMEWORK

3.4.1 Federal Regulation and Policy

The U.S. Environmental Protection Agency (EPA) has no New Source Performance Standards (NSPS) for the reinforced plastics fabrication industry and no regulatory measures are currently being considered (Crumpler, 1980). The EPA's Office of Air Quality Planning and Standards recently sponsored a screening study to determine whether NSPS should be set for the fiberglass manufacturing industry, but neither that study nor the regulations tentatively being considered have any bearing upon polyester resin/fiberglass fabrication (Telander, 1980).

3.4.2 State Regulations

Under the Clean Air Act Amendments of 1977, each state is to formulate and receive EPA approval for a State Implementation Plan (SIP) for preventing significant deterioration of air quality where federal primary ambient air quality standards are currently met and for achieving the standards in current non-attainment areas. Activities and regulations relating to federal and state ambient standards generally fall within one of two arenas--Prevention of Significant Deterioration and Non-Attainment.

Prevention of Significant Deterioration

Under the Prevention of Significant Deterioration (PSD) provisions of the Clean Air Act, three classes of "clean air" areas were created, a clean air area being one in which the federal ambient standards for SO_2, total suspended particulates, carbon monoxide, NO_x, hydrocarbons and ozone are met. In each classification, air quality is permitted to deteriorate by a prescribed maximum increment above the baseline condition existing at the time of the first permit application in a clean air area. These increments must be shared by all present and future sources in and around each air quality control region.

Non-Attainment

Any air quality control region in which the federal ambient standards are violated is designated as a non-attainment area. Construction of new or modified facilities in these areas is governed by EPA's emission offset policy, unless the state's SIP is adequate to manage non-attainment areas. Under this policy, major sources must meet the following requirements before a construction permit may be issued:

- Emissions from the proposed facility must be more than offset by reducing emissions from existing sources, resulting in a positive net air quality benefit and reasonable further progress toward attainment of the ambient standard. A portion of "excess" offset credit may be banked for future use by the applicant, but interpollutant tradeoffs are not permitted.
- The proposed facility must have the Lowest Achievable Emission Rate.
- Any other major sources within the state which are owned by the applicant must be in compliance with applicable emissions standards or compliance schedules.

The Lowest Achievable Emission Rate (LAER) is defined as (1) the most stringent achievable emission limitation for a source category found in any SIP or (2) the most stringent emission limitation achieved in practice (or which can be reasonably expected to occur in practice) for that source category. The most stringent of these options is applicable (Ember, 1978). Draft LAER's are currently circulating for comment.

3.4.3 Local District Regulations

All the California local air pollution control districts (APCDs) having polyester resin/fiberglass fabrication operations within their jurisdiction were contacted in order to determine the extent to which styrene emissions from these processes were regulated. Table 3.4-1 lists the districts and the individuals we contacted.

Most of the districts include styrene emissions under their organic solvent rules or under new source review (NSR) regulations. While styrene, as the cross-linking agent in the polymerization of polyester resin, is incorporated permanently in the resin structure, it also serves as a diluent. Inclusion of polyester resin/fiberglass fabrication in organic solvent regulations is therefore logical. Since, as will be discussed in the next chapter, unambiguous classification schemes for this source category are lacking, the organic solvent approach is perhaps appropriate, even for cases in which styrene is not used as a diluent. We have recommended that the ARB establish category of emission source (CES) numbers for the several polyester resin/fiberglass fabrication processes. (See Chapter 2.).

Table 3.4-1

CONTACTS WITH CALIFORNIA LOCAL AIR POLLUTION CONTROL DISTRICTS WHERE POLYESTER RESIN/FIBERGLASS OPERATIONS CAN BE FOUND

Local Air Pollution Control District	Name of Contact
Fresno County	Charles Maskel Air Pollution Engineer
Glenn County	Ed Romano
Kern County	Leon Hebertson, M.D. Air Pollution Control Officer
Madera County	Bill Stork
Merced County	Richard Wachs Air Pollution Engineer
Monterey Bay Unified[a]	Ed Kindig Air Pollution Engineer
Northern Sonoma County	Michael Tolmasoff Air Pollution Control Officer
Placer County	Kenneth Selover Air Pollution Control Officer
Sacramento County	Bruce Nixon Air Pollution Engineer
San Joaquin County	Mr. Grewall
San Luis Obispo County	Robert Carr Asst. Air Pollution Control Officer
Shasta County	Dale Watson Deputy Air Pollution Control Officer
Sutter County	Alfred Perrin, Jr. Air Pollution Control Officer
Tehama County	Donald Hill Air Pollution Control Officer
Tulare County	Mr. Johnson

Table 3.4-1
CONTACTS WITH CALIFORNIA LOCAL AIR POLLUTION CONTROL DISTRICTS WHERE POLYESTER RESIN/FIBERGLASS OPERATIONS CAN BE FOUND
(continued)

Local Air Pollution Control District	Name of Contact
Ventura County	Jan Bush Air Pollution Control Officer
Yolo-Solano	Mr. Koslow
Yuba County	Dave McBride
Bay Area	Bill deBoisblanc Chief of New Source Review
South Coast	
San Diego County	Ray Skoff Associate Air Pollution Control Engineer
Santa Barbara County	Doug Grappie Air Pollution Engineer

[a] Includes Monterey, Santa Cruz and San Benito Counties.

None of the 22 affected local APCDs has specific emission rate regulations governing the release of styrene from polyester resin/fiberglass manufacture. However, both the Bay Area Air Quality Management District (BAAQMD) and the Shasta County APCD allude to the use of polyester resin in reinforced plastic manufacturing processes in their organic solvent regulations (BAAQMD Regulation 8-4-111, Shasta County Rule 3:4, b.,3.). The Bay Area regulation exempts users of polyester resins if such use, after application, does not result in the emission of organic gases in excess of 6 percent by weight of the resin. Shasta County also grants exemptions for users of polyester resin. Here, the maximum percent loss of organic gas from gel coat and laminating resin processes may not exceed 22 and 8 percent by weight, respectively. This particular exemption expired as of January 1, 1982 and there are presently no plans to update the old rule (Watson, 1982).

New source review regulations were the only other potentially applicable regulations cited by local air pollution officials. For example, in order to comply with non-attainment regulatory obligations, Sacramento County APCD's NSR rules provide that "best available control technology" (BACT) must be used if VOC emissions are between 150 and 250 pounds per day. If the operation emits more than 250 pounds per day VOC, then pollution offsets must be granted to surrounding air pollution sources (Nixon, 1982).

The Monterey Bay Unified APCD's NSR regulation is essentially the same except that if a new or modified operation emits more than 200 pounds per day, then emission offsets and "lowest achievable emission rates" (LAER) apply (Kindig, 1982). The remaining districts located in non-attainment areas either use slight variations of the above NSR scheme or use quidelines such as the old Los Angeles County organic solvent use code, Rule 66.

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4.0

SURVEY OF POLYESTER RESIN USE IN CALIFORNIA

The objective of this part of the project was to characterize the polyester resin/fiberglass industry in California. In order to estimate emissions and formulate control strategies, we needed to know how many plants there were, where they were located, how much polyester resin they consumed, and what production and control processes they used. We therefore conducted a survey of the industry, and, from the information obtained, we constructed an emission inventory. This chapter describes our survey methods and results.

4.1 SURVEY METHODS

4.1.1 Sources of Names of Polyester Resin Users

Before this study was conducted, no comprehensive list of polyester resin users in California was known to exist. Since polyester resin is used in a wide variety of industries, use of the resin could not be unambiguously associated with any Standard Industrial Classification (SIC) code. Furthermore, SIC codes under which many polyester resin users fall are applicable to an equal or greater number of non-users. Those SIC codes most likely to include the types of firms under consideration were 3079 (Miscellaneous Plastics Products) and 3732 (Ship and Boat Building and Repairing). Sources of names of polyester resin users included the following.

California Manufacturers Register

Previous experience had shown the California Manufacturers Register (CMA, 1980) to be useful in identifying companies under given SIC codes. We therefore began our survey by reviewing the listings in this publication under codes 3079 and 3732. Since the products of each firm are reported, we were able to eliminate from consideration those which were obviously not polyester resin users. Nevertheless, only about one-third of the companies remaining after this initial screening turned out, upon being surveyed, to be users. Because inclusion in the California Manufacturers Register is voluntary, a large number of polyester resin users -- including some very large ones -- were not listed. Roughly 100 companies were identified through this source.

Statewide Emission Inventory

Early in the project, we asked the ARB's Stationary Source Emissions Division to run a search on the Emission Data System (EDS), using SIC codes 3079 and 3732, along with the U.S. Environmental Protection Agency's Source Classification Code 3-08-007-99 ("Fabricated Plastic Products, Other/Not Classified") to identify possible polyester resin users. The search identified 87 firms, some of which had already been found through the California Manufacturers Register. Three problems with using the inventory were encountered. First, 34 of the firms were, according to the process descriptions reported by the EIS, not polyester resin users. Second, several firms had gone out of business since 1977, when the inventory had last been updated. Finally, since the inventory generally contains firms having certain minimum emission rates of criteria pollutants, many small polyester resin users were not included. In spite of these problems, the inventory search was useful in providing the names of many of the major users, especially in Los Angeles and Orange Counties.

The EDS printout included Source Classification Codes for each of the processes contributing to hydrocarbon emissions. As a set of these may be useful in future studies of this industry, we list them in Table 4.1-1. It is clear from the table that there is currently no unambiguous way to classify sources of emissions from polyester resin/fiberglass fabrication. Codes for surface coating and solvent evaporation are frequently used, although the pollutants of interest are generally an integral part of the manufactured product. The codes beginning with 3-05-12 are more properly associated with the manufacture of wool-type glass fiber materials, not reinforced plastics (USEPA, 1981), yet they have been used for firms which make the latter. The classification problem is discussed further in Chapter 2, Recommendations.

San Diego County Air Pollution Control District

At our request, the San Diego County Air Pollution Control District ran a search of its own stationary source emission inventory. Most of the 25 firms identified turned out to be polyester resin users. Relevant characteristics of each plant, including hydrocarbon emission estimates, were included in the computer printout.

Table 4.1-1

SOURCE CLASSIFICATION CODES (SCC) ASSOCIATED WITH POLYESTER RESIN/FIBERGLASS OPERATIONS

SCC NO.	Standard Definition	Description in Statewide Emission Inventory
3-05-012-04	Fiberglass mfg: forming line	None
3-05-012-99	Fiberglass mfg: other/not classified	Air-cured fiberglass, fiberglass bath features, fiberglass spray booth
4-02-001-01	Surface coating-paint: general	Fiberglass resin spray
4-02-003-01	Surface coating-varnish/shellac: general	Gel coat, polyester resin, spray booth
4-02-005-01	Surface coating-enamel: general	None
4-02-005-49	Surface coating-enamel: solvent general	Spray booth
4-02-007-01	Surface coating-adhesive: general	None
4-02-008-03	Surface coating-coating oven: baked >175°	Coating-drying, laminated board processing
4-02-009-02	Surface coating-solvent: acetone	Gelcoat, resin
4-02-999-99	Surface coating-solvent: to be specified	Gelcoat, gelcoat spray, polyester spray
4-90-999-99	Miscellaneous HC evaporation: to be specified	Fiberglass, gelcoat, resin

Bay Area Air Quality Management District

On 23 July 1980 SAI staff visited the Bay Area Air Quality Management District (BAAQMD) office in San Francisco and reviewed a list of permit holders. BAAQMD staff pointed out which of the holders were known to be polyester resin users. Names and addresses of 40 plants were obtained. Since this particular list had not been updated in several years, 8 of the firms identified turned out to be defunct, and 12 were not actually polyester resin users.

Shasta County Air Pollution Control District (SCAPCD)

While discussing styrene evaporation tests performed by the Shasta County Air Pollution Control District (see Section 5.1.4), we learned from SCAPCD staff that the agency had compiled a list of polyester resin users within its jurisdiction. At our request, the SCAPCD sent us names, addresses, estimated resin use rates, and estimated emission rates for seven firms (Burns, 1980).

Other Local Air Pollution Control Districts

When the survey was about half completed, it appeared that 24 of California's 58 counties had no polyester resin users. To be sure that no users were missed, we sent a cover letter and questionnaire to the corresponding agencies (see Appendix A). The exercise resulted in the identification of 6 additional firms, as well as confirmation of the nonuse of polyester resin in 21 counties.

Society of the Plastics Industry

Local representatives of the Society of the Plastics Industry, Inc. (SPI) furnished us with the 1980 Membership Directory and Buyers Guide (SPI, 1980), as well as assorted other materials on polyester resin manufacturers and users. While the directory contained only a few manufacturers not listed elsewhere, it proved valuable in our survey of resin formulators (see Section 4.1.3).

Telephone Directory

After all of the above mentioned sources of information had been exhausted, it appeared to us that a significant number of polyester resin users had still not been identified. While, as discussed elsewhere in this report, the number of users and the total resin use rate in California are unknown, our tentative totals were lower than those estimated by the air pollution control agencies and resin manufacturers with whom we discussed the matter. We therefore turned to the telephone directories of all major metropolitan areas in California. Names of putative polyester resin users were chosen from among the listings under "Fiberglass Fabricators," "Boat Building and Repairing," "Surfboards," "Marble-Synthetic," and "Tanks." Though tedious, this search proved highly productive.

Other Information Sources

About a dozen users were identified through miscellaneous means. A major resin manufacturer named two of its largest customers. Some plants told us of branch facilities of which we had been unaware. One of the largest users in the state was not listed in any of the sources mentioned here; the principal investigator happened to drive past it one day.

4.1.2 Keeping Track of Firms in Survey

Since almost 950 firms were surveyed, it was necessary to set up a system to keep track of the status of knowledge on each company. First, 3 x 5 inch cards containing preliminary information such as name, address, phone number, and SIC code (if known) were filled out for each putative user. Each company was identified with a unique number, which was later used on questionnaire forms and/or data coding sheets. Figure 4.1-1 shows a typical index card. The name, address and phone number of the company has been deleted to preserve confidentiality. The meaning of the various notations on the card are explained in the figure. During the survey, cards were stored alphabetically in three groups: non-users, users for which data were complete, and users for which data were lacking. Meanwhile, a survey status register was set up to keep track of all the firms. Companies were listed by survey identification number. For each polyester resin user, we recorded the number of the data coding sheet on which it appeared, the date on which information was received, and whether the data had been stored on floppy disk.

4.1.3 Data Acquisition

In conducting our survey, we gave the highest priority to data which could be used to (1) characterize the industry, (2) choose emission test sites, (3) estimate organic vapor emissions and (4) recommend emission control

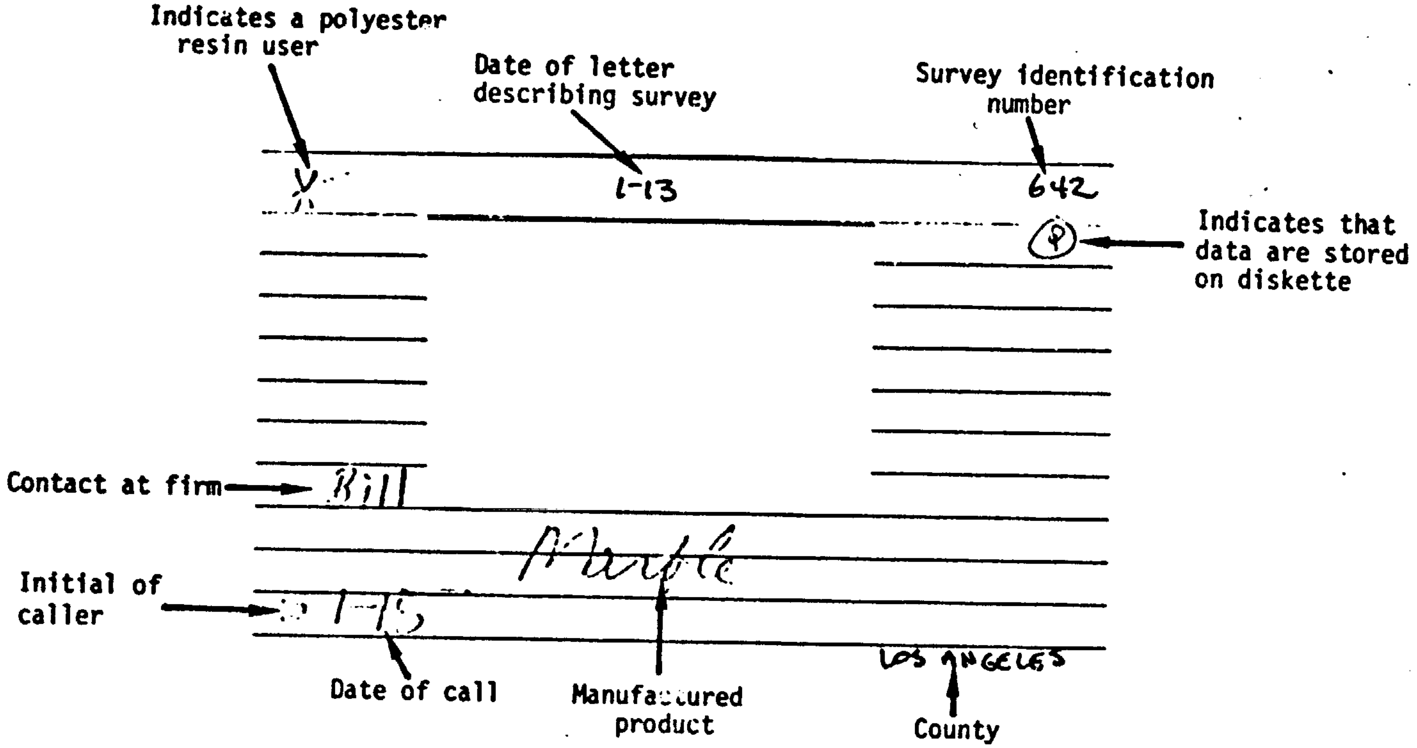


Figure 4.1-1. Example of Survey Index Card

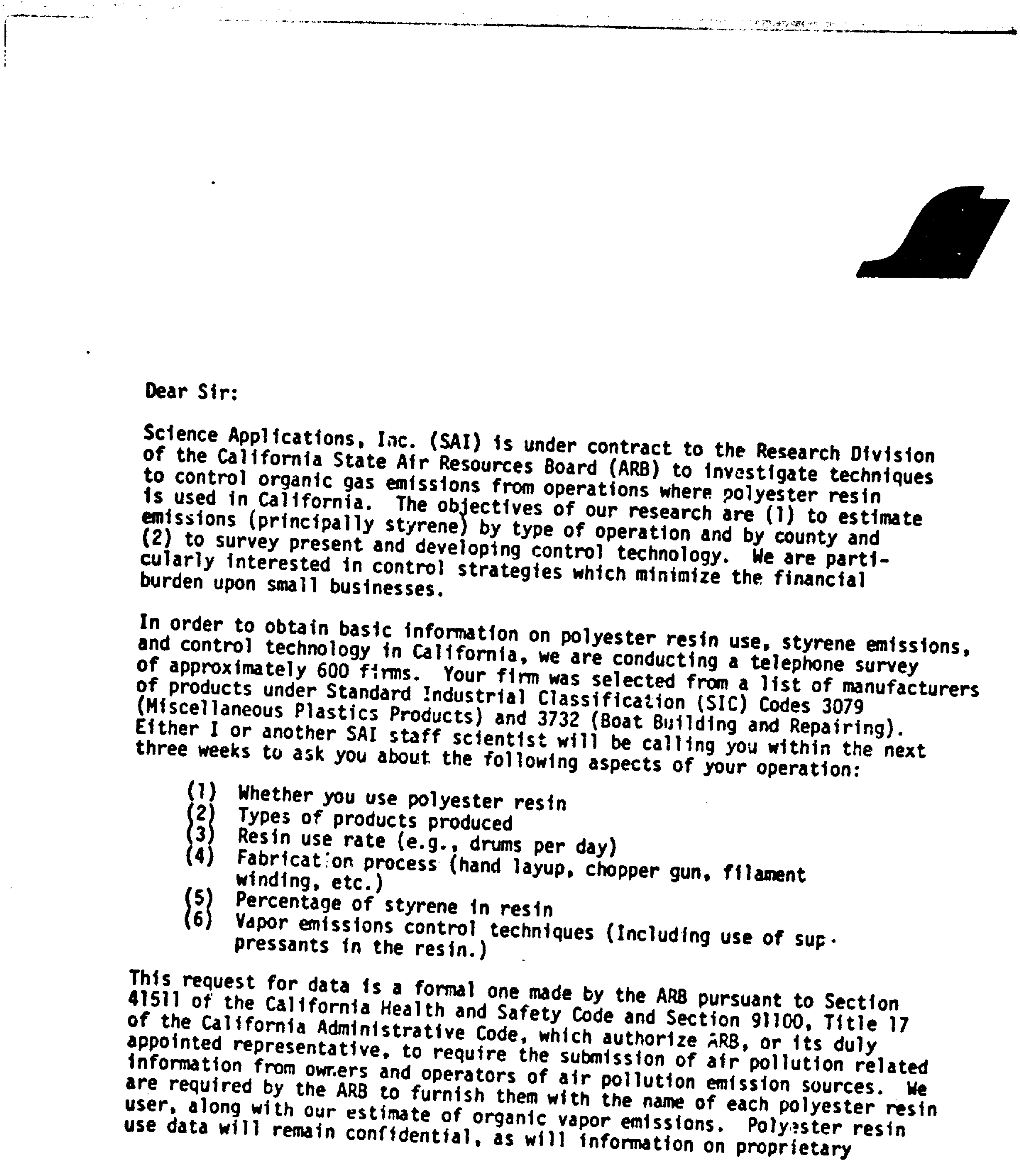
strategies. We therefore limited our survey to what we considered to be the most important items. These were:

- Type of product(s) manufactured
- Fabrication process(es)
- Polyester resin use rate
- Gel coat use rate
- Type of cross-linking agent (monomer)
- Percent of cross-linking agent in resin and gel coat
- Type of catalyst
- Whether a vapor suppressant is used
- Operating schedule
- Emission control system (if any)
- Means of venting vapors to the atmosphere

All but a few of the potential polyester resin users were sent a letter explaining the purpose of the survey and assuring that firm specific information would be furnished only to the ARB. Figures 4.1-2 and 4.1-3 show the letters sent to firms which were contacted by telephone and written questionnaire, respectively. The handful of firms not initially contacted in writing were nevertheless explained ARB's policies regarding confidentiality.

In general, firms which were in the 213 and 714 telephone area codes were interviewed by telephone, while the rest were sent questionnaires. Some companies refused to answer questions by telephone, but did respond in writing. Because we were to establish as complete an inventory of polyester resin users as possible, <u>all</u> firms which did not return questionnaires were later telephoned. In some cases, as many as ten attempts were necessary before an interview could be conducted.

Figure 4.1-4 shows the written questionnaire used in the survey. The same set of questions was used in the telephone interviews, although in many cases considerably more detailed information was obtained. During the telephone interviews, the caller entered certain data items immediately on a coding form, which is discussed below. Resin and gel coat use rates were recorded separately in the form stated by the interviewee (e.g. gallons per day



Dear Sir:

Science Applications, Inc. (SAI) is under contract to the Research Division of the California State Air Resources Board (ARB) to investigate techniques to control organic gas emissions from operations where polyester resin is used in California. The objectives of our research are (1) to estimate emissions (principally styrene) by type of operation and by county and (2) to survey present and developing control technology. We are particularly interested in control strategies which minimize the financial burden upon small businesses.

In order to obtain basic information on polyester resin use, styrene emissions, and control technology in California, we are conducting a telephone survey of approximately 600 firms. Your firm was selected from a list of manufacturers of products under Standard Industrial Classification (SIC) Codes 3079 (Miscellaneous Plastics Products) and 3732 (Boat Building and Repairing). Either I or another SAI staff scientist will be calling you within the next three weeks to ask you about the following aspects of your operation:

(1) Whether you use polyester resin
(2) Types of products produced
(3) Resin use rate (e.g., drums per day)
(4) Fabrication process (hand layup, chopper gun, filament winding, etc.)
(5) Percentage of styrene in resin
(6) Vapor emissions control techniques (Including use of suppressants in the resin.)

This request for data is a formal one made by the ARB pursuant to Section 41511 of the California Health and Safety Code and Section 91100, Title 17 of the California Administrative Code, which authorize ARB, or its duly appointed representative, to require the submission of air pollution related information from owners and operators of air pollution emission sources. We are required by the ARB to furnish them with the name of each polyester resin user, along with our estimate of organic vapor emissions. Polyester resin use data will remain confidential, as will information on proprietary

Figure 4.1-2. Letter Sent in Advance of Telephone Interview

Science Applications, Inc. 1801 Avenue tars, Suite 1205, Los Angeles, CA 90067 (213) 553-2705
Other SAI Offices Albuquerque, Atlanta, Chicago, Dayton, Denver, Hunt ngeles, Oak Ridge, San Diego, San Francisco, Tucson, and Washington D.C

processes and costs. If this arrangement is unsatisfactory to you please inform our caller.

The ARB Research Contracts Monitor for this project is Mr. Joseph Pantalone, whose telephone number is (916) 323-1535. Our contract number is A9-120-30.

Thank you for assisting us in this survey.

Sincerely,

SCIENCE APPLICATIONS, INC.

Michael B. Rogozen, D. Env.
Principal Investigator

MBR/vm

Figure 4.1-2 (Ctd). Letter Sent in Advance of Telephone Interview

Dear Sir:

Science Applications, Inc. (SAI) is under contract to the Research Division of the California State Air Resources Board (ARB) to investigate techniques to control organic gas emissions from operations where polyester resin is used in California. The objectives of our research are (1) to estimate emissions (principally styrene) by type of operation and by county and (2) to survey present and developing control technology. We are particularly interested in control strategies which minimize the financial burden upon small business.

In order to obtain basic information on polyester resin use, styrene emissions, and control technology in California, we are conducting a survey of approximately 1,000 firms. Your firm was selected from a list of manufacturers of products under Standard Industrial Classification (SIC) Codes 3079 (Miscellaneous Plastics Products) and 3732 (Boat Building Repairing). Attached is a set of questions that we have been asking all identified users. Please fill in the blanks and return the questionnaire in the enclosed stamped envelope. We would appreciate it if you could respond within two weeks. The form should be returned even if you are not a user; simply check "no" in Item 1.

This request for data is a formal one made by the ARB pursuant to Section 41511 of the California Health and Safety Code and Section 91100, Title 17 of the California Administrative Code which authorize ARB, or its duly appointed representative, to require the submission of air pollution related information from owners and operators of air pollution emission sources.

We understand that many firms are reluctant to furnish information which they consider to be privileged. The ARB has informed us that actual air pollution emission data cannot be classified as trade secrets, but other data such as privileged processes, costs, formulas, etc., may be eligible for such treatment. The information provided in the questionnaire can be released to the public upon request unless you request trade secret classification in writing (in accordance with the California Public Records Act, Government Code Section 6250 et seq.). All such requests must be accompanied by an adequate justification for the trade secret designation, which should be as detailed as possible without disclosing the trade secret.

Figure 4.1-3. Letter Accompanying Written Questionnaires

Science Applications, Inc. 1801 Avenue of the Stars, Suite 1205, Los Angeles, CA 90067 (213) 553-2705
Other SAI Offices: Albuquerque, Atlanta, Chicago, Dayton, Denver, Hunt ngeles, Oak Ridge, San Diego, San Francisco, Tucson, and Washington DC

Information supplied to ARB which is designated as a trade secret will be kept confidential, although such information may be forwarded to the U.S. Environmental Protection Agency, which protects trade secrets in accordance with federal law. Please note that SAI has formally agreed with the ARB to protect the disclosures of trade secrets to others. Further information on ARB policy may be obtained from the ARB research contract monitor, Mr. Joseph Pantalone, whose telephone number is (916) 323-1535. Our contract number is A9-120-30.

My assistant, Mr. Alan Miller, and I will be happy to answer any questions about the questionnaire and our study. We may be reached at the address and phone number listed at the bottom of the first page of this letter.

Thank you very much for assisting us in this survey.

Sincerely,

SCIENCE APPLICATIONS, INC.

Michael B. Rogozen

Michael B. Rogozen, D.Env.
Principal Investigator

/e

Enc.

Figure 4.1-3 (Ctd). Letter Accompanying Written Questionnaires.

SCIENCE APPLICATIONS, INC.

POLYESTER RESIN USER QUESTIONNAIRE

Firm No.______ Date______

1. Do you use polyester resin? Yes ______ No ______

2. What types of products do you make? ____________________

____

3. Which fabrication processes do you use:

____Hand lay up	____Filament winding
____Spray lay up	____Pultrusion
____Bag molding	____Closed injection molding
____Continuous lamination	____Other (specify); ________

4. Do you apply a separate gel coat? Yes ______ No ______

5. How much resin do you use: (drums/day, gal/week etc.)?

____

6. Is styrene the cross-linking agent? Yes ______ No______

   If not, what is? ____________________

7. What percentage of the resin consists of styrene? ______

8. Is MEK peroxide the catalyst? Yes ______ No ______*

9. Does the resin come with a suppressant mixed in? Yes ____ No ____

   (If uncertain, please specify the manufacturer and type): __

____

10. Is the suppressant also in the gel coat? Yes ____ No ____

11. Do you operate 8 hrs/day, 5 days/wk, 52 wks/yr? Yes ____ No ____

   (If you have a different schedule, please specify): ________

____

* If not, what is? ____________________

Figure 4.1-4. Polyester Resin Use Questionnaire

Page 2

12. What method(s) do you use to control styrene vapors in the plant? Where are vents located? Is there ducting to one or two exhaust points? ______________________________

13. On a separate sheet, please note the name, address and phone number of any other polyester resin user(s) affiliated with your company.

14. How much gel coat do you use? What percentage of the gel coat consists of styrene? ______________________________

Figure 4.1-4 (Ctd). Polyester Resin Use Questionnaire or drums per week) and later converted into lb/year. Descriptions of control and venting systems were also noted separately.

It became apparent early in the survey that over half of the polyester resin users did not know the percentage of styrene (or other monomer) in their resin and gel coat. Most of them were, however, able to give us the names of the resin and gel coat manufacturers. As is discussed in Section 4.2.2, we decided to use product data for cases in which the actual monomer content was known. A telephone survey of the 13 manufacturers of polyester resin and/or gel coat accounting for the overwhelming majority of polyester resin use in California was therefore made.

4.2 EMISSION INVENTORY DATA MANAGEMENT

4.2.1 Initial Coding of Survey Data

To aid in the computer processing of survey results, we set up a system to code the data obtained through the telephone interviews and written questionnaires. Table 4.2-1 shows how data on production processes and resin use were coded. All artificial marble manufacturing process were coded with a 7, even though they could also be considered to be hand layup. Most of the information was coded immediately upon receipt of the written questionnaires or during the telephone interviews. Because resin and gel coat use were expressed in so many different types of units, however, we made the conversion to pounds per year before coding. Many of the firms contacted did not know the percentage of styrene in their resin and/or gel coat, but did know the name of the resin manufacturer. In those cases, we used the percentages obtained in our survey of 13 formulators.

Table 4.2-2 shows the codes used to characterize the pathways by which organic vapors are emitted to the atmosphere. The main purpose of this classification was to identify plants meeting one of our criteria for testing, i.e., those whose emissions were channeled through point emission sources. "Passive" pathways were defined as those through which vapors are emitted by diffusion and convection or through natural ventilation. Examples are open windows and skylights. In all other cases (except outdoor operation), fans or blowers move air from the workplace to the outdoors. Where more than one emission pathway was reported, firms were asked to identify the one corresponding to the greater part of the emissions.

Table 4.2-1

POLYESTER RESIN/FIBERGLASS INDUSTRY SURVEY CODES

CONTACT

0 Not called
1 Interviewed
2 Out of business/moved
3 Refused to answer
4 Sent written reply
5 Not a manufacturing plant
6 Same as other plant
7 Data from local APCD

RESIN USER

0 No
1 Yes
9 Don't know

GEL COAT USER

0 No
1 Yes
9 Don't know

PROCESS TYPE

0 Don't know
1 Hand layup
2 Spray layup
3 Bag molding
4 Continuous lamination
5 Filament winding
6 Pultrusion
7 Marble
8 Matched metal molding
9 Other (specify)

CROSS-LINKING AGENT

1 Styrene
2 Vinyl toluene
3 Methyl methacrylate
4 Other (specify)

CATALYST

0 Don't know
1 MEK peroxide (MEKP)
2 Benzoyl peroxide (BP)
3 Other (specify)
4 BP in resin, MEKP in gel coat
5 Cumene hydroperoxide
6 2,4-pentanedione peroxide
7 MEKP, sometimes BP

VAPOR SUPPRESSANT

0 Not used
1 Used, but not in gel coat
2 Used in resin and gel coat
3 Used in resin; no gel coat used
9 Don't know

Table 4.2-2

EMISSION PATHWAYS CODES

Code	Description
1	Outdoor operation or home repair
2	Ducts: spray booths to wall outlet
3	Ducts: spray booths to roof outlet
4	Ducts: general work area to wall outlet
5	Ducts: general work area to roof outlet
6	Forced air: ceiling vents only
7	Forced air: wall vents only
8	Forced air: wall and ceiling vents
9	Passive wall vents only
10	Passive ceiling vents only
11	Passive ceiling and wall vents
12	Ducts: general work area to wall and roof outlets
13	Unknown
14	Water curtain
15	Afterburner

Table 4.2-3

PRODUCT CODES

Code	Description
0	Unknown
1	Boats
2	Marble
3	Auto, motorcycle, truck, aircraft or RV parts
4	Bathtubs, sinks etc. (not marble or spas or hot tubs)
5	Tanks, boxes, etc. gondolas
6	Furniture
7	Pipes, ducts, flues
8	General fiberglass, including custom
9	Radomes
10	Panels, laminates in general
11	Electronics
12	Helmets, sporting goods
13	Swimming pools and equipment mfg
14	Repairs at homes, etc.
15	Spas, hot tubs, jacuzzis
16	Pultruded rods, antennae etc.
17	Surfboards

In the original survey design, it was considered useful to learn the SIC code of each firm. As mentioned in Section 4.1.1, however, SIC codes constitute a poor guide to this industry. In order to analyze our survey data in a more meaningful way, we defined the set of product codes shown in Table 4.2-3. Most of the categories are self-explanatory. "General" includes firms which make prototype molds or which manufacture a wide variety of short-run products. "Tanks, Containers" includes large storage tanks, gondolas, cargo containers, and small boxes, except for electronics enclosures. Several firms manufacture both tanks and ductwork; these were placed in the "Pipes, Ducts" category. Only firms which specifically reported manufacturing synthetic marble were placed in that category; it is possible that some placed in the "Bathroom Fixtures" category may also be marble manufacturers. "On-Site Repairs" refers to services which resurface swimming pools, shower stalls, and other fiberglass items at the place of use.

4.2.2 Adjustments to Fill Data Gaps

An earnest effort was made to obtain all the desired data from each polyester resin user in the state. In a large number of cases, follow-up calls were made to get information omitted from the questionnaire or not reported in the telephone interview. Nevertheless, many data gaps remained at the end of the survey. The most important types of missing information were gel coat use rate, percentage of cross-linking agent in the laminating or casting resin, and percentage of styrene in the gel coat. Although about one quarter of the firms are deficient in one of these data categories, they represent only a tiny fraction of the polyester resin use in California. Errors in estimating values for the missing parameters would therefore not be expected to have much of an effect upon industry-wide totals and averages. Missing data were synthesized in the following ways.

Gel Coat Use Rate

A review of the survey data showed three important relationships between use of laminating resin and gel coat. First, gel coat is almost never used in connection with certain fiberglass production processes, including continuous lamination and pultrusion. Second, certain products, such as surfboards, are usually not made with a gel coat layer. Finally, the mean ratio between laminating resin use and gel coat use is not significantly different for different final products. We therefore synthesized a gel coat

Table 4.2-4

RATIO BETWEEN GEL COAT USE AND LAMINATING OR CASTING RESIN USE, BY TYPE OF PRODUCT

Product Code[a]	Number of Cases	Mean Value of Ratio	Standard Deviation	t-value[b]
0	25	0.143	0.218	-0.558
1	56	0.138	0.183	-0.632
2	46	0.103	0.264	0.510
3	17	0.127	0.080	-0.156
4	7	0.190	0.095	-0.958
5	22	0.139	0.247	-0.434
6	5	0.082	0.114	0.871
7	5	0.018	0.029	1.174
8	22	0.132	0.133	-0.275
9	NA[c]	NA	NA	NA
10	8	0.018	0.051	1.482
11	5	0.171	0.152	-0.580
12	2	0.019	0.027	0.736
13	3	0.179	0.169	-0.524
14	4	0.200	0.245	-0.817
15	7	0.122	0.078	-0.028
16	5	0.039	0.054	0.932
17	NA	NA	NA	NA

[a] Codes are defined in Table 4.2-3

[b] For hypothesis that mean ratio for a given product code is different from mean ratio for all cases; to be significant at the 0.05 level, $|t \text{ value}| > 1.960$.

[c] NA = Not applicable.

use rate where needed by multiplying the laminating resin use rate by the average resin/gel coat factor, which was 0.12 ± 0.02, or by zero if the process or product does not ordinarily use gel coat. (See Table 4.2-4).

Percentage of Cross-Linking Agent in the Resin and Gel Coat

Since the percentage of cross-linking agent in a polyester resin affects the latter's handling characteristics, it stands to reason that this parameter would vary from process to process. An analysis of all cases for which the cross-linking agent percentage was known showed that the percentage indeed was significantly different for certain processes. Table 4.2-4 shows the values used to supplant missing data.

4.2.3 Computerized Data Management System

Survey data were stored and analyzed with an Apple II microcomputer having 48K bytes of random access memory and a disk drive. To manage the data, a set of program modules were written in BASIC. Figure 4.2-1 shows the interrelationships between the programs and the data, with arrows showing the direction of information flow. Survey data were stored in two ways. First, a separate sequential text file, containing all the information obtained through the survey, was set up for each plant. Figure 4.2-2 shows how these files were arranged. In order to facilitate data analysis, we then created several data element files, each one containing values of one data element for all the firms. For example, one of these files consists of the resin use for each firm. The structure of the random access files is also shown in Figure 4.2-2. The following are brief descriptions.

- DATA INPUT -- This is an interactive program which requests each type of information and then stores it in random access memory. When all the data for given firm are entered, the program displays the data set and asks the user if all are correct. Erroneous data elements can be corrected immediately. At the user's command, the data set is then stored on disk. The name of the data file consists of the first 15 characters of the firm's name.

Table 4.2-5

RESIN STYRENE PERCENTAGES USED WHERE DATA WERE LACKING

Process Combination	Pct. Styrene in Resin
Hand layup alone	41.1
Hand layup, spray layup	42.7
Hand layup, spray layup, bag molding	40.0
Hand layup, spray layup, filament winding	43.1
Hand layup, bag molding	45.0
Hand layup, other	10.0
Spray layup alone	41.5
Spray layup, bag molding	25.0
Spray layup, filament winding	45.0
Continuous lamination alone	40.0
Filament winding alone	45.0

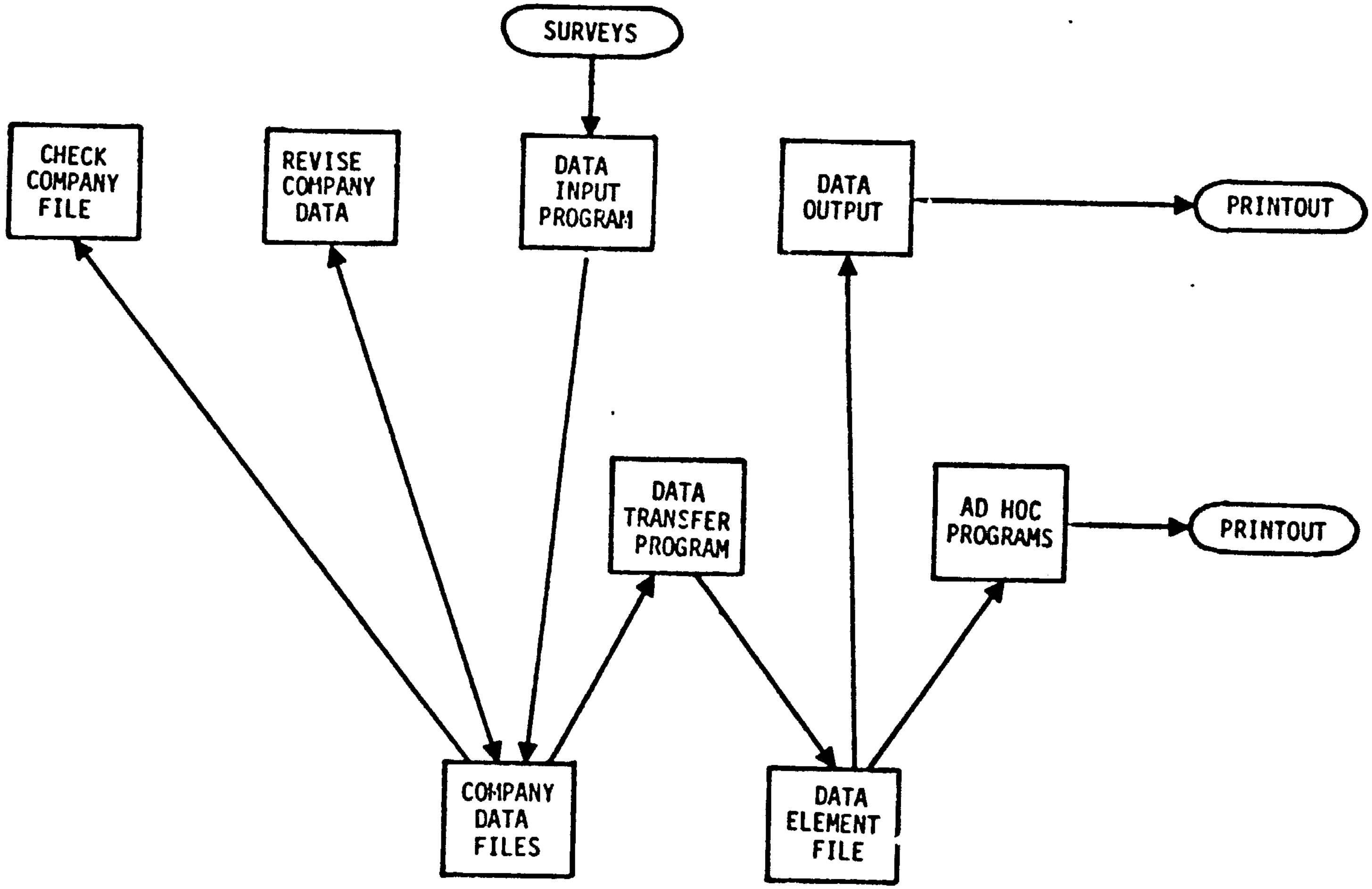


Figure 4.2-1. Data Base Management System

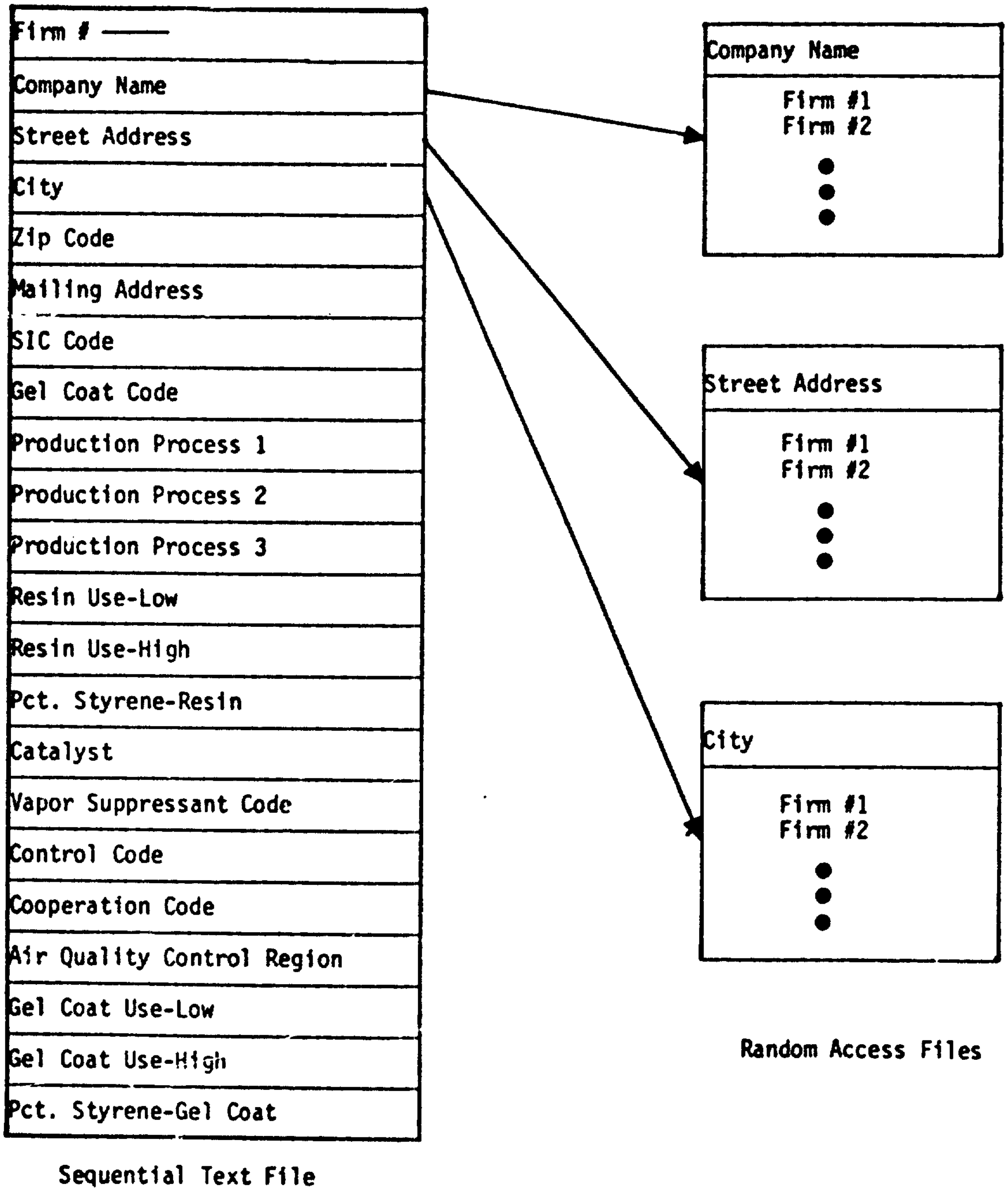


Figure 4.2-2 Structure of Data Files Used For Polyester Resin Use Inventory

- REVISE COMPANY FILE -- This program is used to update a file on a particular company. The user specifies the name of firm, whereupon the program truncates the name to 15 characters and then searches for the corresponding file and stores it in random access memory. The user is then asked to specify the data element to be changed and is shown the value of the element currently stored. After all desired corrections are made, the program erases the old data file and replaces it with the updated version.

- CHECK COMPANY FILE -- If one wishes only to see what data are in a particular company file, then this program is used. The user specifies the company name, which the program truncates to 15 characters and uses to search the disk. When the appropriate file is found, all the data elements contained therein are displayed.

- DATA ITEM TRANSFER -- This program is used to transfer a single data element (e.g., resin use rate) from each company file to a data element file. First, the data element is retrieved from each company file and stored in random access memory. The type of file to be created is called a "random access file," since any of its records may be retrieved immediately by means of a record number. In this case, each company in the inventory is given a unique record number. Because the length of each record in a random access file must be identical, the program sets the record length equal to one plus the size of the largest data element retrieved. For example, the longest company name has 40 characters, so all the records in the COMPANY NAME file are 41 characters long. After all of the individual company files have been searched, the data are transferred from the random access memory onto the disk.

- DATA OUTPUT -- The function of this program is to translate the coded data in the company files to a conveniently read form. It was used to generate the emission inventory summaries provided under separate cover to the ARB.

4.3 CHARACTERISTICS OF THE INDUSTRY IN CALIFORNIA

4.3.1 Survey Response

Using the information sources described in Section 4.1, we identified and attempted to contact 947 putative unsaturated polyester resin users. Table 4.3-1 summarizes the status of our survey as of 15 May 1981, after which date no further attempts were made to obtain new information. In the table, "unsuccessful contacts" are those firms which were either obviously not polyester resin users (for example, those which had gone out of business) or whose user status could not be determined. Only 15 firms out of the 947 refused totally to cooperate with the survey.

It may be seen in Table 4.3-1 that about 15 percent of the firms in the survey had gone out of business or had moved out of California. This result was but one of several symptoms of the depressed state of the industry during the survey period (August 1980 to May 1981). Quite a few companies told our interviewers that they were operating fewer days per week than usual, and/or using less than the normal amount of resin and gel coat. As was described in Section 3.2.3, the marine industry was especially affected.

"Successful contacts" include firms which completed and returned questionnaires, or which were interviewed on the telephone by SAI staff. Also included are three companies for which we received information from local air pollution control districts.

In the following discussion, it is necessary to distinguish between two survey data sets. The first includes complete information on 291 firms, and was used to calculate various industry characteristics, such as median firm size; it is called the "statistical data set." The other, which is displayed in Table 4.3-2, includes the partial data obtained for an additional 14 firms, and is called the "supplementary data set." Wherever possible, we have combined information from the two. An inventory of all 305 firms has been supplied to the ARB as a separate document.

4.3.2 Statewide Unsaturated Polyester Resin Use

A major "unknown" at the start of this study was the size of the polyester resin/fiberglass industry in California. Discussions with a major resin formulator in July 1980 led to an initial estimate of 59 to 63 million

Table 4.3-1

POLYESTER RESIN/FIBERGLASS SURVEY STATUS

Total Plants in Survey		947
Unsuccessful Contacts		229
- Out of Business/Moved from California	139	
- Not a Manufacturing Plant	64	
- Refused to Cooperate	15	
- Duplicate Plant	7	
- Unable to Reach	4	
Successful Contacts		718
- Telephone Interviews	635	
- Written Questionnaires	80	
- Information from APCD's	3	
Polyester Resin Users		305
- Complete Information Obtained	291	
- Partial Information Obtained	14	

Table 4.3-2
SUPPLEMENTARY DATA SET

Survey I.D. No.	County	Product	Processes	Total Resin Use (lb/yr)	VS	Control Code
40	Santa Clara	Auto parts	Hand, Spray	ND	Yes	6
77	Santa Clara	ND[a]	Spray	ND	ND	ND
151	San Diego	Boats	ND	ND	ND	ND
177	Los Angeles	Panels	ND	26,000	No	6
190	Los Angeles	Boats	Hand	ND	No	ND
227	Orange	ND	ND	ND	ND	ND
577	Los Angeles	General	Bag molding	ND	ND	ND
643	San Diego	Marble	Casting	ND	ND	ND
654	Los Angeles	Spas	Spray	312,000	No	6
669	Orange	Rods	Pultrusion	ND	ND	ND
688	Los Angeles	Boats	ND	ND	ND	ND
810	Orange	ND	Hand	ND	ND	8
832	Marin	ND	ND	ND	ND	ND
901	Alameda	Spas	ND	ND	ND	ND

[a] ND = No data

kg/yr (130 to 140 million lb/yr) total polyester resin consumption in the State. The full impact of the recession in the boat building industry had not yet been felt, however, and in January 1981 the same source told us that 45 million kg/yr (100 million lb/yr) would be more likely. In both cases, one estimate was made by multiplying national resin use by a "rule-of-thumb" factor. Attempts were made to obtain another estimate. The Society of the Plastics Industry, Inc.'s Committee on Resin Statistics, which compiles nationwide use data for a wide variety of resins and plastic products, does not have data for individual states (Anon., 1981a), nor does the Readers Service of Modern Plastics (Anon., 1981b).

We feel reasonably confident, therefore, that our estimate of 44.4 to 45.5 million kg/yr (97.9 to 100.4 million lb/yr) for California unsaturated polyester resin use is the best available to the general public. Although many very small firms might have remained unidentified, their combined resin use would constitute but a tiny fraction of the statewide total. Furthermore, after discussions with cognizant air pollution control agencies, we believe that no major user has escaped our detection.

4.3.3 Distribution of Resin Users by Size and Location

Distribution by Size

It is clear from our survey data that the California polyester resin/fiberglass industry consists of a relatively large number of small firms which, in combination, account for only a small fraction of the state's unsaturated polyester resin consumption; and a few very large firms, which use the great majority of the total resin. Figure 4.3-1 shows the cumulative frequency distribution of fabricators by firm size, which is defined here as total resin use (laminating and casting resin, plus gel coat) per firm. A logarithmic scale was necessary for firm size, since this variable ranged from 99.77 kg/yr to 8.76 million kg/yr (220 lb/yr to 19.3 million lb/yr). As seen in the figure, the median firm size is about 27,500 kg/yr (60,200 lb/yr). More than 168 companies use less than 45,000 kg/yr (100,000 lb/yr).

Figure 4.3-2 gives another picture of the way that large companies dominate resin consumption in California. The graph is an analogue of the Lorenz curve in economics, which is used to measure the distribution of market share or income among firms (Asch, 1970). The diagonal line represents a

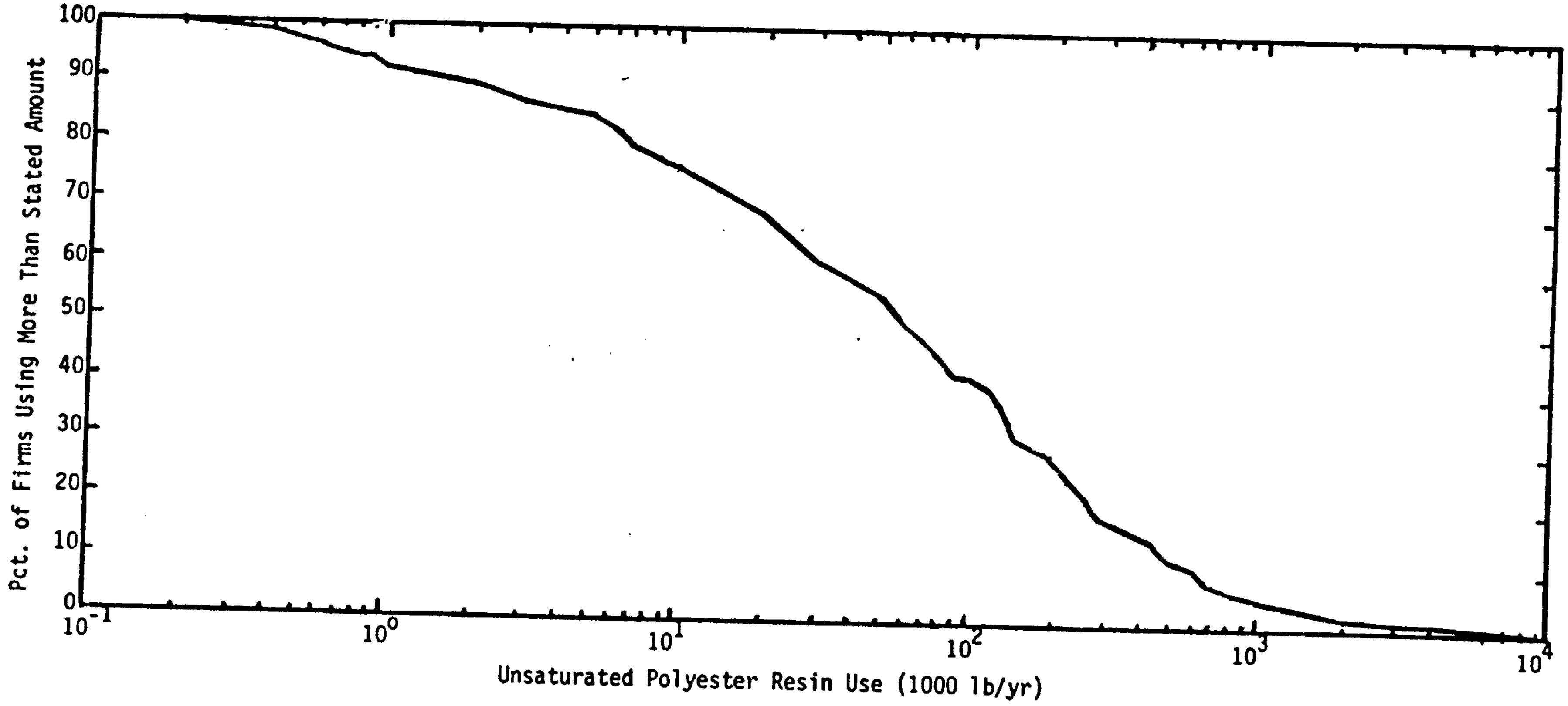


Figure 4.3-1. Cumulative Frequency Distribution of Polyester Resin/Fiberglass Fabricators, by Resin Use

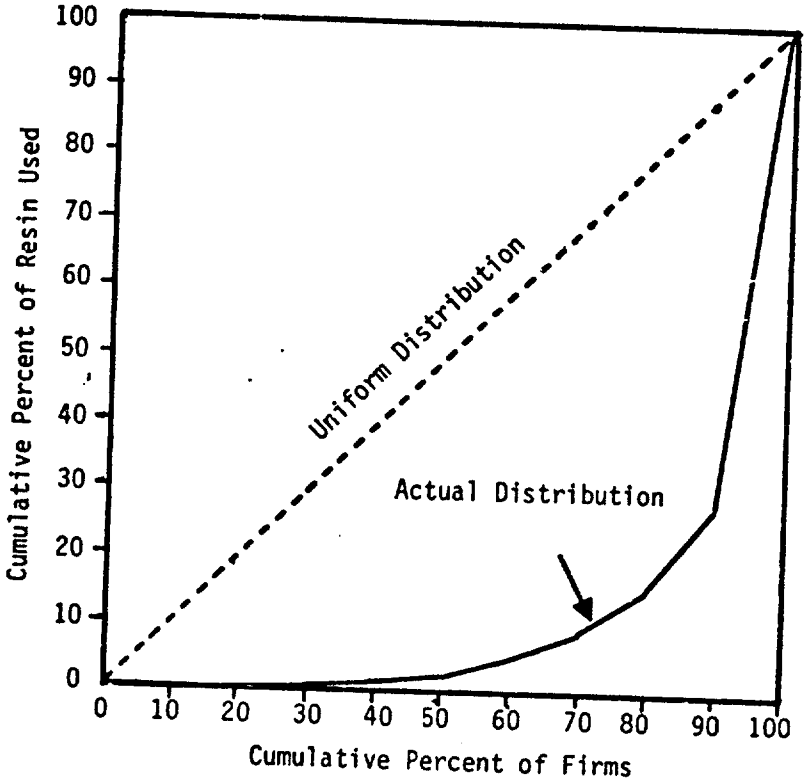


Figure 4.3-2. Lorenz Curve for Distribution of Polyester Resin Use in California

percent stronger than the one-stage laminate made from the identical resin.

9.3.2 Bending Tests

Results of the bending tests are shown in Table 9.3-4. The pattern of flexibility among laminates is different from that of interlaminar shear strength. In this case, Laminate C, which was made from the "specially formulated" resin had the greatest stiffness. In order of decreasing stiffness, the ranking of laminates was:

Laminate	Characteristic
C	Special formulation
E	No vapor suppressant
B	Vapor suppressant/two-stage fabrication
A,D	Vapor suppressant (A), No vapor suppressant (D)

Laminates A and D are ranked the same, since there was no significant difference between their bending moduli. Since the resin used for these laminates differed only in whether it had a vapor suppressant, the use of vapor suppressant apparently did not affect the flexibility of the laminates. On the other hand, constructing Laminate B in two stages appears to have increased its stiffness, since its bending modulus is significantly higher than that of Laminate A, which was made from the same resin. Correlation between bending modulus and interlaminar shear strength was rather low ($r = 0.482$).

9.4 DISCUSSION

It is not surprising that an appreciable fraction (9 of 30) of the test laminates failed in tension, rather than in shear. Indeed, McKenna (1975) points out that, while ASTM D 2344-76 is the only accepted standard for interlaminar shear testing, the values obtained are "apparent." This is due to the fact that the shear stress distribution through the composite is not constant. Mixed mode failures can occur if the composite flexural strength/interlaminar shear strength ratio is too low.

From these limited tests, it does not appear that the use of vapor suppressant degrades interlaminar shear strength significantly. In the one case for which laminates varied only in their vapor suppressant content (A vs

Table 4.3-3

COUNTIES WITH NO REPORTED POLYESTER RESIN USE

Alpine
Amador
Butte
Calaveras
Colusa
Del Norte
El Dorado
Humboldt
Imperial
Inyo
Kings
Lake
Lassen
Mariposa
Mendocino
Modoc
Mono
Monterey
Nevada
Plumas
Riverside
Sierra
Siskiyou
Stanislaus
Trinity
Tuolumne

Table 4.3-4

REPORTED POLYESTER RESIN USE, BY COUNTY

County	No. of Firms[a]	Reported Polyester Resin Use Lower Estimate (lb/yr)	Upper Estimate (lb/yr)
Alameda	11	817,800	1,018,900
Contra Costa	7	812,400	818,000
Fresno	8	323,580	323,580
Glenn	1	x[b]	x
Kern	2	x	x
Los Angeles	76	31,243,400	31,593,200
Madera	1	x	x
Marin	5	74,600	74,600
Merced	1	x	x
Napa	1	x	x
Orange	74	40,638,600	41,474,600
Placer	1	x	x
Sacramento	12	710,600	993,200
San Benito	1	x	x
San Bernardino	3	1,936,700	1,936,700
San Diego	43	8,549,600	8,587,700
San Francisco	4	120,900	149,400
San Joaquin	3	1,561,400	1,626,400
San Luis Obispo	1	x	x
San Mateo	5	822,200	822,200
Santa Barbara	1	x	x

(continued on next page)

Table 4.3-4
REPORTED POLYESTER RESIN USE, BY COUNTY
(continued)

County	No. of Firms[a]	Reported Polyester Resin Use Lower Estimate (lb/yr)	Upper Estimate (lb/yr)
Santa Clara	20	2,091,100	2,091,100
Santa Cruz	2	x	x
Shasta	6	998,300	998,300
Solano	1	x	x
Sonoma	2	x	x
Sutter	1	x	x
Tehama	1	x	x
Tulare	4	393,800	426,300
Ventura	3	244,800	257,900
Yolo	3	1,987,800	1,987,800
Yuba	1	x	x
Totals	305	97,888,000	100,414,200

[a] Includes 12 firms for which resin use data are lacking.

[b] To preserve the anonymity of individual firms, county totals are presented only for counties have three or more users.

Distribution by Air Quality Control Region

To aid in coordination with statewide emission inventory data, our results were also grouped according to Air Quality Control Region (AQCR), as defined by the U.S. Environmental Protection Agency. (See Figure 4.3-3). AQCR boundaries correspond fairly well to those of the California Air Basins, which are shown in Figure 4.3-4; the chief exception is that Ventura County is included in AQCR 24 rather than 32. It should be noted that San Bernardino and Riverside Counties are divided between AQCR's 24 and 33; however, the polyester resin/fiberglass fabricators identified by our survey in these counties all are within AQCR 24, which corresponds to the South Coast Air Basin.

Table 4.3-5 shows number of firms and reported polyester resin use for each California AQCR having at least one firm. It is clear that the great majority of the firms and the resin use are centered in AQCR 24. The San Diego Air Basin (AQCR 29) is a distant second in resin use, while the San Francisco Bay Area (AQCR 30) and the Sacramento Valley (AQCR 28) Air Basins are tied for third.

4.3.4 Products and Production Processes

Products

As mentioned in Section 4.2.1, SIC codes are inadequate to identify unsaturated polyester resin users. We therefore defined the set of finished product classifications shown in Table 4.2-4 and asked each firm in our survey to specify the type(s) of products it produced. In many of the cases in which firms did not answer this question, we were able to obtain the information from the California Manufacturers Register. The results are reported in Table 4.3-6.

It was noted above that polyester resin use in California is concentrated among a small number of firms; the same holds true for product categories. The 16 firms which manufacture panels and bathroom fixtures use almost 25 million kg/yr (55 million lb/yr) of resin and gel coat, or about 55 percent of the state total. The greatest number of firms are in the boat building, synthetic marble and general job shop categories. While comprising over half of the user population, however, they account for only about one quarter of the total unsaturated polyester resin use.

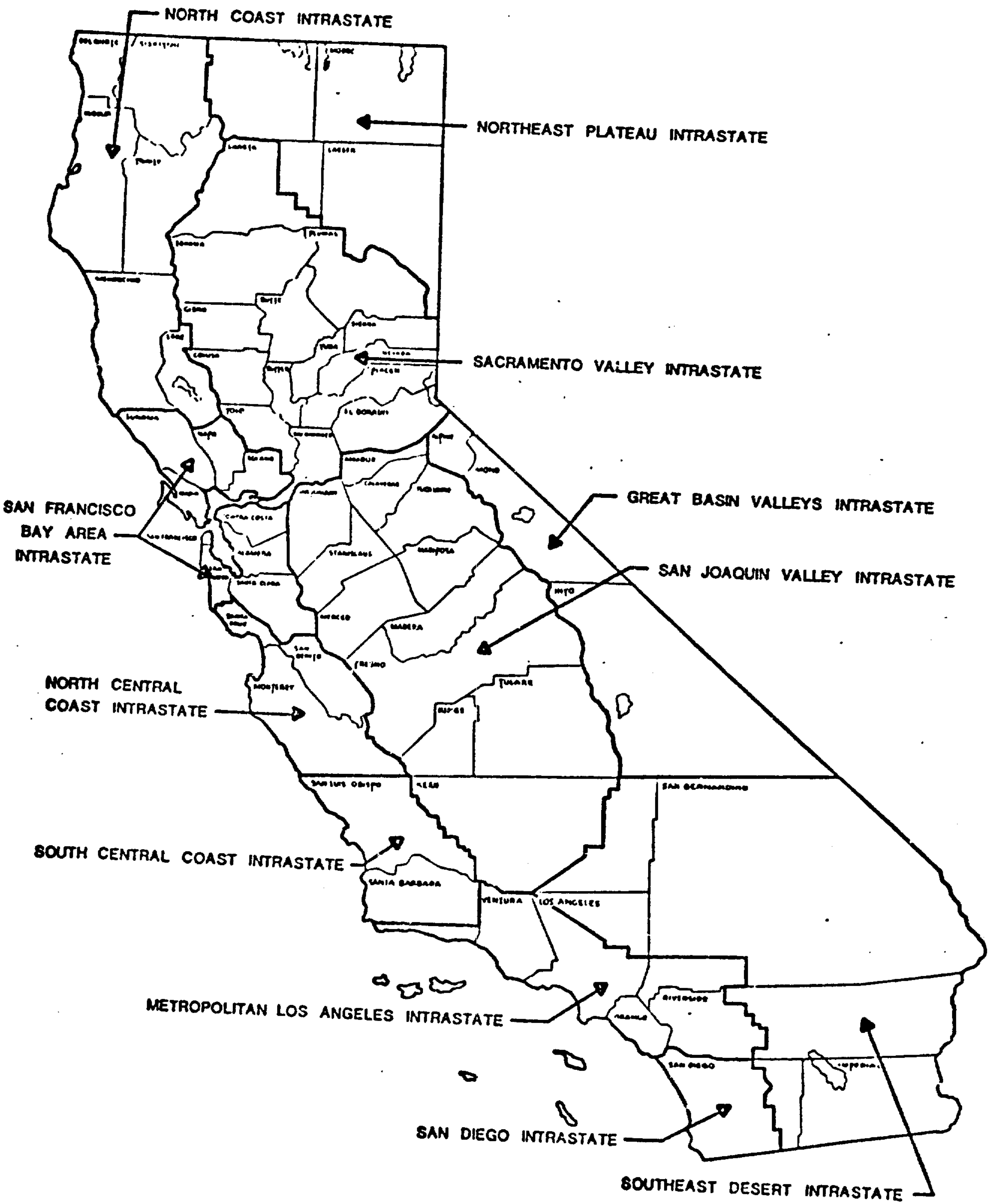


Figure 4.3-3. Federal Air Quality Control Regions in California.

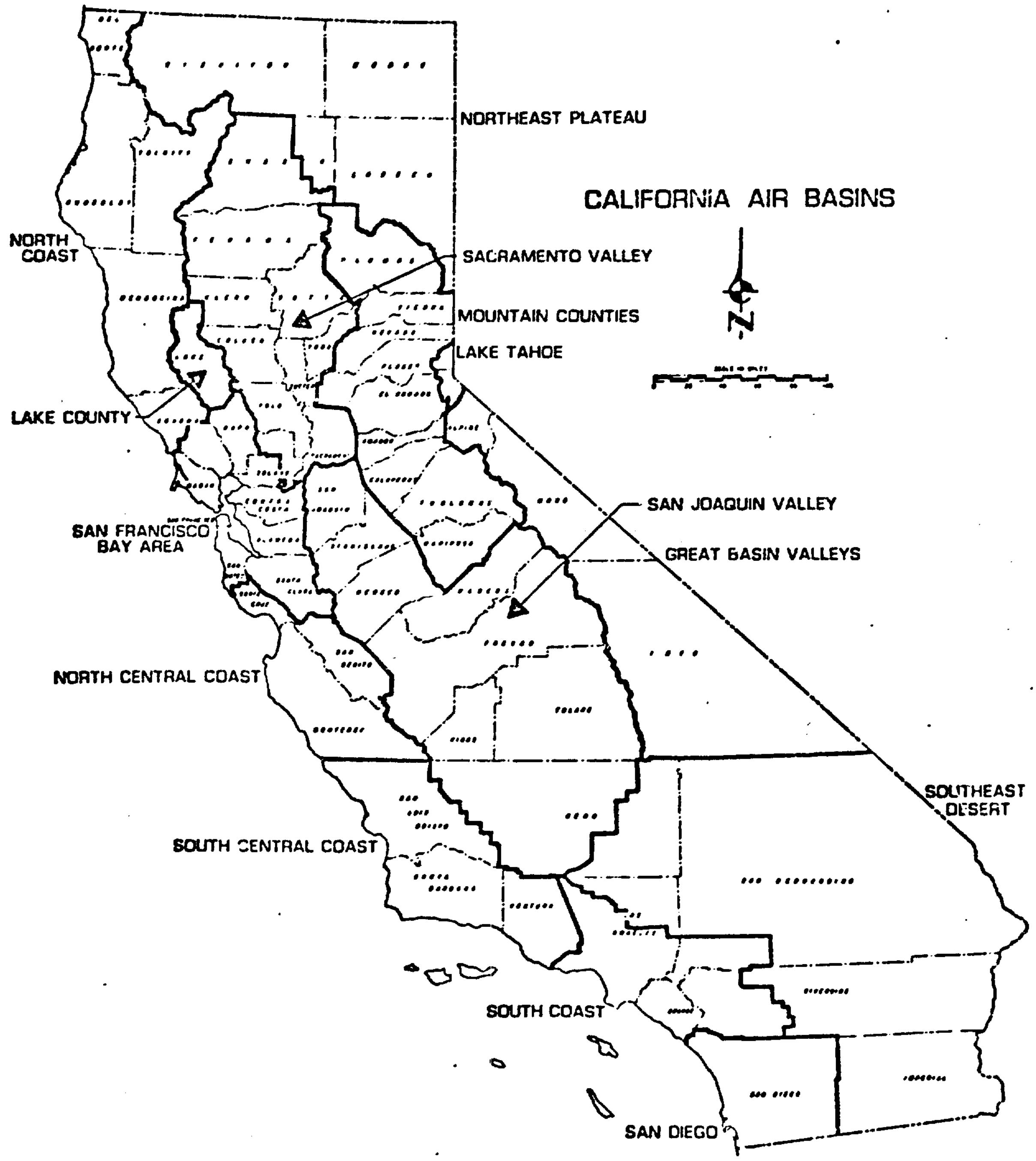


Figure 4.3-4. California Air Basins

Table 4.3-5

REPORTED POLYESTER RESIN USE, BY AIR QUALITY CONTROL REGION

AQCR No.	California Air Basin Name	No. of Firms	Estimated Resin Use[a] Lower (lb/yr)	Upper (lb/yr)	Percent of State Total Resin Use[b]
24	South Coast[c]	156[d]	74,063,500[c]	75,262,400[c]	74.95
25	North Central Coast	3	774,400	1,424,400	1.42
28	Sacramento Valley	26	5,203,500	5,489,200	5.47
29	San Diego	43[d]	8,549,600	8,587,700	8.55
30	San Francisco Bay Area	56[d]	5,262,100	5,497,300	5.47
31	San Joaquin Valley	19	3,441,300	3,551,800	3.54
32	South Central Coast[e]	2	593,600	601,400	0.60
	Totals	305	97,887,400	100,414,100	100.00

[a] Includes laminating and casting resin and gel coat.
[b] Based upon upper use estimate.
[c] Includes Ventura County.
[d] Includes firms for which only partial data are available.
[e] Excludes Ventura County.

TABLE 4.3-6

CALIFORNIA UNSATURATED POLYESTER RESIN USE BY PRODUCT TYPE
(Statistical Data Set)

Product	No. of Firms	Polyester Resin Use(lb/yr)		Pct. of Total UP Resin Use in California[a]	Average UP Resin Use Per Plant (lb/yr)
		Lower Estimate	Upper Estimate		
Boat Building, Repair	79	13,474,000	14,085,000	14.1	178,300
Synthetic Marble	50	9,701,000	9,773,000	9.8	195,500
General	25	1,300,000	1,316,000	1.3	52,600
Tanks, Containers	22	4,473,000	5,364,000	5.4	243,800
Auto, Aircraft, Truck	19	1,186,000	1,259,000	1.3	66,300
Spas,Hot Tub	9	1,491,000	1,712,000	1.7	190,300
Surfboards	8	122,000	122,000	0.1	15,200
Panels	8	44,864,000	44,936,000	44.9	5,617,000
Bathroom Fixtures[b]	8	9,781,000	9,781,000	9.8	1,222,600
Furniture	7	2,791,000	2,791,000	2.8	398,700
Pipes,Ducts	6	493,000	493,000	0.5	82,200
Electronics	5	903,000	938,000	0.9	187,700
Antennas, Rods	5	1,643,000	1,643,000	1.6	328,600
On-site Repairs	4	138,000	138,000	0.1	34,500
Swimming Pools	3	542,000	542,000	0.5	180,600

(Continued next page)

TABLE 4.3-6

CALIFORNIA UNSATURATED POLYESTER RESIN USE BY PRODUCT TYPE

(Statistical Data Set)

(continued)

Product	No. of Firms	Polyester Resin Use(lb/yr) Lower Estimate	Upper Estimate	Pct. of Total UP Resin Use in California[a]	Average UP Resin Use Per Plant(lb/yr)
Helmets, Sporting Goods	2	269,000	317,000	0.3	158,600
Radomes	1	29,000	29,000	0.1	29,000
Not Reoorted	30	4,348,000	4,835,000	4.8	161,179
TOTALS	291	97,548,000	100,074,000	100.0	343,900

[a] Based upon upper use rate estimate

[b] Does not include fixtures made of synthetic marble

The resin use rate per firm varies significantly from product to product. Panel and bathroom fixture plants are relatively large, averaging 2.5 million kg/yr (5.6 million lb/yr) and 550,000 kg/yr (1.2 million lb/yr) per firm, respectively. The smallest operations are the surfboard manufacturers, who average only 6,900 kg/yr (15,000 lb/yr) per firm. We believe that the number of surfboard firms is probably significantly under-reported, since there are many backyard or garage operations which we could not identify. Because these enterprises are so small, however, their omission most likely has no effect upon estimates of statewide totals.

Production Processes

Table 4.3-7 shows the results of our survey of fabrication processes used in the California polyester resin/fiberglass industry. The table shows reported uses of each process; since many firms use more than one process, the total number of firms and total resin use exceed the values reported in other tables. It is clear that, despite recent increases in use of more sophisticated production processes, the firms surveyed which use hand layup are by far the most common. About one third of the firms surveyed use hand layup only, while almost three quarters of them use either hand or spray layup or a combination of the two.

The average resin consumption per reported use of each process is also shown in Table 4.3-7. It is clear that continuous lamination and pultrusion are high-volume operations, while hand layup processes use relatively little resin per firm. In fact, firms which use only hand and/or spray layup, though many in number, account for only 60 percent of the statewide total consumption.

4.3.5 Cross-Linking Agents and Catalysts

All but three plants reported that they used styrenated resin or did not know the cross-linking agent. Discussions with resin and gel coat formulators lead us to believe that use of monomers other than styrene is quite rare in California. The three exceptions all use resin containing methyl methacrylate (MMA). Since two of these plants are among the largest in the state, the use of these resins accounts for almost 12 percent of the statewide total. The two large firms make fiberglass panels, while the third is a boat manufacturer. A fourth company, also a panel manufacturer, uses a mixture of styrene and methyl methacrylate on occasion.

TABLE 4.3-7

USE OF PRODUCTION PROCESSES BY CALIFORNIA POLYESTER RESIN/FIBERGLASS FABRICATORS

Process	No. of Firms	Total Resin Use[a] (lb/yr)	Average Consumption per use of Process[b] (lb/yr)
Hand layup	214	26,827,000	127,140
Spray layup	149	56,741,300	386,500
Marble casting	49	9,248,400	192,670
Filament winding	9	2,972,100	330,240
Bag Molding	9	1,463,900	182,980
Pultrusion	6	5,138,000	856,330
Continuous lamination	4	21,110,000	5,277,500
Matched metal molding	1	737,000	737,000
Other	5	479,620	95,924
Unknown	1	ND[c]	ND
Hand layup only		98	97,243
Spray layup only		41	981,521
Hand and spray layup only		77	132,059

[a] Based upon upper estimate of resin and gel coat use.
[b] Based upon 291-firm statistical data set
[c] ND = No data

It should be noted that one major gel coat manufacturer told us that its formulations contain a 60:40 mixture of styrene and MMA. We do not have sufficient data to estimate the share of the total statewide gel coat use represented by this formulation.

As seen in Table 4.3-8, methyl ethyl ketone peroxide (MEKP) is by far the most widely-used catalyst; only eight percent of the firms in the survey use anything else. The second most commonly-used catalyst is benzoyl peroxide (BP). Although this chemical is frequently associated with high-temperature processes, there did not appear to be any clear pattern of use among the firms surveyed, except that firms using BP tend to be rather large. The only other catalyst cited more than once was 2,4-pentanedione peroxide, which is used by two marble manufacturers and one maker of electronic parts.

4.3.6 Emission Control Techniques

Although each firm was asked whether it attempted to remove or reduce organic vapor emissions, the major objective of this part of the survey was to determine the pathways by which the vapors are transferred from the production processes to the outdoor ambient air. Knowledge of these pathways was important both for selection of emission test sites and for estimating the extent of ventilation changes necessary should an exhaust gas treatment strategy be considered. Since treatment processes such as absorption and incineration require channelling of exhaust gases, those plants already having a ducting system would have smaller retrofitting requirements.

Table 4.3-9 shows the result of this portion of our survey. Definitions of the different emission modes were given in Section 4.2.1. About 36 percent of the firms, representing over 62 percent of the state's resin use, already have some form of ducting. Given state and federal limitations on occupational exposure, it is not surprising that only 38 firms, representing less than 5 percent of statewide resin use, use natural ventilation to control indoor exposures. Another 30 firms operate outdoors or make repairs off-site.

Only two firms reported using organic vapor removal equipment. In each case, incineration was the reported method. (Emissions from one of these plants were measured as part of this project; see Section 5.2.1.) Two other plants direct their exhaust through a water spray "curtain," but the purpose of this treatment is to remove particulate matter. One large plant reported that

TABLE 4.3-8

USE OF CATALYSTS BY CALIFORNIA POLYESTER RESIN/FIBERGLASS FABRICATORS

Catalyst Type	No. of Firms	Pct. of Firms	Total Resin Use[a] (lb/yr)	Pct. of Total Resin Use
MEK peroxide (MEKP)	269	92.44	73,183,100	73.13
Benzoyl peroxide (BP)	6	2.07	9,454,120	9.45
Cumene hydroperoxide	1	0.34	6,500,000	6.49
Cumene peroxide + BP	1	0.34	5,200,000	5.20
BP in resin, MEKP in Gel coat	2	0.69	2,693,600	2.69
2,4-pentanedione peroxide	3	1.03	1,086,580	1.09
Peroxydicarbonate	1	0.34	421,000	0.42
Other	5	1.72	1,054,960	1.05
Do not know	3	1.03	482,900	0.48
TOTALS	291	100.00	100,076,260	100.00

[a] Based upon upper estimate of resin and gel coat use.

TABLE 4.3-9

DISTRIBUTION OF VAPOR EMISSION MODES IN THE CALIFORNIA POLYESTER RESIN/FIBERGLASS INDUSTRY

Emission Mode	No. of Firms	Pct. of Firms	Total Resin Use[a] (lb/yr)	Pct. of Total Resin Use
Outdoor Operation	30	10.31	742,920	0.74
Passive Ventilation				
Wall vents only	18	6.18	1,778,660	1.78
Ceiling vents only	10	3.44	1,673,240	1.67
Wall and ceiling vents	10	3.44	1,201,010	1.20
Forced Air/Vents				
Wall vents only	31	10.65	4,003,450	4.00
Ceiling vents only	43	14.78	9,444,600	9.44
Wall and ceiling vents	23	7.90	5,119,880	5.12
Ducted Pathways				
General work area to wall	4	1.37	2,279,640	2.28
General work area to roof	25	8.59	19,409,180	19.39
General work area to wall and roof	2	0.69	1,445,300	1.44
Spray booths to wall	9	3.09	2,850,380	2.85
Spray booths to roof	66	22.68	36,168,930	36.14

(continued on next page)

TABLE 4.3-9

DISTRIBUTION OF VAPOR EMISSION MODES IN THE CALIFORNIA POLYESTER RESIN/FIBERGLASS INDUSTRY (continued)

Emission Mode	No. of Firms	Pct. of Firms	Total Resin Use[a] (lb/yr)	Pct. of Total Resin Use
Special Controls				
Water curtain	2	0.69	267,800	0.27
Afterburner	2	0.69	11,920,000	11.91
Unknown	16	5.50	1,771,260	1.77
TOTALS	291	100.00	100,076,250	100.00

it had been considering purchasing a wet scrubber system, while another is considering substituting foamed polyester for conventional liquid resin. It should be noted that the plants using afterburners are both quite large, use a continuous lamination process, and consume about 12 percent of the industry's unsaturated polyester resin. The combination of high operating temperatures and large potential organic vapor emissions apparently made use of incineration economical.

Firms were also asked to report whether they used resin or gel coat containing vapor suppressant compounds. A total of 54 companies, representing 25 percent of the statewide polyester resin and gel coat use, definitely use vapor-suppressed resins, while 113 firms, representing 40.5 percent of the unsaturated polyester resin use, definitely do not. The most frequent response to our survey was "do not know." All but one of the resin and gel coat formulators we contacted said that they do not add a suppressant to a resin unless the customer specifically asks them to do so. The exception stated that all its resin and gel coat contains a vapor suppressant, unless the customer does not want it. Although identification of resin and gel coat source was not requested in all cases, 22 firms, representing 2.5 percent of statewide resin use, reported that they used the brand in question. It is possible, therefore, that at least 1.25 million kg/yr (2.75 million lb/yr) of resin and gel coat contain a vapor suppressant.

An attempt was made to see whether producers of various products tended to use vapor suppressant. The greatest number of firms using suppressed resins were in the boatbuilding industry. It may be recalled, however, that this product category contains the most firms among polyester resin users in general. Chi square analysis showed that there is no statistically significant association ($p > 0.05$) of vapor suppressant use with product category ($x^2 = 19.452$, d.f. = 16).

4.4 REFERENCES

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TABLE 4.3-10

USE OF VAPOR SUPPRESSANTS BY CALIFORNIA POLYESTER RESIN/FIBERGLASS FABRICATORS

User Status	No. of Firms	Pct. of Firms	Total Resin Use[a] (lb/yr)	Pct. of Total Resin Use
Yes, in resin and gel coat	17	5.84	4,997,020	4.99
Yes, but not in gel coat	35	12.03	19,374,530	19.36
Yes, no gel coat used	2	0.69	720,000	0.72
No	113	38.83	40,525,730	40.50
User does not know	124	42.61	34,458,960	34.43
TOTALS	291	100.00	100,076,240	100.00

[a] Based upon upper estimate of resin and gel coat use.

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5.0

DERIVATION OF EMISSION FACTORS

Air pollution control agencies and the industries they regulate are faced continually with the problem of estimating pollutant emissions in the absence of hard, site-specific scientific data. A very common practice is to assume that emissions are a fixed fraction of the material consumed, processed, produced, stored or disposed of by a facility. These fractions, whose scientific bases range from "engineering judgment" to comprehensive field and laboratory studies, are called emission factors. In the case of the polyester resin/fiberglass industry, emission factors are generally expressed as mass of volatile organic compound (VOC) emitted per unit mass of polyester resin consumed in the manufacturing process. For example, the South Coast Air Quality Management District instructs its permit holders to compute their annual emission fees under the assumption that VOC emissions are five and ten percent of laminating resin and gel coat consumption, respectively (MacKnight 1981).

After reviewing the literature, performing laboratory and source emission tests, and discussing the matter with polyester resin users, we believe that using a single emission factor for all cases can lead to serious inaccuracies in predicting VOC emissions. First, as was discussed in Section 3.3, polyester resin/fiberglass processes vary considerably in their emission potential. Second, resins have a wide range of volatile monomer content, so that emission factors based only upon resin mass would often be incorrect. Third, the use of vapor suppressants is frequently not accounted for. Finally, the microenvironment of a production process (temperature, wind speed etc.) can strongly influence evaporation rates. A more realistic approach to defining and applying emission factors would take these realities into account. We have therefore chosen to develop emission factors for each of the major production processes, and to base them upon the input of monomer, rather than resin. These emission factors are defined as:

$$\text{Emission Factor} = \frac{(\text{Mass VOC emitted})}{(\text{Mass VOC input})}$$

Another way of stating this is:

$$\text{Emission Factor} = \frac{\text{(Mass VOC emitted)}}{\text{(Mass resin consumed)}\times\text{(Fraction monomer in resin)}}$$

The next three sections are devoted to our literature review, emissions tests, and laboratory tests. Process-specific emission factors are then derived in Section 5.4.

5.1 REVIEW OF PREVIOUS ESTIMATES

Several attempts have been made to measure the emission of volatile organic gases from the application of polyester resin. Table 5.1-1 summarizes the findings of previous tests identified by this project. 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. We have therefore included, for each emission factor estimate, a rating based upon the relative use of experimental data and assumptions. Table 5.1-2 shows the rating system.

5.1.1 Dade County, Florida Study

One of the earliest attempts to gain an understanding of the nature and quantity of styrene emissions from the polyester resin/fiberglass industry was a study performed by the predecessor of the Metropolitan Dade County Department of Environmental Resources Management in Miami, Florida (Schmitz, 1968). Polyester resin use in Dade County was at that time roughly the same as in Southern California today, and the agency was receiving "frequent complaints" about organic vapor odors around boatbuilding plants and other polyester resin/fiberglass fabrication facilities. In one set of tests, three-ply resin/glass laminates were made by hand layup in a laboratory. A statement that the "resin contained wax" is assumed to imply that a vapor suppressant was present. The author gives the brand name of the resin, but not the styrene percent; our calculations are based upon the knowledge, from our industry survey, that this particular brand of resin contains from 40 to 44 percent styrene. Another set of tests were made at a fabrication plant. The data for only one test, that of a gel coat spray gun, were considered complete enough to use here. Because the Dade County study was done 13 years

5.1-1

EMISSION FACTORS ESTIMATED FROM PREVIOUS STYRENE MEASUREMENT STUDIES

Process	Resin Type[a]	Location	Calculated Emissions Factor (pct)[b]	Rating of Test[c]	Reference[d]
Hand layup	Laminating	Laboratory	8.5 - 10.5	13	1,4
Hand layup	Laminating	Laboratory	15.6 - 35.4	18	5
Hand layup	Laminating	Laboratory	8	16	2
Hand layup	Laminating*	Laboratory	5.6 - 6.3	16	6
Hand layup	Laminating*	Laboratory	1.9 - 2.6	18	4
Hand layup	Laminating*	Laboratory	13.6 - 19.6	18	5
Hand layup	Gel coat	Laboratory	47	16	2
Hand layup	Filament winding	Laboratory	71 - 82	18	4
Hand layup	Filament winding*	Laboratory	16	18	4
Hand layup	(Fire retardant)	Laboratory	6.6	14	2
Hand layup	Casting	Laboratory	3.8 - 4.1	18	4
Hand layup	Casting*	Laboratory	1.0 - 1.4	18	4
Spraygun	Laminating	Field	8 - 18	18	3
Spraygun	Laminating	Field	16 - 25	14	3
Spraygun	Laminating	Field	13	15	3

5.1-1

EMISSION FACTORS ESTIMATED FROM PREVIOUS STYRENE MEASUREMENT STUDIES

(continued)

Process	Resin Type[a]	Location	Calculated Emission Factor (pct)[b]	Rating of Test[c]	Reference[d]
Spraygun	Gel coat	Field	26 - 28	14	3
Spraygun	Gel coat	Field	7[e] - 12[e]	16	3
Spraygun	Gel coat	Field	24 - 38	16	3
Chopper gun	Laminating	Field	27	16	3
Chopper gun	Laminating	Field	>12[f]	10	3

[a] Asterisks indicate use of vapor suppressant

[b] Emission factor = 100 x (styrene emission/styrene input)

[c] Rating system is explained in Table 5.1-2.

[d] 1=Ashland Chemical Company (undated); 2 = Berryman (1978); 3 = DeBoisblanc (1980); 4=Duffy (undated); 5 = Pritchard and Swampillai (1978); 6 = Schmitz (1968).

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

[f] Since exhaust air was diluted to an unknown extent, this figure is a lower bound on the estimate.

TABLE 5.1-2

SYSTEM FOR RATING EMISSION FACTOR TEST DATA

	Rating
Styrene Emissions	
Direct measurement	5
Assumed to be percentage of total organic vapor	1
Styrene Content of Resin	
Direct assay	5
Manufacturer's data	3
Typical for industry	1
Measurement Site	
Workplace/continuous operation	5
Workplace/intermittent	3
Laboratory	3
Resin Use Rate	
Direct measurement	5
Typical batch	3
Estimate from other data	1

ago, it is likely that the spray guns used were significantly less efficient than those used today.

5.1.2 Bay Area Air Quality Management District Tests

During our visit to the offices of the Bay Area Air Quality Management District (BAAQMD), we were permitted to review reports on emissions tests made at six polyester resin/fiberglass fabrication facilities between 1974 and 1978. When interpreting results, one should bear in mind that the purpose of these tests was to verify compliance with hourly and daily emission standards, not to develop emission factors. The following brief descriptions tell how BAAQMD data were used for our purpose.

BAAQMD Source Test 74146. These tests were made on the exhaust of a booth where gel coat is sprayed onto shower and bathtub molds. In their report, BAAQMD personnel noted that the spray booth intake air was heavily contaminated with styrene from laminating resin spraying. We therefore used the data to estimate an overall emission factor for gel coat and laminating resin. Since the styrene content of the materials was not reported, we assume 38 to 42 percent for the gel coat and 40 to 45 percent for the laminating resin.

BAAQMD Source Test 74192. The test site was a pipe manufacturing plant which has since gone out of business. Measurements were taken during chopper gun application of laminating resin and glass to a rotating mandrel. It is not apparent from the report whether the operation was enclosed, or whether emissions were directed through ducts. Emissions were reported as a percentage of the resin used; to convert these to emission factors, we assumed that the resin contained between 40 and 45 percent styrene.

BAAQMD Source Test 74200. This plant manufactures shower, tub and sink fixtures. Gel coat is applied in a separate spray booth. Since the styrene content of the gel coat was not reported, we assumed 38 to 42 percent. For chopper gun spraying of laminating resin, we assumed that the styrene percentage in 1974 was the same as reported by this company in our survey. The test engineers reported that the exhaust from the chopper gun operations was diluted with an unknown amount of fresh air. Our calculated emission factors are therefore probably too low.

<u>BAAQMD Source Tests 75028 and 75029.</u> At this plant, which manufactures a variety of fiberglass products, gel coat and chopper gun operations are performed at separate stations, each of which is equipped with exhaust fans and ducts to the roof. Gel coat styrene was assumed to be 38 to 42 percent, while laminating resin styrene was reported by the company to be 40 percent.

<u>BAAQMD Source Test 75101.</u> Details on test procedures were unavailable for this case. Emissions were reported for a chopper gun spray booth. For the percentage of styrene in the resin, we used the figure reported by this company in our industry survey (45 percent).

<u>BAAQMD Source Test 76061.</u> At this plant, which manufactures fiberglass containers, resin is applied in three spray booths, each equipped with an exhaust fan and stack. The styrene content of the resin was determined by a special laboratory analysis to be 53.3 percent. On the first test day, three measurements were made on one stack. On the second day, one sample was taken from the same stack, and two were taken from a second stack; the third stack was not tested. The low and high styrene emission rates per stack were 1.8 and 4.2 lb/hr, respectively. For three stacks, then, emissions would be between 5.4 and 12.6 lb/hr. In this case, resin use was reported in gallons per day. To convert to weight, we assumed that the resin had a specific gravity of 1.2.

5.1.3 Ashland Chemical Company Tests

In order to test the effectiveness of vapor suppressants in reducing styrene emissions, Ashland Chemical Company of Columbus, Ohio conducted several tests of weight loss from various resin and resin/glass formulations. In the laminating resin tests summarized in Table 5.1-1, 1-ft^2, 3-ply laminates were made with a "standard spray-up" resin having a 20-minute gel time. The <u>rate</u> of weight loss is highest up to and slightly beyond the gel time. The emission factors presented in Table 5.1-1 are based upon the weight loss after one hour.

In another test, an isophthalic polyester resin normally used in filament winding and having a nine-minute gel time was formed into 10- and 20-mil films and allowed to cure. Emission factors presented in the table are based upon weight losses after 24 hours. Note that the test does not simulate filament winding operations. Finally, a composite consisting of 23.5 percent polyester, 26.5 percent styrene, and 50 percent alumina trihydrate (ATH) by weight was tested. Our emission factors are based upon a 30-minute cure time. This last formulation is similar to that used in manufacture of artificial marble.

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.

5.1.4 Shasta County Studies

In 1978, Shasta County performed laboratory tests of gel coat and resin types used at one of the plants within its jurisdiction (Berryman, 1978). One-foot-square glass plates were coated with wax. A gel coat layer was then applied, and the weight loss due to volatile organic emissions was measured over 66 minutes. Glass roving and laminating resin were then added and weight loss was observed for 50 minutes. Finally, weight loss measurements were made after application of a layer of roving and fire-retardant resin. For our estimates of the emission factor, we have used the styrene percentages reported to us by the company in question during our industrial survey.

5.1.5 Kingston Polytechnic Studies

To our knowledge, the only systematic styrene evaporation study published in the peer-review literature was that performed at Kingston Polytechnic's School of Chemical and Physical Sciences in Kingston-on-Thames, England (Pritchard and Swampillai, 1978). Four types of isophthalic polyester resin, with and without a paraffin wax-based vapor suppressant, were used with woven roving or chopped strand glass mat to make laminates. All test laminates were made by hand layup. Styrene losses were determined gravimetrically. In order to determine the effect of various process variables upon styrene emission rates, Pritchard and Swampillai controlled the ambient temperature, air velocity, amount of hand rolling, glass reinforcement type, styrene concentration, and wax concentration.

In general, styrene evaporation increased with increasing wind speed and increasing ambient air temperature. Use of woven roving resulted in higher emissions than when chopped strand mat was used. One interesting finding was that increasing the hand-rolling time from 10 to 15 minutes resulted in significantly higher styrene losses, for both vapor-suppressed and non-suppressed resins. Because experimental conditions varied from test to test, we calculated ranges of emission factors for resins with and without vapor suppressant.

5.2 SAI SOURCE TESTS

As none of the abovementioned studies included direct measurement of styrene from modern fabrication processes, SAI conducted a field sampling program at three polyester resin/fiberglass fabrication facilities. To identify appropriate facilities to test, we first searched our emission inventory survey file for those plants whose exhaust air was channeled through definable outlets; i.e. those which vented styrene-laden air chiefly through open windows and/or doorways were not considered. Explanatory letters were sent to the manager of each potential testing site, who was then contacted by telephone about a week later. Once the first two facilities were enlisted in the testing program, another selection criterion was added. Because of the interest in determining the effect of vapor suppressants upon styrene emissions, we required that the third facility use a vapor-suppressed resin. Field sampling protocols are included in each of the three field test descriptions. Instrument calibration and analytical procedures are reported in Appendix B.

5.2.1 Source Tests at Facility A

Facility A is a large continuous lamination plant in Los Angeles County. A preliminary site visit was made on 5 March 1981. Emissions measurements were made on the morning and afternoon of 18 March 1981 and on the morning of 19 March 1981. The first day began sunny with no wind and gradually turned cool and overcast. The second morning was cold and overcast, with a moderate wind from the south; rain began as we took our last three samples.

Facility Description

The facility consists of two independent units: the fiberglass panel plant, which was of interest to this study, and a polyvinyl chloride molding plant, which was not. Panels are made on a production line running almost the entire length of the west side of the facility. The following description is based upon information supplied by the company, as well as our personal observations. Proprietary process information has been omitted.

During our tests, two types of orthophthalic polyester resin were used. The first, which is used to make general purpose panels, contained 35 percent styrene by weight and no methyl methacrylate (MMA). The second, which is used to improve weather resistance, contained 35 percent styrene and 5 percent MMA. Resins and other chemicals are stored in a yard on the north side of the facility. Blending of resin, colorants, catalyst and fillers (calcium carbonate and ATH) occurs in an open vat inside the plant. After the resin batch is thoroughly mixed, it is pumped to the impregnation table.

The impregnation table consists of a heated metal bed over which a cellophane film is passed at a steady rate. The resin is pumped onto the cellophane and spread evenly over the surface by a "doctor blade." Above the conveyor is a chopper which reduces glass roving to short-length fibers. The fibers are deposited gently and evenly over the moving resin-coated cellophane and then forced into the resin by a special squeeze roll. The wetted glass mat is then transported to the end of the impregnation table, where a top layer of cellophane or polyester film is added. A squeeze roll sets the final thickness of the "sandwich" of film, resin, and glass fibers, and seals the edges. The table temperature is about 57°C (135°F) and the belt speed is 0.06 - 0.21 m/s (12 - 42 ft/min). Since the open area is about 6.1 m (20 ft) long, any portion of the resin-glass mixture is exposed to the air for about 28 to 100 seconds.

Curing takes place in a thermostatically-controlled, gas-fired oven. Wooden "shoes" placed transverse to the direction of travel mold the sheet into the desired cross-sectional pattern. The curing time varies with resin type, desired product properties, and production schedule. Oven temperatures are roughly 104°C in the gel zone (Zone 1), 204°C (400°F) in the cure zone (Zone 2) and 177°C (350°F) in the post cure zone (Zone 4). Zone 3 is a covered area with open sides, located between Zones 2 and 4. After curing, the panels are cut longitudinally and crosswise, sprayed with water, and stripped of the film layers.

Emission Control and Exhaust Points

The assembly line is outfitted with a complex system of hoods, ducts, and fans to minimize the contamination of workplace air with organic vapors and particulate matter. In many cases, ducts from two or more potential emission sources are connected to a header and conveyed to the roof. After reviewing plant plans and touring the assembly line and the roof, we identified the roof-level exhaust points listed in Table 5.2-1. Points 111-37 through 111-40 exhaust air directly from the production line, with no attempt at pollutant removal or dilution. Point 111-41 is in a duct conveying air from the impregnation table to an afterburner, while Point 111-42 is the afterburner exhaust. Point 111-43 is the outlet of an electrostatic precipitator which removes resin and glass particles from air collected from several points in the production line.

The plant has several potential passive emission sources, i.e. those through which air flows principally by convection. Among these are 39 skylights, of which 10 were open on the days of our testing. We observed two elbow vents which are permanently open; one of these was sampled as Point 111-45-1. Finally, the rear door of the plant, near the impregnation table, is usually left open. It is designated as Point 111-45-2 in this study.

Figure 5.2-1 shows the locations of the rooftop sampling points. Point 111-45-2, the rear door, is on the north side of the plant. Although the figure is not to scale, it gives an idea of the relative position of the different pollutant-generating operations along the assembly line, which runs from north to south. Figure 5.2-2 shows the physical configuration of each exhaust vent or duct. Dots indicate the points at which our sampling probe was placed.

Sampling Procedure

We began by using a Foxboro Instruments Model OVA-128 organic vapor analyzer ("OVA") as a "sniffer" at all of the exhaust points listed in Table 5.2-1, to obtain a rough idea of the relative importance of each. Points 111-37 through 111-43 were then sampled in numerical order; seven sample collections constituted one round. The first round was conducted on the morning of 18 March, during which time a resin containing 40 percent styrene and no other monomer was being used on the production line. During the other

Table 5.2-1

DISCRETE EXHAUST POINTS AT FACILITY A

Code Number	Contributing Styrene Sources	Exhaust Air Flow m^3/s (cfm)	Exhaust Air Temp ^oC (^oF)	Observations
111-37	Crosscut saw at end of production line	3.8 (8000)	28-30 (82-86)	No odor
111-38	Curing ovens near end of cure; room air	1.4 (3000)	40-48 (104-118)	
111-39	Curing ovens for early part of cure	0.57 (1200)	76-77 (169-171)	Strong styrene odor
111-40	Glass chopper above impregnation table	2.25 (4770)	26-29 (79-84)	Very strong styrene odor; glass fibers
111-41	Impregnation table (Inlet to afterburner)	0.94 (2000)	29-36 (84-97)	
111-42	Afterburner outlet	1.88 (4000)[a]	540-550 (1004-1022)	
111-43	Various sources (exhaust from particle collection system)	0.57 (1200)[a]	20-30 (68-86)	
111-45-1	Passive duct above impregnation table	Negligible	~25 (77)	Strong styrene odor
111-45-2	Rear door of plant; near impregnation table	Negligible	~25 (77)	Extremely strong styrene odor

[a] Includes 0.94 m^3/s (2000 cfm) of dilution air.

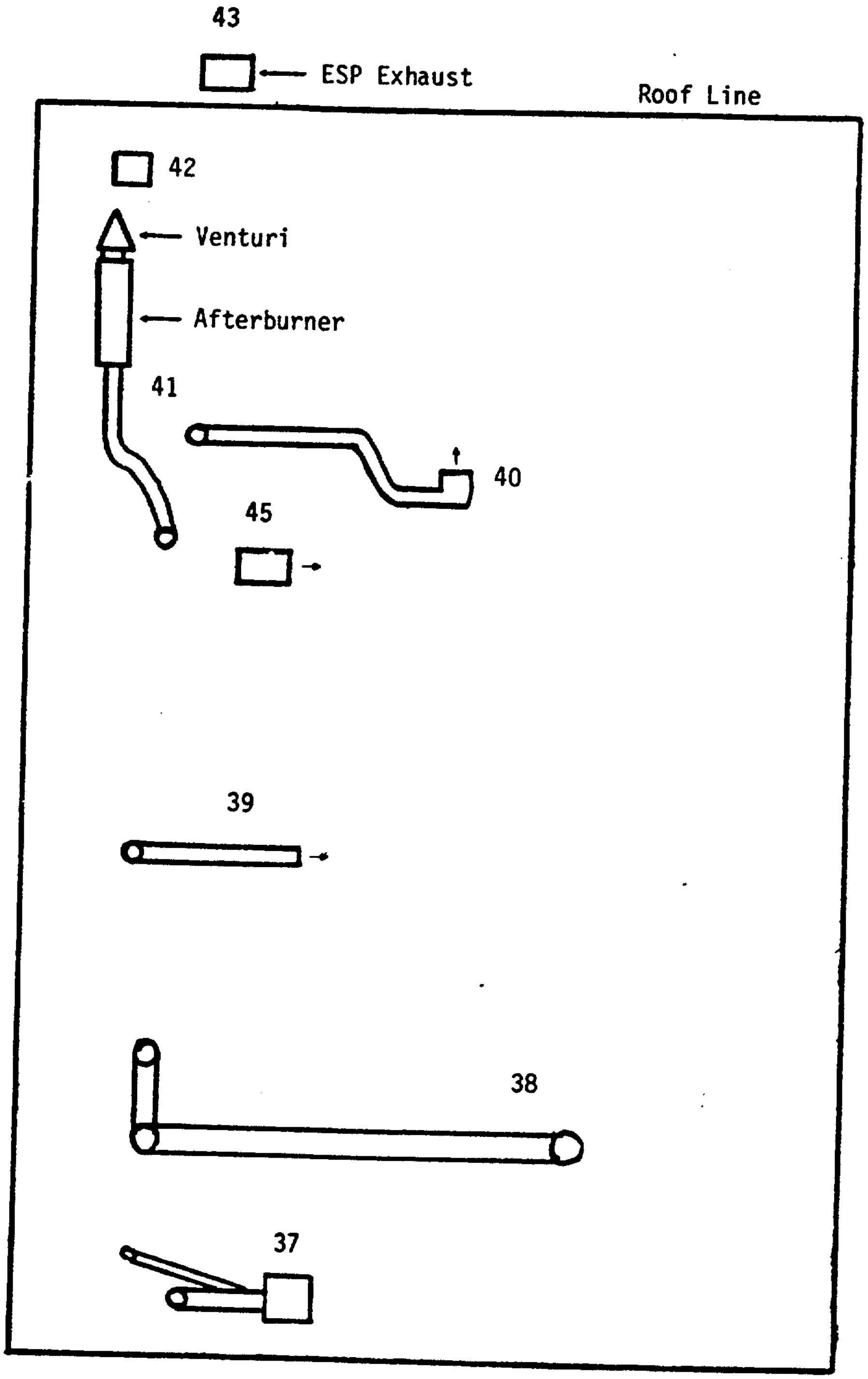

Figure 5.2-1. Locations of Rooftop Sampling Points at Facility A

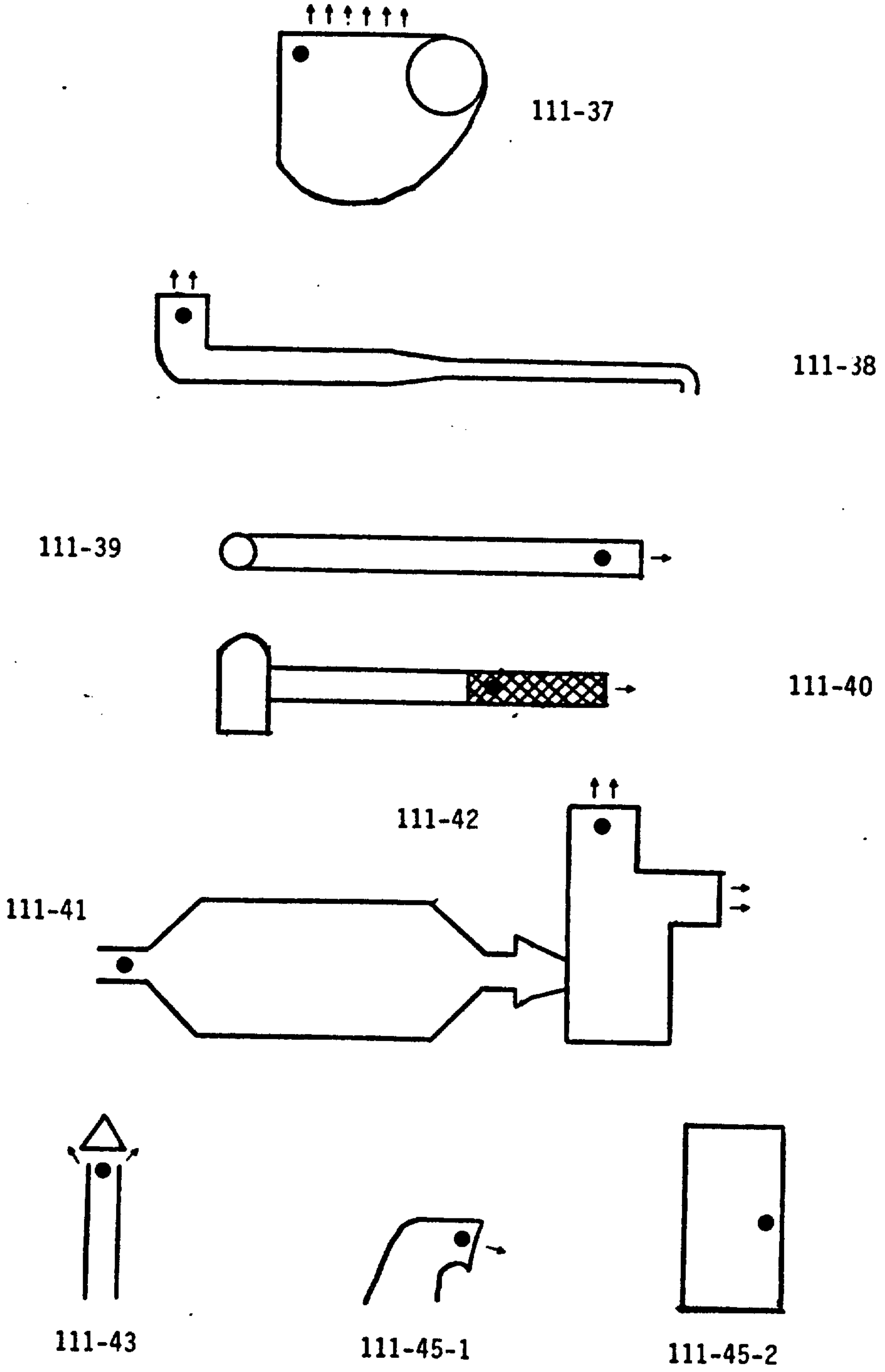

Figure 5.2-2. Configurations of Exhaust Vents and Ducts at Facility A

rounds--two on the afternoon of 18 March and two on the morning of 19 March--a second type of resin, containing 35 percent styrene and 5 percent MMA, was used in production. After the five rounds of forced-air emission sampling, we collected samples from the roof vent (Point 111-45-1) and the rear door (Point 111-45-2). Frequent checks were made with the plant management to assure that production was continuous throughout our testing.

Additional "sniff" tests were made at each point to determine whether pollutant concentrations were likely to vary significantly across the duct or outlet diameter. The only exhaust point at which more than a few percent variation was observed was Point 111-38, for which the minimum and maximum OVA readings were 40 and 55 ppm, respectively. It should be noted, however, that mass flow appeared to be nonsteady; i.e. the OVA readings at any given point in the cross-section varies by several ppm with time. In addition, as is discussed below, OVA readings at this exhaust point were probably influenced heavily by the present of species other than styrene. We therefore assumed that the styrene concentration of the air drawn into our sampling device was typical of the actual exhaust concentration.

Two types of probes were used for sample collection. For Points 111-39 and 111-42, where the exhaust was quite hot, the probe was a 2.4-m (8-ft) copper tube. In all other cases, we used a 43-cm (17-in) stainless steel, ell-shaped tube. Both probes have a 0.32-cm (0.125-in) inside diameter. After the sampling, it was verified that the sampling flow rate was not diminished by the use of either probe. At Points 111-39 and 111-41, where a sampling port was available, the probe was inserted to roughly half the duct diameter. OVA sampling and collection of styrene on charcoal traps followed the procedures described in Appendix B.

Results and Discussion

Table 5.2-2 shows the results of our analyses of the charcoal trap samples collected at Facility A. Given the uncertainty in every aspect of sampling and analysis, concentrations are expressed as ranges. The low value results from assumption of a 1.0-L/min sampler flow rate and a styrene recovery factor of 0.9, while the high value results from use of 0.86 L/min and 0.8 for the two parameters, respectively. It is clear that the highest styrene concentrations are found in air vented from the impregnation table and the portions of the ovens where curing is not fully underway. It is for this

Table 5.2-2

STYRENE CONCENTRATIONS[a] IN EXHAUST AIR AT FACILITY A

Sample ID No.	Emission Source	Styrene Concentration (μg/L)		Styrene Concentration (ppmv)[b]	
		Low	High	Low	High
111-37-1	Crosscut saw	6.2	8.1	1.5	1.9
111-37-4	Crosscut saw	4.6	6.0	1.1	1.4
111-37-5	Crosscut saw	14	18	3.2	4.2
111-38-1	Ovens	29	38	7.2	9.5
111-38-4	Ovens	110	140	27	36
111-39-1	Ovens	10	14	2.9	3.7
111-39-4	Ovens	13	17	3.5	4.6
111-40-1	Impregnation table	130	160	30	39
111-40-4	Impregnation table	330	430	78	100
111-41-1	Pre-Incinerator	2050	2700	500	660
111-41-5	Pre-Incinerator	3300	4300	780	1000
111-41-6	Pre-Incinerator	3600	4700	860	1100
111-42-1	Post-Incinerator	17	22	11	14
111-42-2	Post-Incinerator	19	25	12	16
111-42-4	Post-Incinerator	29	38	19	25
111-42-5	Post-Incinerator	19	25	13	16
111-43-1	ESP	8.0	11	1.9	2.5
111-43-4	ESP	37	48	8.5	11
111-45-1	Open roof vent	380	500	89	120
111-45-2	Rear doorway	250	330	58	77

[a] Low: Sampler flow rate = 1.0 L/min, Recovery fraction = 0.9.
High: Sampler flow rate = 0.86 L/min, Recovery fraction = 0.8

[b] Adjusted for exhaust air temperature.

reason that emissions from the impregnation table are directed to the rooftop incinerator.

On order to estimate mass flows of styrene from the facility, it is necessary to take air flow rates into account. Flow rates for all the exhaust points were obtained from the facility's engineering staff. While it would have been feasible to make our own flow measurements, we believed that the day-to-day variability of air flows would be considerably greater than the uncertainty in any measurements we could make. We therefore relied upon data provided by the facility's engineering staff, which had measured flows at several points within the last year.

Table 5.2-3 shows the mass flow rate of styrene from each forced-air exhaust point. Since emissions from Points 111-45-1 and 111-45-2 were principally by convection, it was not possible to estimate their magnitudes without considerably more information. That the styrene concentrations at these last two points were relatively high does not necessarily mean that emissions therefrom were high; indeed, given the ventilation system, the flow through the rear door (Point 111-45-2) could be expected to be inward at least part of the time. Additional comment is necessary in the case of Point 111-42, the afterburner outlet. Immediately downstream from the combustion chamber, dilution air is added by means of a venturi. We collected samples downstream from the dilution point, so that while styrene concentrations were half what they were upstream, the air flow rate was double. Therefore, the mass flow rate of pollutant was the same both upstream and downstream of the venturi.

The afterburner efficiency may be estimated from the data shown in Table 5.2-3. According to our results, the device removed from 98.4 to 98.8 percent of the incoming styrene mass.

Derivation of Emission Factors

For each charcoal trap sampling run, the starting and ending clock times were noted so that measured concentrations could later be associated with resin use rates. After all the sampling was completed, we obtained copies of the schedule by which resin was added to the production line. From this schedule we were able to compute, for any sampling interval, the average resin use rate, and hence the styrene input rate. As seen in Table 5.2-3, the

Table 5.2-3

ESTIMATE OF PROCESS EMISSION FACTORS FOR FACILITY A

Sample ID No.	Est. Styrene Emission Low (lb/min)	Est. Styrene Emission High (lb/min)	Resin Use (lb/min)	Styrene Flow (lb/min)	Emission factor (as Pct.) Low	Emission factor (as Pct.) High
111-37-1	0.0031	0.0040	24.0	9.6	0.032	0.042
111-37-4	0.0023	0.0030	9.6	3.4	0.068	0.088
111-37-5	0.0068	0.0089	20.2	7.1	0.096	0.13
111-38-1	0.0055	0.0072	30	12	0.046	0.060
111-38-4	0.020	0.027	12.5	4.4	0.45	0.61
111-39-1	0.00078	0.0010	12.7	5.1	0.015	0.020
111-39-4	0.00095	0.0013	23.8	8.3	0.011	0.016
111-40-1	0.037	0.049	12.7	5.1	0.73	0.96
111-40-4	0.099	0.13	20.0	7.0	1.4	1.9
111-41-1	0.26	0.34	12.7	5.1	5.1	6.7
111-41-5	0.41	0.54	20.0	7.0	5.9	7.7
111-41-6	0.45	0.59	16.1	5.7	7.9	10
111-42-1	0.0041	0.0054	12.7	5.1	0.080	0.11
111-42-2	0.0047	0.0062	20.8	7.3	0.064	0.085
111-42-4	0.0072	0.0095	21.7	7.6	0.095	0.13
111-42-5	0.0048	0.0063	22.7	8.0	0.060	0.079
111-43-1	0.00060	0.00079	12.7	5.1	0.012	0.015
111-43-4	0.0028	0.0036	21.7	7.6	0.037	0.047

flow of styrene through the system varied from 3.4 to 12 lb/min during our testing. The last two columns of Table 5.2-3 show the low and high ends, respectively, of our estimated confidence interval for the emission factor. As in the rest of this report, the emission factor is defined as the ratio of styrene emitted to styrene input to the system.

Emission factors for each major in-plant source are summarized in Table 5.2-4. The total uncontrolled emission factor was computed by including the afterburner intake but excluding the afterburner exhaust; i.e. by assuming that the afterburner did not exist. The total controlled emission factor includes the afterburner exhaust but not the input. It is seen that, while the afterburner is highly efficient in removing styrene from the impregnation table exhaust air, enough uncontrolled sources remain to result in an emission factor of 0.9 to 2.8 percent.

A review of all of the concentration, mass emission and emission factor data presented in this section shows an unexpected pattern: styrene emissions are generally higher when Resin 2 (35 percent styrene, 5 percent MMA) is used than when Resin 1 (40 percent styrene) is the main ingredient of the panels.

In summary, two emission factors will be used in estimating styrene emissions from continuous lamination plants. Where controls are absent, the emission factor will vary from 0.059 to 0.13. Where an afterburner is used, the emission factor will be 0.0092 to 0.028.

5.2.2 Source Tests at Facility B

Facility B is a medium-sized (120,000 lb resin per year) tank manufacturing plant in San Diego County. A preliminary site visit was made in March 1981. Emissions measurements were made on the afternoons of 31 March and 15 April 1981. Both days were sunny and clear, with afternoon temperatures around 29°C (75°F). Our initial conversations with plant management led us to believe that exhaust air flow data were available. As this proved not to be the case, we returned to the facility on 13 November 1981 to perform velocity traverses on the exhaust stack.

Facility and Process Description

The chief activity at this plant is the spray application of glass-reinforced polyester resin coating to 38- to 45-m^3 (10,000- to 12,000-gal)

Table 5.2-4
SUMMARY OF ESTIMATED EMISSION FACTORS FOR PLANT A
(EF = 100 x mass styrene out/mass styrene throughput)

In-Plant Source	Resin 1 (40 Pct. Styrene) Mean	Resin 1 (40 Pct. Styrene) Range	Resin 2 (35 Pct. Styrene, 5 Pct. MMA) Mean	Resin 2 (35 Pct. Styrene, 5 Pct. MMA) Range
Crosscut saw	0.037	0.037 - 0.042	0.096	0.068 - 0.13
Ovens (early in cure)	0.053	0.046 - 0.060	0.53	0.45 - 0.61
Ovens (late in cure)	0.018	0.015 - 0.020	0.014	0.011 - 0.016
Glass chopper	0.85	0.73 - 0.96	1.7	1.4 - 1.9
Impregnation table	5.9	5.1 - 6.7	7.9	1.4 - 1.9
Afterburner exhaust	0.095	0.08 - 0.11	0.086	0.060 - 0.13
Electrostatic precipitator	0.014	0.012 - 0.015	0.042	0.037 - 0.047
Total (Uncontrolled)	6.9	5.9 - 7.8	10	7.1 - 13
Total (Controlled)	1.1	0.92 - 1.2	2.5	2.0 - 2.8

steel tanks. All coating operations are conducted in a 4.6 x 12.2 x 4.6 m (15 ft x 40 ft x 15 ft) steel shed, a diagram of which is shown in Figure 5.2-3. At the start of the process, the tanks are sandblasted outdoors. Spray operations are conducted only during conditions of low or moderate humidity; during the season in which we made our tests, spraying generally began after 10 a.m.

One tank is sprayed at a time in the shed. The tank is carried into the shed on a low cart equipped with rollers and is moved to the approximate position shown in Figure 5.2-3. The entry door, which is at the opposite end of the shed from the exhaust stack, is left open, while the exit door remains closed during the spraying. One quarter of the tank's surface is coated at a time. Each coating cycle consists of three steps. First, the operator walks from the open end of the shed toward the closed end, applying a coat of resin with a spraygun attached to a travel arm. After this precoat is applied to the length of the tank, the operator returns to the starting point and then applies a coat of mixed resin and glass roving to the same quarter surface. These two passes take about 45 minutes. Finally, the tank is rotated 90 degrees and the cycle is repeated. The spraygun is thus operating for 180 minutes per tank. The actual manufacturing time is somewhat longer, since the first quarter coat must be substantially cured before coming into contact with the rollers for the application of the fourth quarter coating. This pause in spraying lasts about 20 minutes.

Emission Control and Exhaust Points

Makeup air enters the shed through the open door at one end. During spray operations (and only then), a 5-hp, 1735-rpm, 8-blade exhaust fan draws air through ducts located on the ceiling on either side of the closed end of the shed. The cylindrical exhaust stack is 91 cm (36 in) in diameter and extends 46 cm (18 in) above the roof line. No emission controls are installed.

Sampling Procedure

As will be described below, our sampling procedure differed between the two test days. In each case, however, air samples were drawn through a train consisting of 94 cm (20 ft) of 0.32-cm (0.125-in) inside diameter copper tubing, a cotton plug to remove fiberglass, and a charcoal trap. The cotton plug was replaced every half hour to avoid reduction of flow. The OVA pump

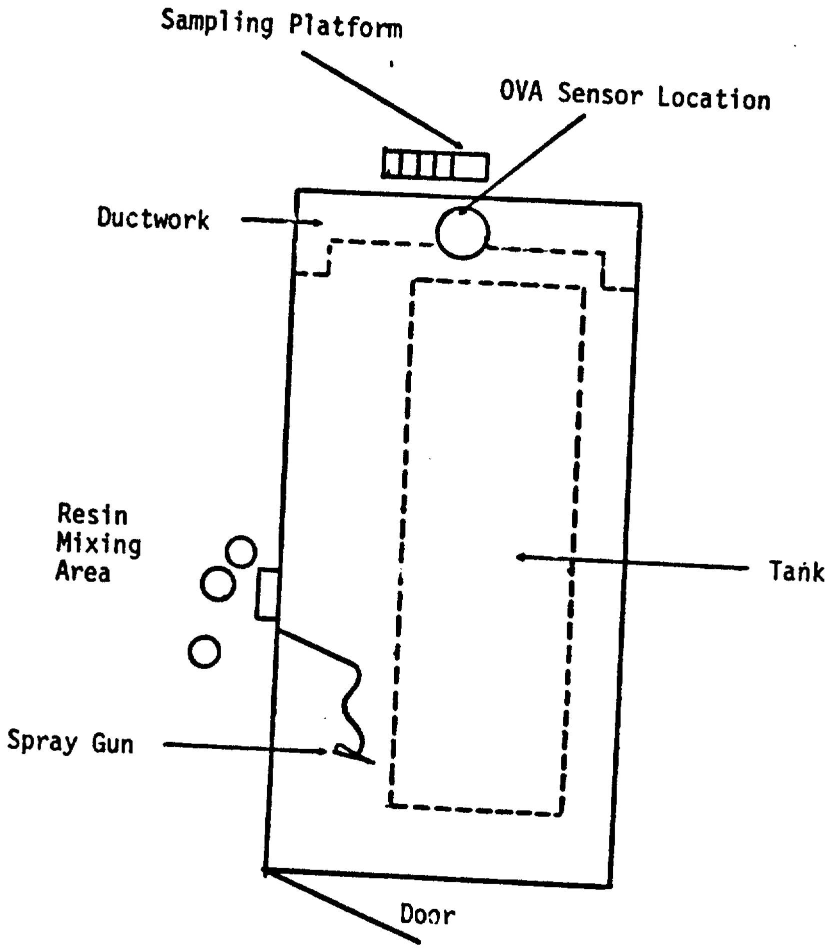

Figure 5.2-3. Plant Layout at Facility B (Scale: 1" = 10').

provided the suction for the sample collection. The copper tube inlet was placed approximately 20 cm (8 in) from the lip of the exhaust stack. The calibrated sampling flow rate was 1.0 L/min on the first day and 0.9 L/min on the second day.

On the day before each test, the OVA was calibrated by the procedures described in Appendix B. On each test day one or two charcoal traps were spiked in the field with known amounts of styrene and immediately sealed. As an additional quality control measure, blank traps were opened and immediately sealed in the field.

To measure exhaust velocity, a Kurz Model 415M hot-wire anemometer and an Ota Keiki Model 29-DGDC digital air velocity meter were placed at 16 points along two perpendicular diameters of the fanstack. Because the air flow was quite turbulent, velocity readings fluctuated considerably. We therefore maintained the sensor at one position for at least three minutes and noted a range of velocities in which about 90 percent of the readings fell. Readings were accurate to 0.05 m/s. Exhaust air velocity and volumetric flow rate were determined with values obtained by averaging six readings (three with the anemometer and three with the digital air velocity meter) at each measurement position. Readings with the air velocity meter were, on the average, 0.60 m/s higher than those on the anemometer; however, this difference was not significant at the 0.05 level ($t = 0.7584$, d.f. = 70).

Results and Discussion

First Day's Sampling. The purpose of the first day's sampling efforts was to obtain estimates of the ranges of styrene concentrations likely to be found in the plant exhaust during different portions of the production cycle. We thus kept a detailed log of activities in the spraying shed, so that they could be correlated with instantaneous OVA readings and concentrations determined from two- to five-minute integrated charcoal trap samples. The mean measured exhaust air velocity and flow rate were 3.2 m/s and 1.5 m^3/s, respectively.

Table 5.2-5 presents the results of our GC analyses of the integrated charcoal trap samples. Analysis of Sample 111-48-1, which was spiked with 4530 ng of styrene in the field, indicated that 80.0 percent of the styrene present was recovered by our measurement technique. (Values reported in Table

Table 5.2-5

RESULTS OF GC ANALYSIS OF EXHAUST AIR GRAB SAMPLES TAKEN AT FACILITY B, FIRST VISIT

Sample ID No.	Sampling Time (min)	Plant Activity During Sampling	Styrene Concentration mg/m^3	Styrene Concentration ppm
111-48-2	5	Spraying of resin only	1105	259
111-48-3	3	Pause after resin spraying	441	103
111-48-4	5	Resin/glass spraying	1383	324
111-48-5	2	Resin/glass spraying, rollout[a]	879	206
111-48-6	5	Intermittent resin spraying at far end	1134	265
111-48-7	2.5	Resin spraying at near end	1730	405
111-48-8	2	No spraying; one door open[b]	410	96
111-48-9	3	Resin spraying (far end)	793	186
111-48-10	3	Resin spraying (near end)	1165	273
111-48-11	3	No spraying; both doors open	351	82

---

[a] Spraying for 30 seconds, rollout for 30 seconds, spraying for 60 seconds.

[b] Sample taken at open door, at opposite end of shed from the principal sampling point.

5.2-5 are for concentrations adjusted by a factor of 1.25). Concentrations in ppm by volume were calculated under the assumption that the exhaust air stream was at the measured ambient air temperature, 24°C.

Figure 5.2-4 shows instantaneous styrene concentrations as measured by the OVA during the test period. Readings made during consecutive one-minute intervals are joined by solid lines. In contrast to the situation at Facility A, where a continuous lamination process is used, styrene levels in the plant exhaust fluctuate considerably. Even the integrated samples taken on charcoal show that concentrations may vary by a factor of four during the spraying of one tank. It was therefore necessary to develop a sampling method which could provide an estimate of the integrated average styrene concentration in the exhaust air over a typical spraying cycle.

Fortunately, as seen in Figure 5.2-5, the correlation between the results of simultaneous OVA and charcoal trap sampling in the field was fairly high ($r = 0.78$). For the second visit, we attached a strip chart recorder to the OVA and devised a method of relating the height of the chart trace to the "true" styrene concentration measured by charcoal trap sampling. By field-calibrating the OVA in this way, we could then calculate integrated average styrene concentrations by planimetry. The method is described in detail in Appendix B.

Second Day's Sampling. Plant operations at Facility B on the second test day were identical to those on the first day, except that a different brand of polyester resin was used. According to the manufacturer, the resin on the second day had a specific gravity of 1.07 to 1.09 and contained 47 ± 2 percent styrene by weight. At approximately 1300 hours, the OVA sampler inlet was placed in the exhaust stack and the chart recorder began recording instantaneous organic vapor concentrations. Spraying operations began at 1336 hours and ended at 1451 hours. The chart recorder was turned off at 1453 hours.

Figure 5.2-6 shows portions of the chart recorder trace corresponding to the first 57 minutes of plant operations. The sudden drops in recorded organic vapor concentrations occurred each time that a charcoal trap was placed in series with the OVA; all styrene was presumably adsorbed onto the trap before it could reach the OVA's FID. Charcoal traps 111-53-1 and 111-53-2 were field-spiked with known amounts of styrene, as mentioned above.

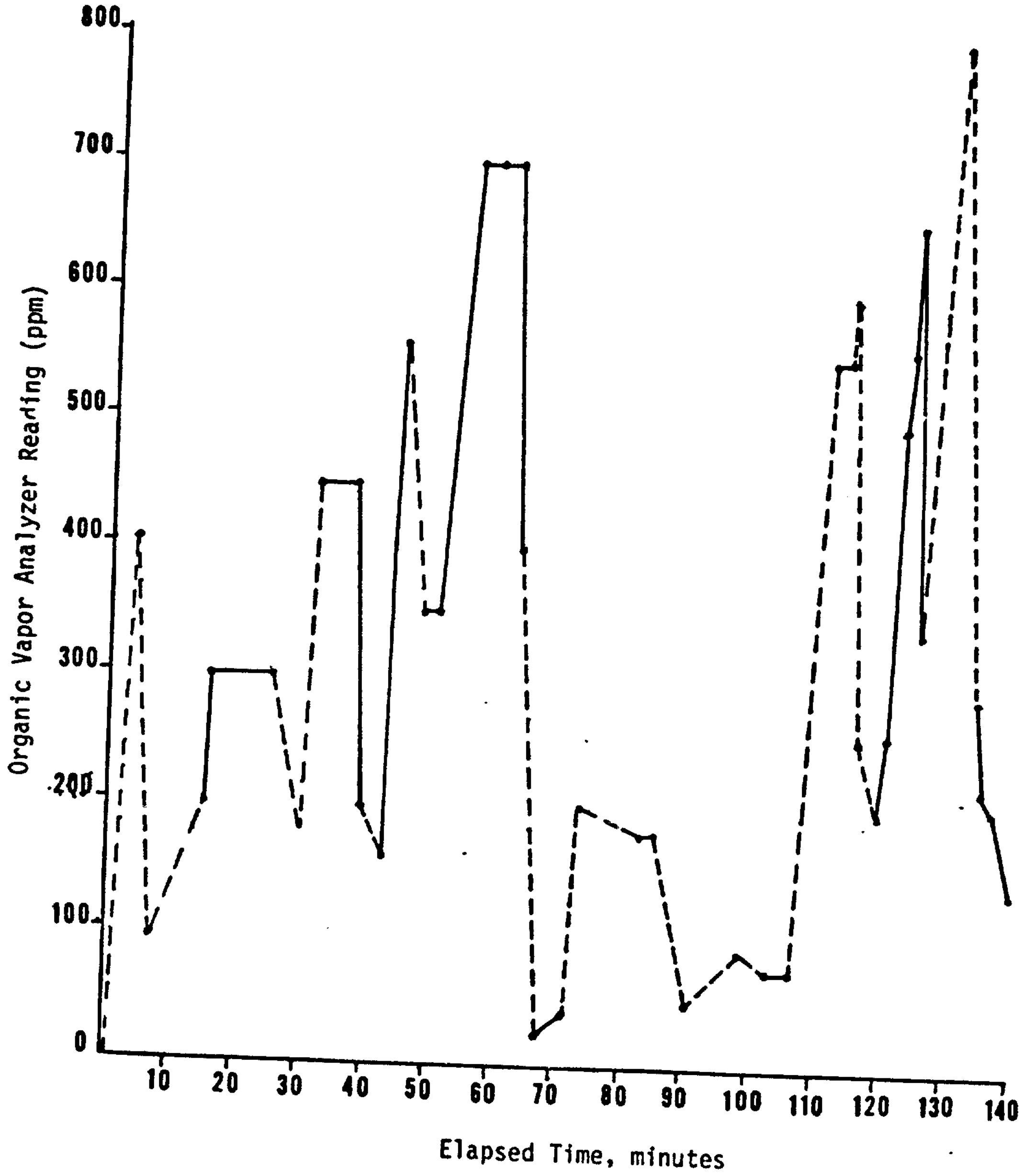

Figure 5.2-4. Instantaneous Exhaust Styrene Concentrations as Measured by Organic Vapor Analyzer at Facility B, First Visit. Solid Lines Connect Readings Made in Consecutive One-Minute Intervals

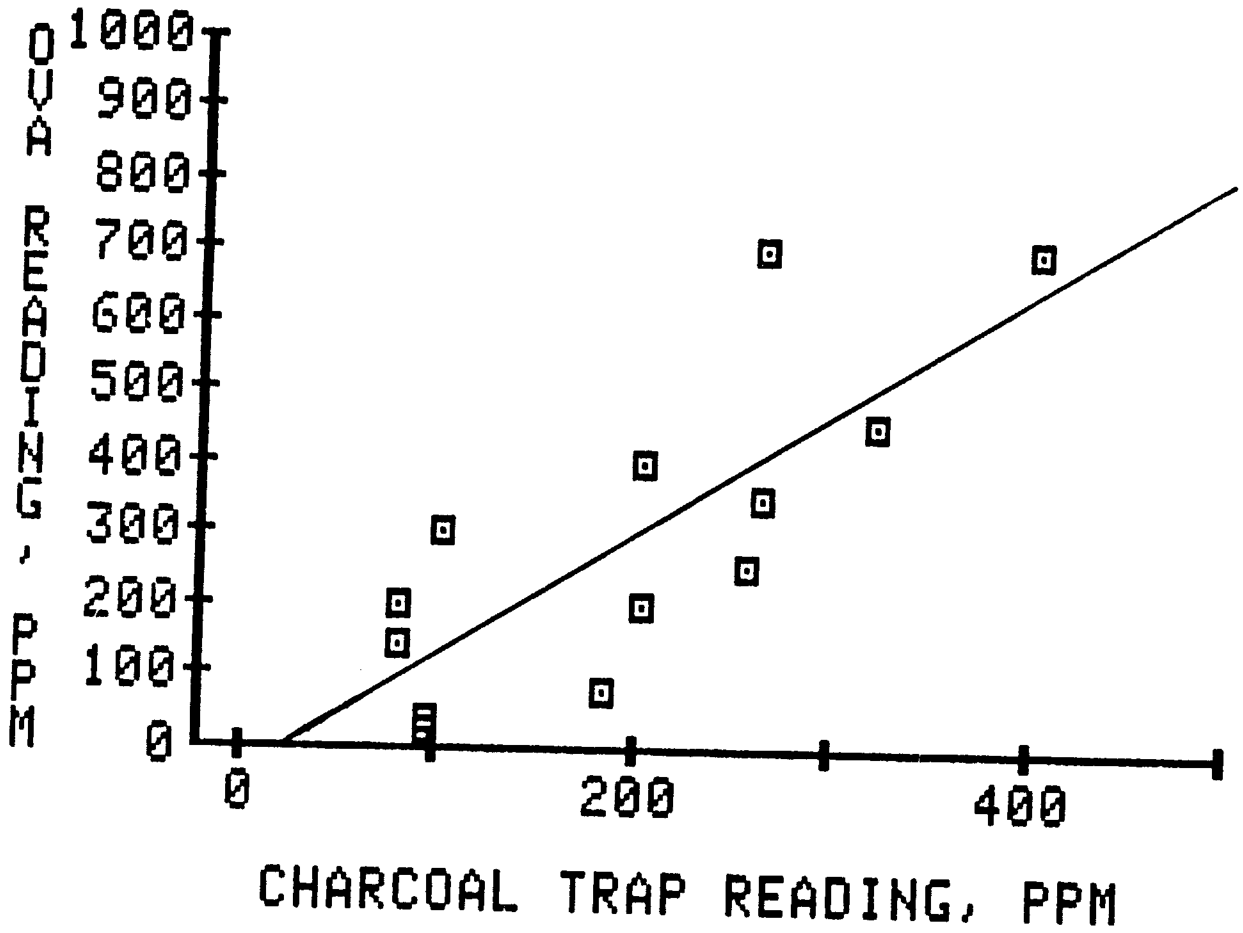

Figure 5.2-5. Organic Vapor Analyzer Readings vs. Charcoal Trap Sampling Results at Facility B, First Visit. Equation of the Regression Line is OVA = 1.69 (TRAP) - 40.0.

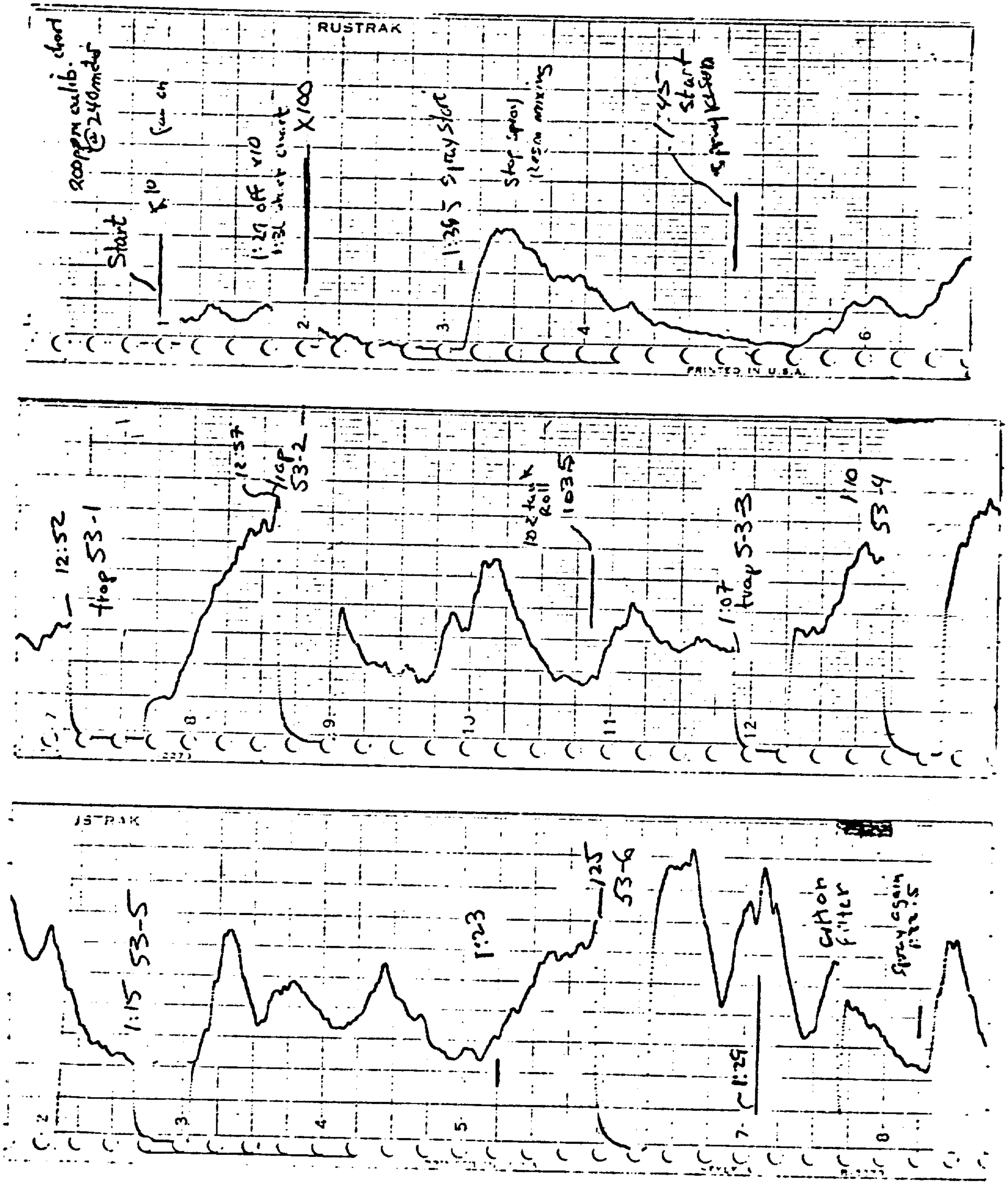

Figure 5.2-6. Recorder Trace of Instantaneous OVA Readings at Facility B, Second Visit

Traps 111-53-3 through 111-53-6 were used for calibrating the OVA trace. (Two additional calibration samples, not shown in Figure 5.2-6, were taken.) The shaded areas were measured by planimetry so that trap readings and integrated chart readings could be compared.

Table 5.2-6 shows, for each sample, the mass of styrene collected on the charcoal trap and the measured area under the recorder trace for the one-minute interval during which the trap sampling was conducted. Ideally, the ratio between chart area and mass collected should be the same for each sample. That it is not is due to variability in planimetry, in styrene recovery efficiency and instrument error. We have attempted to set rough bounds for this variability by adjusting the styrene mass/chart area ratio by the two recovery factors (0.82 and 0.86) determined from the spiked samples. The mean ratio was 63 g styrene per unit chart area, and the 95-percent confidence band for the mean was 55 to 71 g/unit area. Thus the maximum likely error for this calculation would be about 12 percent.

The area under that portion of the OVA trace corresponding to 145 minutes of plant operations, as measured by planimetry, was 2157 chart area units. Therefore by our method, the 95-percent confidence band for the amount of styrene emitted during that time interval would be 55 x 2157 to 71 x 2157 g. Given our sampling rate of 0.9 L/min and the 145-minute sampling time, the concentration of styrene in the plant exhaust was estimated to be 909 to 1174 g/L. As noted above, the measured exhaust air flow rate was 1.5 m^3/s. Mass emission rates were therefore determined to be the following:

	Emission Rate	
	g/s	lb/hr
Low Estimate	1.4	11
High Estimate	1.8	14

Derivation of Emission Factors

According to the plant operator, 263 kg (580 lb) of polyester resin was used during the test period. Since the styrene content of the resin was between 45 and 49 percent, between 118.4 and 128.9 kg of styrene entered the system. Low and high estimates of emission factors were calculated as follows:

Table 5.2-r
CALIBRATION OF OVA CHART RECORDER AT FACILITY B, SECOND VISIT

Charcoal Trap No.	Styrene Measured on Charcoal Trap (µg)[a]	OVA Chart Area[b]	µg Styrene per Unit of Chart Area Low[c]	High[d]
111-53-3	630.4	17.0	47.9	50.2
111-53-4	1378.5	27.3	65.2	68.4
111-53-5	508.8	12.0	54.8	57.5
111-53-6	1529.2	38.8	50.9	53.4
111-53-10	267	5.0	69.0	72.4
111-53-11	237	3.8	80.6	84.5

[a] Uncorrected

[b] Average of three or four planimetric measurements

[c] Based on recovery factor of 0.86 and flow rate of 0.9 L/min

[d] Based on recovery factor of 0.82 and flow rate of 0.9 L/min

$$\text{Low estimate} = \frac{\text{Minimum emission rate}}{\text{Maximum styrene input rate}}$$

$$\text{High estimate} = \frac{\text{Maximum emission rate}}{\text{Minimum styrene input rate}}$$

These quantities are:

$$(EF)_{low} = \frac{(909 \times 10^{-6}\ \text{g/L})\ (1.5\ \text{m}^3/\text{s})\ (10^3\ \text{L/m}^3)\ (145\ \text{min})\ (60\ \text{s/min})}{(128.9\ \text{kg})(1000\ \text{g/kg})}$$

$$= 0.092$$

$$(EF)_{high} = \frac{(1174 \times 10^{-6}\ \text{g/L})\ (1.5\ \text{m}^3/\text{s})\ (10^3\ \text{L/m}^3)(145\ \text{min})(60\ \text{s/min})}{(118.4\ \text{kg})(1000\ \text{g/kg})}$$

$$= 0.13$$

These emission factors are somewhat lower than those we derived in Section 5.1 from reports on previous tests of spraying operations (see Table 5.1-1). We believe, however, that our results are more credible, inasmuch as we took a 142-minute integrated sample rather than a few grab samples, and we measured the exhaust air flow, rather than depending upon fan ratings or other estimates. One very interesting finding is that if the emission factors calculated from our data are based upon resin use, rather than styrene mass input, then they bracket the emission factor used by the South Coast Air Quality Management District (SCAQMD) for this type of emission source; our low and high emission factors would be 0.041 and 0.064, respectively, compared to the SCAQMD emission factor of 0.05.

5.2.3 Source Tests at Facility C

Facility C is a fairly large (420,000 lb resin per year) synthetic marble plant in the South Coast Air Basin. A preliminary site visit was made on 17 June 1981, at which time it was arranged that the plant would use non-suppressed and vapor-suppressed resins on successive test days. Emissions measurements were made on 7 and 8 July 1981.

Facility and Process Description

All manufacturing activities at Facility C are conducted in a one-story rectangular building. Figure 5.2-7 is a schematic of the plant layout. On the two test days, the plant was manufacturing bathroom sinks of various sizes and shapes. The process begins on the west end of the building, where the casting resin is mixed with catalyst, fillers and colorants. Buckets of mixed resin are conveyed on an overhead trolley to the center of the plant. The resin is then hand-poured between the inner and outer shells of partially closed molds, which are conveyed by a belt to the east end of the plant. After a few minutes of curing, the outer shells of the molds are removed, and the sinks are placed in a drying oven. The inner shells are then removed, and the sinks are conveyed to a spray booth on the north side of the plant, where they are sprayed with gel coat. Finally, the gel-coated sinks are cured in an oven next to the spray booth.

Emission Control and Exhaust Points

A preliminary survey of the plant identified the following potential exhaust points for organic vapor emissions:

- Five fan vents along the east-west axis of the roof;
- Doors at either end of the building; and
- An exhaust vent connected to the spray booth and final curing oven

As is discussed below, organic vapor measurements were made at each potential emission point. No organic vapor emission control devices are used in this plant.

Sampling Procedure

On the first test day, the Foxboro Instruments Model OVA-128 organic vapor analyzer (OVA) described in previous sections was used to monitor styrene concentrations at the roof vents and the open doors. A Kurz Model 415M hot-wire anemometer was used to perform velocity traverses on the spray booth exhaust stack and the open doors.

On the afternoon of the first day and throughout the second day, emissions from the spray booth stack were measured by the same combination of charcoal trap sampling and OVA chart recording as was used for Facility B (see Section 5.2.2). On 7 July, the plant used a regular casting resin (i.e. with-

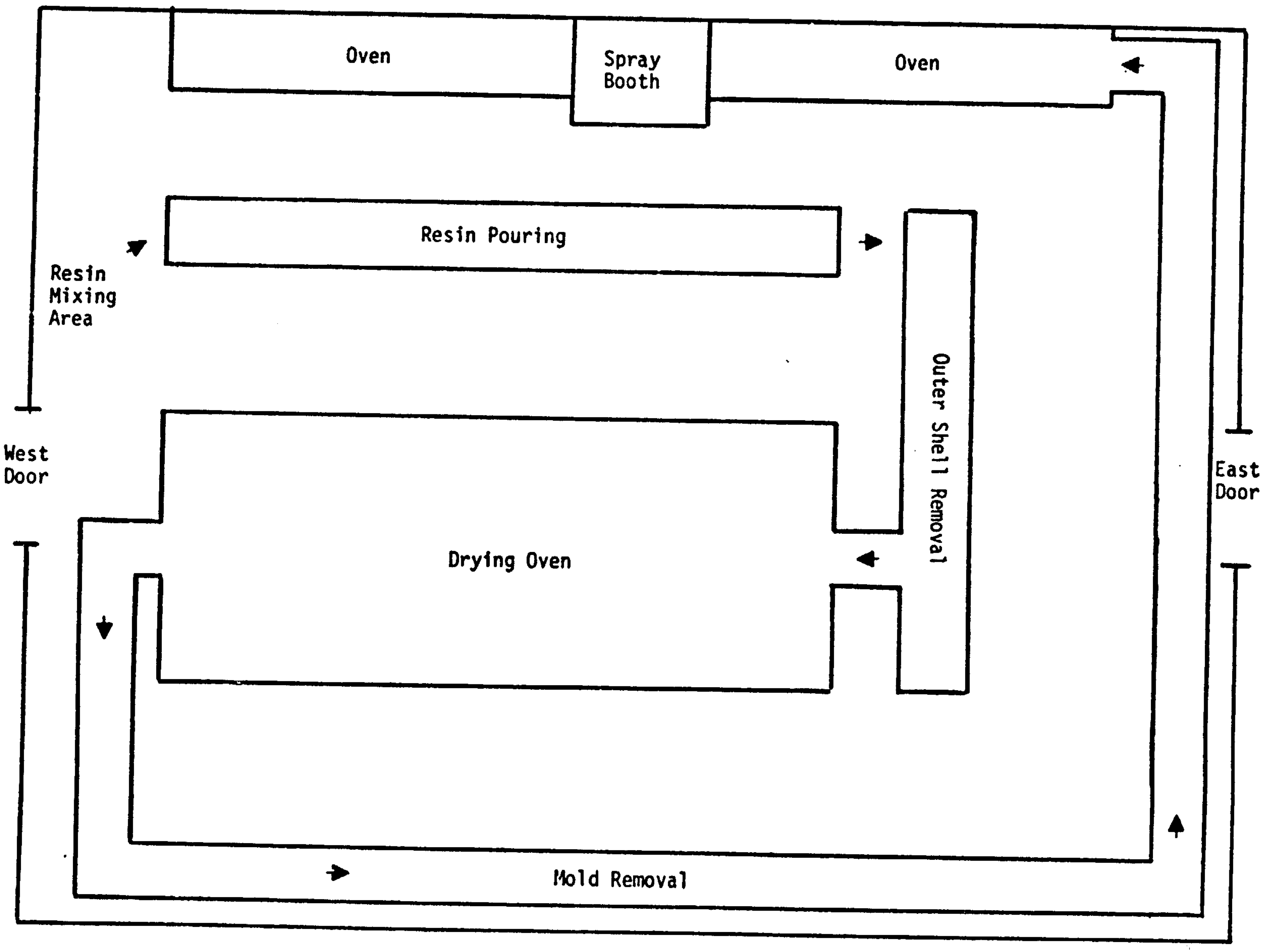

Figure 5.2-7. Plant Layout at Facility C (Not to Scale).

out vapor suppressant) having 37 percent styrene by weight. Continuous stack monitoring began at 1400 hours and ended at 1620 hours, for a total of 140 minutes. When we arrived at the plant on the morning of 8 July, the same resin was being used. The plant operators switched to a vapor-suppressed resin at 1030 hours, at which time we resumed our monitoring. The 173-minute monitoring period for the vapor-suppressed resin was 1037 to 1330 hours.

Results and Discussion

Roof vents: Styrene concentrations in the roof vent exhausts ranged from 5 to 9 ppm. Since these concentrations were far below those of the spray booth exhaust stack, and exhaust air flow was negligible, the roof vents were discounted as significant emission points.

End Doors: After our preliminary site inspection, we were concerned that an appreciable portion of the plant's organic vapor emissions could occur through the 4.3 x 3.7 m (14 x 12 ft) open doors at the ends of the building. These emissions would be quite difficult to monitor, given frequent changes in ambient wind speed and direction. We therefore divided the plane of each opening into quadrants and measured the wind speed and styrene concentration in each one. According to the OVA, the styrene concentration was essentially zero in all four quadrants of the west door and the lower half of the east door, and ranged from 1 to 2 ppm in the upper half of the west door. Spot measurements with the OVA confirmed that organic vapor concentrations were nearly zero inside the plant, near the doorways. Furthermore, we did not observe an appreciable flow of air from the major vapor-emitting processes (i.e. resin mixing, pouring, and gel coat spraying) towards the doors; instead, the main flow appeared to be toward the spray booth, which was equipped with an exhaust fan. Indeed, given the rather high spray booth exhaust air flow rate (see below), the net flow of air through the doors would have to be inward. We therefore discounted the doors as significant points of emissions to the outdoors.

Spray Booth Vent: The flow rate and mean velocity of the spray booth exhaust air were calculated to be 3.4 m^3/s and 3.7 m/s, respectively. Figure 5.2-8 shows three typical sections of the recorder trace of the instantaneous OVA readings. Plant activities concurrent with the sampling are shown at the bottom of the trace. It is evident that styrene emissions are highest when gel coat is being sprayed in the booth. During times of no

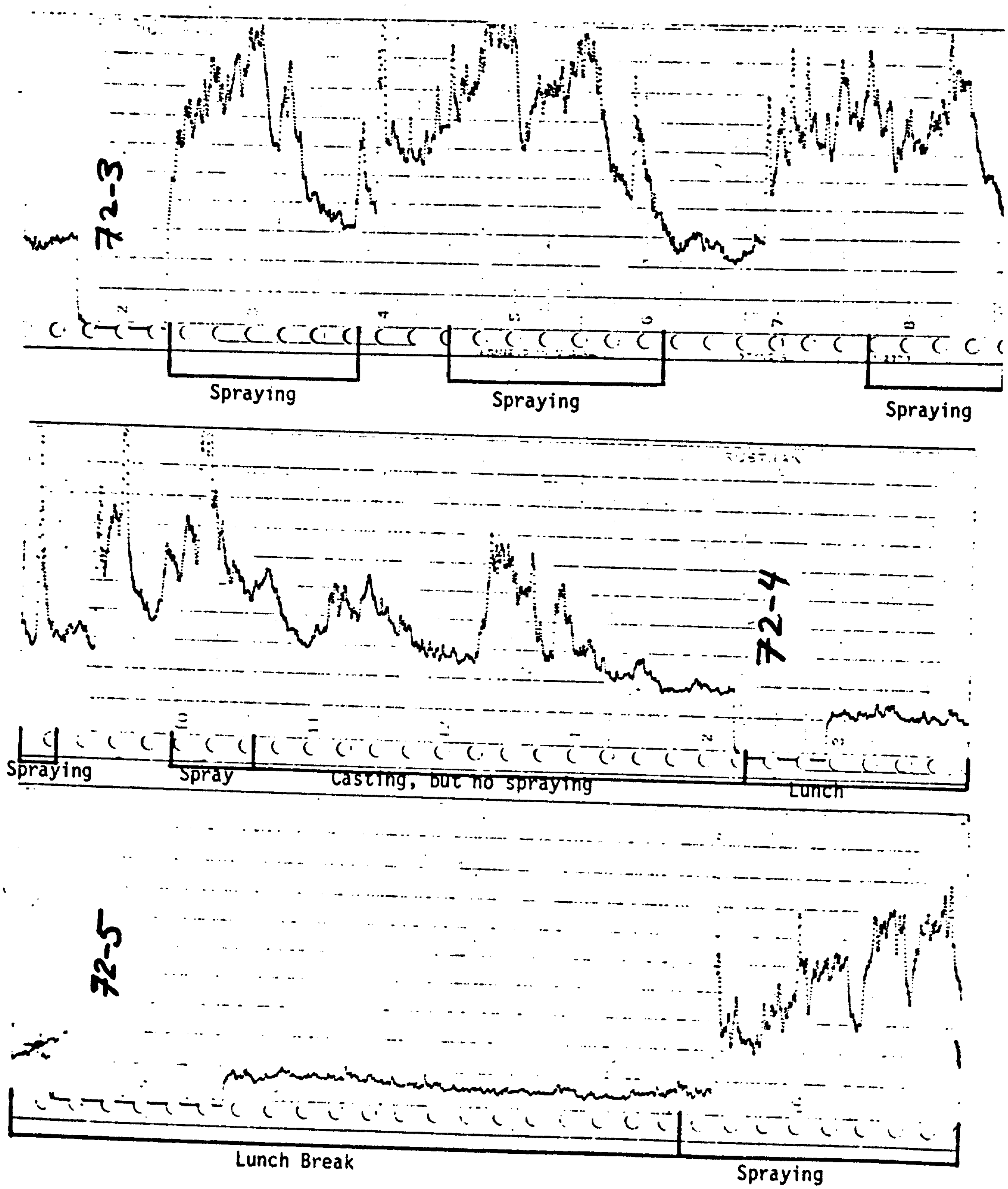

Figure 5.2-8. Recorder Trace of Instantaneous OVA Readings at Facility C, Second Day (Vapor-Suppressed Resin)

spraying, styrene concentrations in the exhaust decline but do not disappear; some of the styrene is probably carryover from the spraying, while some is due to emissions from casting. As seen in the second and third sections of the trace, the exhaust air styrene concentration began to drop at 1107 hours, when pre-lunch break spraying ended. For the next 12 minutes, casting operations continued, and styrene concentrations in the exhaust rose briefly and then began a gradual decline. During the lunch break, exhaust air styrene concentrations remained at about 5 to 10 ppm.

Table 5.2-7 shows the results of our GC analyses of charcoal trap samples and our planimetric measurements of corresponding OVA chart recorder traces. As was done for Facility B, minimum and maximum values for the ratio between styrene mass and chart area were calculated by using two recovery factors (0.80 and 0.81) determined from analysis of field-spiked samples, and two OVA sampling flow rates (0.95 and 0.97 L/min) determined from laboratory calibration. On 7 July, the mean value for the styrene mass/chart area ratio was 55.6 g/area unit, and the 95-percent confidence band was 5.1 to 6.2. On the following day, the ratio was (for an unknown reason) significantly smaller; the mean was 3.2 g/area unit and the 95-percent confidence band was 2.1 to 4.3.

Table 5.2-8 summarizes the calculation of emission rates from the stack monitoring data. It appears that the mass emission rate of styrene is slightly lower when the vapor-suppressed resin is used, although we hasten to note that there is so much overlap in the 95-percent confidence intervals about the means for the two resin types that the difference in means may not be statistically significant. In either case, however, the mass emission rate is lower than that observed for the general purpose polyester resin spraying operations conducted at Facility B.

Derivation of Emission Factors

Because styrene-laden air from the casting operations is commingled with air in the gel coat spray booth, it is impossible to derive separate emission factors for the two processes. The recorder traces from the spray booth exhaust monitoring make it clear that the bulk of the styrene emissions are due to the spraying. We have therefore estimated two types of emission factors: one for the overall operation, and one for gel coat spraying alone.

Table 5.2-7

CALIBRATION OF OVA CHART RECORDER AT FACILITY C

Charcoal Trap No.	Styrene Measured on Charcoal trap (μg)[a]	OVA Chart Area[b]	μg Styrene per Unit of Chart Area	
			Low [c]	High[d]
7 July 1981 Sampling				
117-71-1	87.0	20.0	5.5	5.7
117-71-2	51.5	13.0	5.0	5.2
117-71-3	131.1	27.5	6.1	6.3
8 July 1981 Sampling				
117-72-1	95.5	31.7	3.8	4.0
117-72-4	14.2	9.1	2.0	2.1
117-72-6	42.4	28.0	1.9	2.0
117-72-11	114.6	30.0	4.9	5.0

[a] Uncorrected.

[b] Average of two or three planimetric measurements.

[c] Based on recovery factor of 0.81 and flow rate of 0.97 L/min.

[d] Based on recovery factor of 0.80 and flow rate of 0.95 L/min.

Table 5.2-8

CALCULATION OF STYRENE EMISSIONS FROM FACILITY C

	Sampling Date	
	7 July	8 July
Resin type	Non-suppressed	Suppressed
Sampling time	140 min	173 min
OVA chart area	2131 units	3601 units
Styrene/chart area	5.1 - 6.2 μg/unit	2.1 - 4.3 μg/unit
Mass emission	10.9 - 13.2 mg	7.6 - 15.5 mg
Sampling volume[a]	140 L	173 L
Styrene conc. in exhaust	78 - 94 μg/L	44 - 90 μg/L
Exhaust air flow	3.4 m^3/s	3.4 m^3/s
Mass emission rate	0.27 - 0.32 g/s	0.15 - 0.31 g/s
Mass emission rate	2.2 - 2.6 lb/hr	1.2 - 2.6 lb/hr

[a] Correction for volume flow rate was made in calculating styrene/chart area ratio.

According to the plant operator, the normal production rate is 20 sinks per hour. During the 173-minute monitoring period on the second test day, we counted 60 sinks starting on the casting line. Assuming a steady flow of fixtures through the assembly line, the observed production rate was therefore 20.8 sinks per hour. Given the variability in production from day to day, we have assumed in the following calculations that the nominal 20 sink/hour rate was valid for both test days. On the first test day, the plant operator provided us with a tabulation of resin and gel coat use for the entire day's production. To make 47 sinks, 481 lb of casting resin and 42 lb of gel coat were used. The resin use rates were therefore 4.62 kg (10.2 lb) casting resin and 0.408 kg (0.9 lb) gel coat per sink. The casting resin and gel coat used at the plant contain 37 and 40 percent styrene by weight, respectively.

Table 5.2-9 summarizes the calculation of emission factors for this plant. From 1.4 to 3.1 percent of the styrene entering the plant as cross-linking agent in the casting resin and gel coat is emitted to the atmosphere. By basing the emission factor upon styrene input we can avoid the problem of distinguishing between casting resin and gel coat emissions. By assuming that all the emissions are due to gel coat spraying, however, we can set an upper bound for a gel coat emission factor. The styrene-based emission factor for the gel coat is estimated to be 0.30 to 0.35 for the first test day and 0.166 to 0.34 for the second test day; the absolute upper bound would thus be about 0.35. As has been mentioned several times before, various regulatory agencies have traditionally based the emission factor upon total gel coat use, rather than upon styrene. In our case, the upper bound for this "conventional" type of emission factor is estimated by multiplying the styrene-based factor by the fraction of styrene in the gel coat, 0.4. The result, 0.14, is higher than the value of 0.10 used by the South Coast Air Quality Management Dsitrict. But then, at least some of the styrene emissions entering into the calculation were probably really due to casting resin use.

Finally, it is not possible to draw a firm conclusion about the effectiveness of vapor suppressants in reducing styrene emissions from this facility. The fact that the lower bound of the emission factor estimate is lower for the vapor-suppressed resin than for the conventional casting resin is probably due more to the greater variance in our measurements of the styrene/OVA chart area ratio than to a real difference in emissions. In addition, differences in casting resin styrene emissions could have been masked by emissions from the gel coat spraying.

Table 5.2-9

CALCULATION OF EMISSION FACTORS FOR FACILITY C

Casting Resin Type[a]	Styrene Emission Rate (g/s)	Test Period (min)	Styrene Emitted (kg)	Casting Resin Use (kg)	Gel Coat Use (kg)	Total Styrene Input (kg)	Emission Factor[b]	
							Low	High
NVS	0.27 - 0.32	140	2.3 - 2.7	216	19.0	87.5	0.026	0.031
VS	0.15 - 0.31	173	1.6 - 3.2	267	23.5	108.2	0.014	0.030

[a] NVS = Non-vapor-suppressed resin, VS = vapor-suppressed resin.

[b] Emission factor = Mass styrene out/mass styrene throughput.

5.3 SAI LABORATORY TESTS

In order to supplement the emission data obtained in the field, we conducted a series of controlled laboratory experiments. The objectives of these tests were (1) to compare the emission potential of various brands and types of polyester resin; (2) to determine the effects, if any, of vapor suppressants upon styrene emissions; and (3) to gain insights into mechanisms of styrene emissions. Since no attempt was made to simulate an actual production process, emission factors cannot properly be derived from our results.

5.3.1 Methods

Our test protocol resulted from a synthesis of methods recommended by previous researchers. The "pour pan test method" and test for gel time is based upon procedures used by the Bay Area Air Quality Management District (Balestrieri, 1978). Use of a wind tunnel followed the example of Pritchard and Swampillai (1978), whose tests were described in Section 5.1.5. Finally, minor modifications in the test procedure were made at the suggestion of an industry researcher (Reinhardt, 1981).

Apparatus and Procedures

Figure 5.3-1 shows the apparatus used for our laboratory tests. The basic procedure was to allow a thin film of catalyzed polyester resin to evaporate into a steady, turbulent air stream, and to monitor the weight loss over time. Preliminary measurements showed that 50 ml of resin were needed to obtain a uniform thickness of 1 cm on the petri dish. At the start of each test, this quantity of resin was added to a polyethylene centrifuge tube. A predetermined amount of methyl ethyl ketone peroxide (MEKP) catalyst was then added dropwise to the centrifuge tube, and the mixture was shaken by hand for exactly 3 minutes. The resin/catalyst mixture was then immediately poured into a pre-weighed petri dish, which rested on the pan of a Sartorius Model 2205 top loading mechanical balance sensitive to 0.01 g. An initial mass reading was taken, and then a wind tunnel effect was created by placing a 19.1-cm (7.5-in) square box between the air inlet and outlet ports, as shown in Figure 5.3-1. The top and one side of the box were made of glass, the bottom was open, and the remaining sides were made of wood. Circular holes, 6.6 cm (2.6 in) in diameter, in the wooden sides of the box allowed air to pass through.

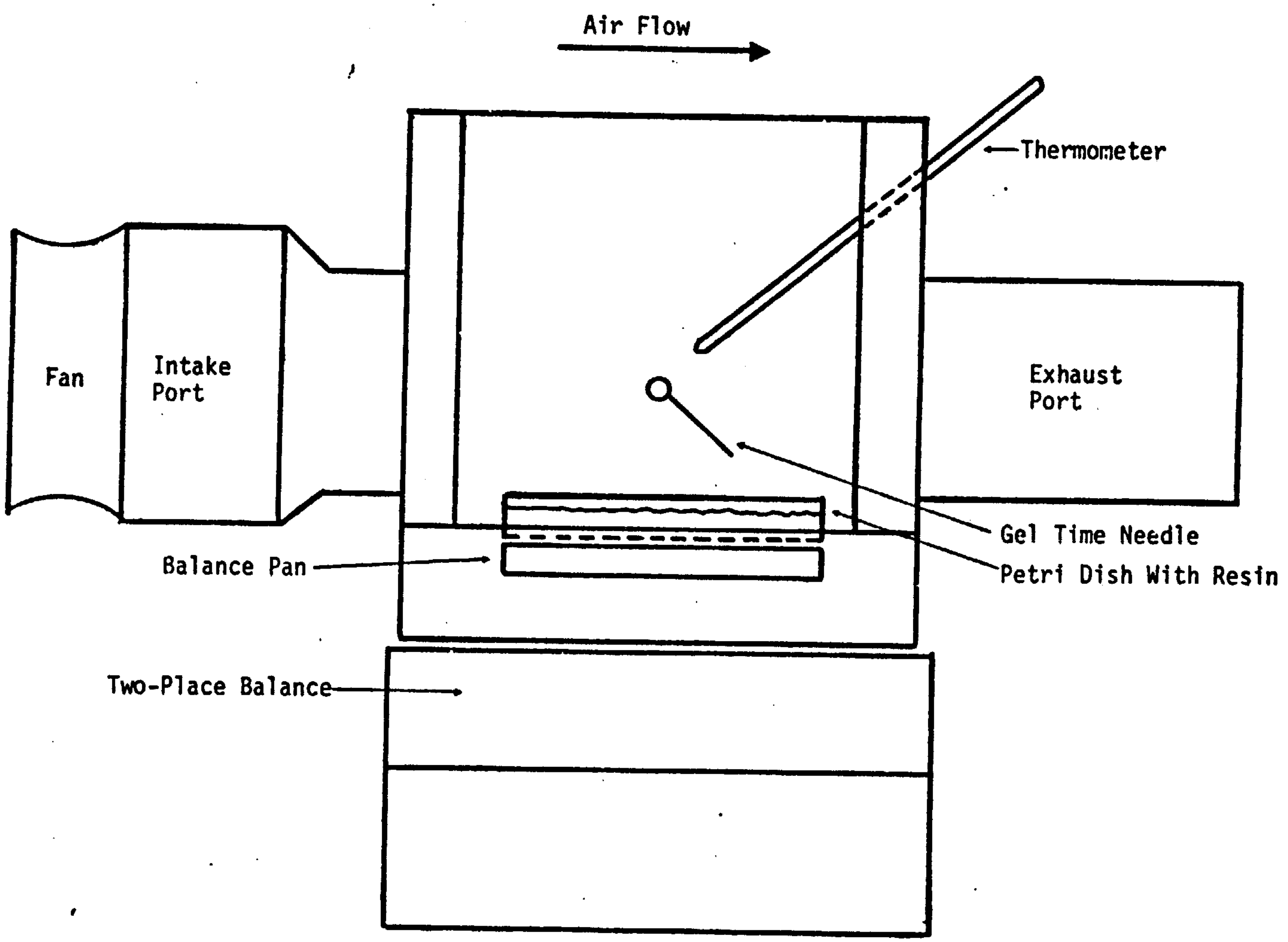

Figure 5.3-1. Resin Evaporation Test Apparatus (Scale: 1" = 2")

Air flow was provided by a 9.5-watt Pamotor Model 4800X three-blade fan. To characterize the air flow, measurements were made with a hot wire anemometer (described in Section 5.2.2) at the inlet and outlet ports and along a line transverse to the air flow and 2.5 cm (1 in) above the resin surface. Because the flow was turbulent, velocity readings were taken over several minutes and averaged. The mean air velocity above the resin surface was 0.9 m/s, and the air flow through the system was approximately 0.02 m^3/s (38 cfm). Temperature was measured at the exhaust port with a 0 to 50^oC immersion thermometer. Relative humidity was determined at the same point with a sling psychrometer.

In order to monitor weight loss accurately, it was necessary to read the balance only when the petri dish was under still air. At various times, the box was lifted and rotated so that one side blocked the flow of air towards the petri dish. Readings were taken and the box was replaced.

Gel time was determined by dipping a glass rod into the resin surface about four times per minute; when the string of resin attached to the rod snapped, gel time was considered to have been reached. Preliminary tests showed that the mass of resin adhering to the glass rod after this test was a negligible percentage of total resin mass. As seen in Figure 5.3-1, the glass rod was rotated towards and away from the resin surface by a wooden dowel protruding from one of the wooden sides of the box.

Selection of Resins to be Tested

Table 5.3-1 summarizes the seven types of polyester resins used in the laboratory tests. Note that Resin Nos. 3 and 4 are from different batches made from the same formula. Resin Nos. 1, 2 and 5 were also used to make laminates for the material tests described in Chapter 9. Resin Nos. 6 and 7 are grab samples taken from the production line in Facility C during our emissions testing there.

5.3.2 Laboratory Test Results

Wind tunnel temperature and humidity, catalyst percentages and resulting gel times and weight losses for the seven test resins are shown in Table 5.3-2. The catalyst percentage and the weight loss were defined as

Table 5.3-1

SUMMARY OF POLYESTER RESIN TYPES USED IN LABORATORY TESTS

Resin No.	Use	Pct Styrene	Material Tests Designation	Emission Test Site	VS
1	General purpose	35 - 37	C	-	No[b]
2	General purpose	42 - 48[a]	E	-	No
3[c]	General purpose	42 - 48[a]	-	-	Yes
4[c]	General purpose	42 - 48[a]	-	-	Yes
5	General purpose	43.8	D	-	No
6	Casting	37	-	C	No
7	Casting	37	-	C	Yes

[a] Range reported by manufacturer for resins of this type; actual percentage for the batch tested here was not known.

[b] Resin does not contain a vapor suppressant additive, but its manufacturer claims it is specially formulated to reduce evaporation.

[c] Resins 3 and 4 are different batches of the same product.

Table 5.3-2

SUMMARY OF LABORATORY RESIN EVAPORATION TEST RESULTS

Resin No.[a]	Run	Temp (^oC)	Relative Humidity (Pct)	Pct. MEKP[c]	Gel Time (min)	Pct. Weight Loss at Gel Time[d]	Pct. Weight Loss at 60 Minutes[d]
1	1	23.0	NM[b]	1.04	19.5	1.83	2.21
1	2	22.8	NM	1.07	19.0	1.74	2.15
2	1	22.4	64	1.02	16.5	1.91	2.32
2	2	21.5	66	0.93	20.0	2.06	2.57
2	3	22.2	66	0.89	17.5	1.87	4.19
3	1	22.5	67	1.02	26.5	1.10	1.54
3	2	22.5	66	1.08	24.5	1.00	1.36
3	3	22.0	68	1.26	24.0	0.97	1.34
4	1	21.5	67	1.46	23.0	0.84	1.13
4	2	21.5	69	1.46	23.0	0.80	1.13
5	1	21.1	70	1.01	12.0	0.60	1.03
5	2	21.1	73	0.90	13.5	0.71	1.06
5	3	20.0	65	0.79	16.5	1.17	1.46
6	1	20.6	70	0.70	19.8	1.30	1.45
6	2	20.0	69	0.68	34.5	2.12	2.26
7	1	20.0	71	0.77	14	0	0
7	2	20.0	71	0.58	19.5	0	0
7	3	21.7	69	0.52	23.5	0	0

[a] Resins are described in Table 5.3-1.

[b] NM - Not measured.

[c] Pct. MEKP = 100 x $\frac{\text{MEKP added}}{\text{Mass resin before addition}}$

[d] Pct. Weight loss = 100 x $\frac{(\text{Resin + MEKP})_{t=t} - (\text{Resin + MEKP})_{t=0}}{(\text{Resin + MEKP})_{t=0}}$

follows:

$$\text{Catalyst Pct.} = 100 \times \frac{\text{(Wt. of catalyst)}}{\text{(Resin wt. before catalyst added)}}$$

$$\text{Weight Loss} = \text{Wt. of resin before catalyst added} + \text{Wt. of Catalyst} - \text{Final wt. (resin and catalyst)}$$

The percentage of weight lost was then defined as:

$$\text{Weight Loss Pct.} = 100 \times \frac{\text{Weight Loss}}{\text{Wt. of resin before catalyst} + \text{Wt. of Catalyst}}$$

Figure 5.3-2 shows, for each test run, the percentage of the original styrene in the resin lost after 60 minutes of evaporation. These values were calculated by dividing the total resin weight loss percentage by the fraction of styrene contained in the original resin. Ranges are given for Resin Nos. 2 through 4 since precise data on styrene content were unavailable.

Before commenting on these results, we would like to point out that our original plan was to compare emissions from pairs of resins identical in every respect except for presence or absence of vapor suppressant, as was done in the materials testing described in Chapter 9. We were able to do this only for Resin Nos. 6 and 7, which were non-suppressed and suppressed, respectively. Unfortunately, resin manufacturers and distributors were unable to furnish us with other formulations we requested in time for the laboratory testing.

It is evident from Figure 5.3-2 that styrene emissions from the vapor-suppressed resins we tested (indicated by triangles) were lower than those from all the non-suppressed resins except No. 5. Indeed, no weight loss was observed in three tests of Resin No. 7, a vapor-suppressed casting resin. We may therefore conclude that, under our test conditions, vapor suppressants do reduce styrene emissions.

Cumulative organic vapor loss over time is plotted for a vapor-suppressed resin (No. 3) and a normal resin (No. 5) in Figures 5.3-3 and 5.3-4, respectively. All resins tested, it should be noted, had evaporation curves of the same general form. The rate of evaporation decreased with time,

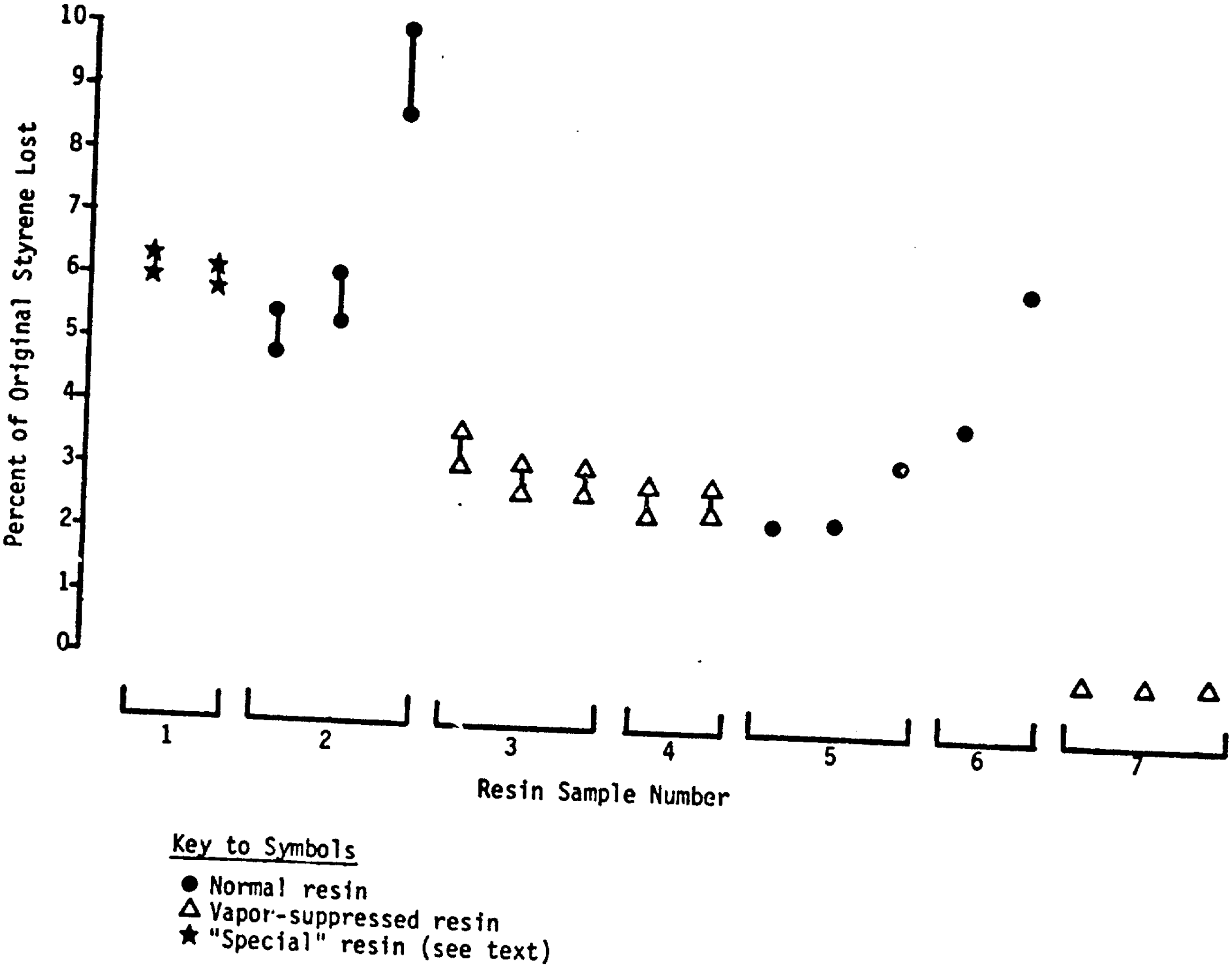

Figure 5.3-2. Cumulative Weight Loss at 60 Minutes

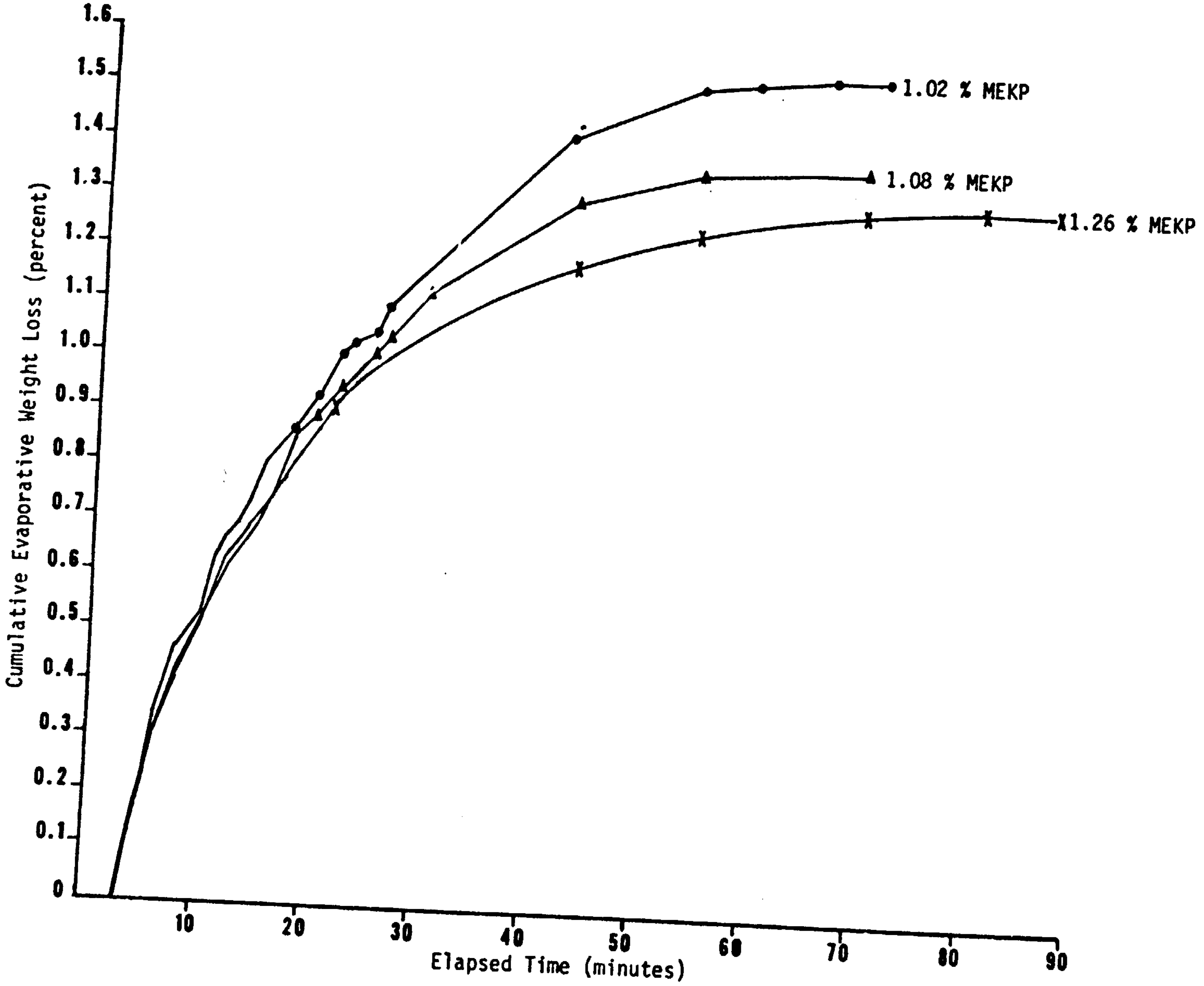

Figure 5.3-3. Weight Loss vs Time for a Vapor-Suppressed Resin

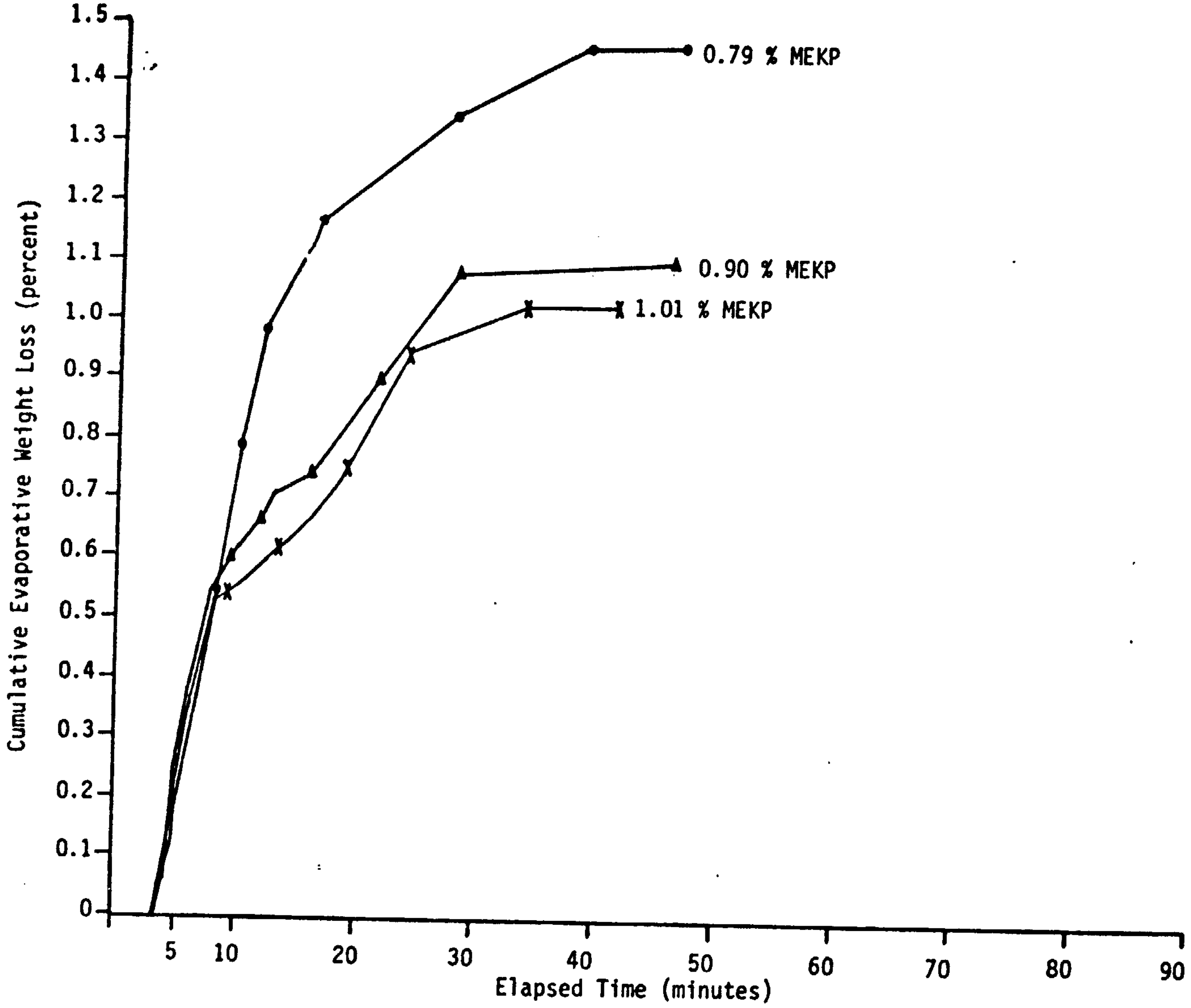

Figure 5.3-4. Weight Loss vs Time for a Normal Resin

especially after the gel time was reached. This finding is consistent with others' observation that, as the cross-linking reaction proceeds, more and more styrene is incorporated in the polyester matrix or otherwise made unavailable for release.

In each figure, curves corresponding to three different concentrations of MEKP catalyst are shown. As was expected, the gel time decreased with increased catalyst concentration. For both resins, the cumulative styrene emission was about the same for all three catalyst concentrations up until the gel time. One very interesting finding was that the long-term cumulative weight loss appeared to be inversely related to the catalyst percentage. For example, when the MEKP concentration in Resin 3 was increased by 28 percent, cumulative weight loss at the 60-minute point was decreased by 29 percent. As seen in Figure 5.3-5, this inverse relationship between long-term weight loss and MEKP concentration held for all of the resins except No. 7, which had zero weight loss at all catalyst concentrations. The control strategy implications of this finding are discussed in Chapter 7.

5.4 RECOMMENDED EMISSION FACTORS

5.4.1 Rationale for Selection

Table 5.4-1 lists the ranges of emission factors which we have chosen to use for estimating organic vapor emissions from the polyester resin/fiberglass industry in California. Details of how these factors were used are provided in the next chapter. The rationale for our selection of the particular ranges shown in the table was as follows.

Hand Layup

In our judgement, the data from the laboratory tests of Pritchard and Swampillai (1978) are both the best documented and most representative of actual operating conditions; they were thus used for the emission factors for laminating resins. For gel coat, we used the only experimental data available, those of the Shasta County Air Pollution Control District (Berryman, 1978).

Spray Layup

This category includes both chopper gun spraying and application of unreinforced resin and/or gel coat. As stated in Section 5.2.2, we believe that our tests at Facility B yielded more reliable data than reported

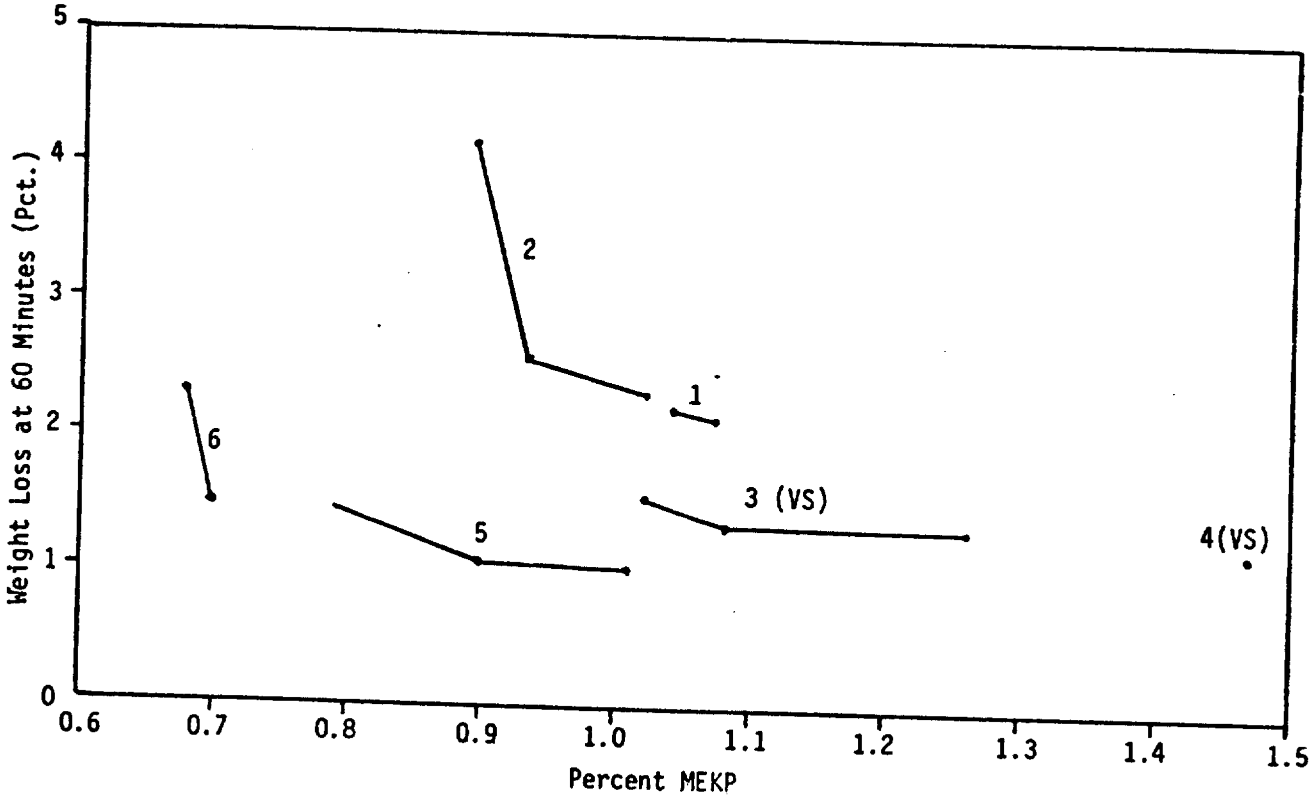

Figure 5.3-5. Resin Weight Loss After 60 Minutes, as a Function of Catalyst Percentage

Table 5.4-1

RECOMMENDED MONOMER-BASED EMISSION FACTORS FOR POLYESTER RESIN/FIBERGLASS OPERATIONS
(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[a]		NA[b]	
Pultrusion	6 - 13		NA	
Filament winding	6 - 13	3 - 9	26 - 35	13 - 25
Closed molding	1 - 3	1 - 3	NA	

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

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

heretofore in the literature. We have therefore used our calculated range of emission factors. For gel coat spraying, our tests at Facility C (described in Section 5.2.3) yielded an upper bound of 35 percent. We have combined that value with a lower limit derived from Bay Area Air Quality Management District field tests (DeBoisblanc, 1980).

Hand and Spray Layup Combined

Because our resin use survey revealed that a significant number of firms use both hand and spray layup processes in the same plant, it was necessary to assign a range of emission factors for this combination. We did so by assuming that spraying would be the major activity, and that the hand layup in these plants would be done for repairs and other minor jobs. The emission factors for spraying and hand layup were weighted by 0.75 and 0.25, respectively, to derive a composite range of emission factors. The same weighting was used for gel coat.

Marble Casting

For casting resin emissions, we used the emission factor range determined from our measurements at Facility C. While our range of one to three percent may appear to be low, this estimate may actually be too high, since our sampling included emissions from gel coat spraying as well as from casting operations. Our selected emissions factors for gel coat application at marble plants are the same as for gel coat spraying in general.

Continuous Lamination and Pultrusion

The emission factors reported for continuous lamination are those derived from our source tests at Facility A. Note that the range of 6 to 13 percent is for uncontrolled emissions. Where incinerators are used, the emission factor drops to 1 to 3 percent. Because of the similarity of processes, the same ranges of emission factors were assigned to pultrusion. As gel coat is not normally used in these two operations, no additional emission factors were assigned.

Filament Winding

While tests of emission from filament winding resins have been reported (Duffy, undated), to our knowledge no process emissions tests have been performed. The most similar operation from the standpoint of emission potential would be continuous lamination. We therefore assigned the continuous lamination emissions factors to filament winding.

Closed Molding Processes

No test data on emissions from bag molding, matched metal molding and other closed molding processes were available. From the nature of the processes, however, one would expect emissions to be quite low. We have therefore assigned the emission factors for marble casting (a semi-closed process) to this last category.

5.4.2 Adjustments for Use of Vapor Suppressants

As will be discussed in Chapter 7, no single measure of the effectiveness of a vapor suppressant can be applied to all cases; resins, processes, and operating conditions vary too much. It is our judgement, based upon our literature review and discussions with industry researchers, that vapor suppressants are likely to reduce styrene emissions by between 30 and 50 percent under most circumstances. We have therefore adjusted the emission factors in Table 5.4-1 by multiplying the low and high ends of each range by 0.5 and 0.7, respectively.

5.4.3 Discussion

One aspect of our selection of emission factors which may appear surprising is that the factors for hand layup are higher than those for spray layup, especially in light of our statement in Section 3.3.2 that "of all the production processes reviewed here, spray layup probably has the highest potential for emission of organic vapors." By breaking the resin up into tiny droplets, the spraying process creates an enormous surface area for evaporation. On the other hand, it is more convenient to perform hand layup operations with resins having long gel times and, as was demonstrated in our laboratory experiments, long-term emissions increase with increasing gel times. Unfortunately, no useful field data on hand lamination emissions could be found.

Finally, we recognize the inconvenience of using ranges of emission factors rather than single values, especially since most compilations of emission factors report only the latter. The complexity of the real world must be taken into account, however, if emissions estimates derived from process flows are to be truly useful. Given the limited data at our disposal, we believe that the best way to keep this complexity explicit and manageable is to present reasonable ranges for all the variables going into our emission predictions.

5.5 REFERENCES

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6.0
ESTIMATION OF ORGANIC VAPOR EMISSIONS IN CALIFORNIA

The last step in our assessment of the polyester resin/fiberglass industry in California was to estimate the emissions of volatile organic compounds from all the facilities identified in our survey. In the following discussion, it should be understood that the organic vapor emissions to which we refer are in the vast majority of cases those of styrene monomer. Although it is true that other cross-linking agents, chiefly methyl methacrylate, are emitted by many facilities, no significant change in our results would occur if we did not treat all emissions as styrene.

6.1 METHODOLOGY

Emissions from each facility identified by our survey were calculated by multiplying laminating or casting resin use rates by the appropriate emission factors. Our general methodology is described in the next section. Adjustments were made for the three plants at which we conducted field tests and for the 14 firms for which we obtained only partial information. These departures from the general methodology are described in Section 6.1.2.

6.1.1 General Methodology

The general equation for the emissions from a facility was:

$$\begin{aligned}\text{Emissions} = {} & \left[(\text{Resin use}) \times \begin{pmatrix}\text{Fraction}\\ \text{styrene}\\ \text{in resin}\end{pmatrix} \times \begin{pmatrix}\text{Emission factor}\\ \text{for process}\\ \text{combination}\end{pmatrix} \times \begin{pmatrix}\text{Vapor}\\ \text{suppressant}\\ \text{use factor}\end{pmatrix} \right] + \left[(\text{Gel coat use}) \times \begin{pmatrix}\text{Fraction}\\ \text{styrene}\\ \text{in gel coat}\end{pmatrix} \times \right. \\ & \left. \begin{pmatrix}\text{Emission factor}\\ \text{for process}\\ \text{combination}\end{pmatrix} \times \begin{pmatrix}\text{Vapor}\\ \text{suppressant}\\ \text{use factor}\end{pmatrix} \right]\end{aligned}$$

It should be noted that all emission factors are based upon the quantity of <u>styrene</u> (or other monomer) entering the facility, rather than upon the amount of resin and/or gel coat. The rationale for basing emission factors on styrene content was presented in the previous chapter. In addition, all of the variables in the equation except the styrene fractions are considered as ranges, rather than as single values.

Table 5.4-1 presented our best engineering judgments of the emission factors to be used for all the common polyester resin/fiberglass fabricating processes. These numbers, it should be noted, were adjusted for use or non-use of vapor suppressants. In a great number of cases, plants actually use two or more processes. In the marble casting plant we tested, for example, the main process was casting in a semi-closed mold, but gel coat was also sprayed onto the semi-cured units. Although our survey respondents identified the production processes they used, in only a few cases did they report on how much resin was used in which process. It was therefore necessary to develop emission factors for combinations of production processes. Table 6.1-1 shows what we believe are reasonable composite emission factors for the combinations reported in our survey. These emission factors have not been adjusted for vapor suppressant use.

Table 6.1-2 presents the vapor suppressant adjustment factors. If no vapor suppressant is used, then emissions are unaffected, and the adjustment factor is unity. We have assumed that the suppressants reduce styrene emissions by between 30 and 50 percent. The adjustment factors for the low and high cases of emissions are therefore (1 - 0.5) and (1 - 0.3), or 0.5 and 0.7, respectively.

Finally, maximum hourly and daily emissions were calculated by dividing the emission estimate by the operating time fraction and by the appropriate time units. For example, a plant operating 75 percent of the time and emitting 4 tons per year would have the following short-term emissions:

Daily emissions = (4 tons/yr) (1/260 days/yr) (1/.75) (2000 lb/ton)
= 41 lb/day

Hourly emissions = (41 lb/day)/(8 hr/day) = 5.1 lb/hr.

Annual emissions aggregated by geographic region, firm size, production process and other variables of interest are presented in Section 6.2. Data on individual firms, including daily and hourly emissions are contained in a separate document. To protect confidentiality, the latter compilation has been made available only to the Air Resources Board.

Table 6.1-1

EMISSION FACTORS FOR PROCESS COMBINATIONS

(Units are 100 x mass monomer emitted/mass monomer input)

Process Combination[a]	Resin Emission Factor Low	Resin Emission Factor High	Gel Coat Emission Factor Low	Gel Coat Emission Factor High
1	16	35	47	47
1,2	11	19	31	38
1,2,3	1	3	31	38
1,2,5	9	13	31	38
1,2,7	1	3	31	38
1,3	1	3	47	47
1,5	9	13	47	47
1,7	1	3	47	47
1,9	13	13	25	25
2	9	13	26	35
2,3	1	3	26	35
2,5	9	13	26	35
2,5,7	9	13	26	35
2,7	1	3	26	35
2,8	1	3	26	35
3	1	3	31	38
4	6	13	31	38
5	9	13	31	38
6	6	13	31	38
7	1	3	31	38
7,9	1	3	31	38
8	1	3	31	38
9	13	13	25	25

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[a] Key: 1 = hand layup, 2 = spray layup, 3 = bag molding, 4 = continuous lamination, 5 = filament winding, 6 = pultrusion, 7 = marble casting, 8 = closed molding, 9 = other.

Table 6.1-2

VAPOR SUPPRESSANT USE FACTORS

Use of Vapor Suppressant	Resin Factor		Gel Coat Factor	
	Low Case	High Case	Low Case	High Case
Not used at all	1	1	1	1
Used only in laminating or casting resin	0.5	0.7	1	1
Used in resin and gel coat	0.5	0.7	0.5	0.7
Don't know	1	1	1	1

6.1.2 Special Adjustments

Source Test Firms

Since plant-specific emissions data were available for three plants as a result of our field tests, we did not use the general methodology for those cases. For Plant A, we assumed that the incinerator operates at the same efficiency as when we performed our test. For Plants B and C, we used measured emission factors, along with the plant operators' estimates of total annual use of gel coat and/or resin.

Supplementary Data Set

It will be recalled from Chapter 4 that, in addition to our complete set of data on 291 firms, we assembled a set of partial data on 14 firms. We were able to obtain resin use data from only two of the latter. These included a panel-making plant and a spa manufacturer, both of which are in Los Angeles County. Using the appropriate emission factors, we estimated ranges of emissions of 0.8 - 1.8 and 5.6 - 8.2 tons/yr for the two plants. Emission totals for Los Angeles County and for aggregations by product and manufacturing process were increased by these amounts.

6.2 RESULTS

6.2.1 Emissions By Geographic Unit

According to our estimates, between 1406 and 2544 metric tons/yr (1550 and 2805 tons/yr) of reactive hydrocarbons were emitted from polyester resin/fiberglass fabrication operations in California during August 1980 - May 1981. Table 6.2-1 shows estimated emissions by county. Los Angeles, Orange and San Diego Counties, where the polyester resin/fiberglass industry is concentrated, account for 81 percent of the total emissions. Distributions of emissions by federal air quality control region (AQCR) and state air basin are shown in Tables 6.2-2 and 6.2-3, respectively. Again, the preponderance of the emissions are in Southern California. It is interesting to note that emissions in the Sacramento Valley are higher than those in the San Francisco bay area, even though polyester resin use is nearly identical in the two basins. A likely reason for the difference is that the Sacramento Valley has a higher proportion of firms using processes with high emission factors.

Table 6.2-1

ESTIMATED EMISSIONS FROM POLYESTER RESIN/FIBERGLASS FABRICATION: DISTRIBUTION BY COUNTY

County	Annual Emission (tons/yr) Low	Annual Emission (tons/yr) High	Pct. of State[a]
Alameda	5.39	13.86	0.49
Contra Costa	18.14	26.49	0.94
Fresno	9.46	18.30	0.65
Glenn	0.30	0.47	0.02
Kern	16.93	24.77	0.88
Los Angeles	262.18	512.52	18.27
Madera	0.55	0.94	0.03
Marin	2.43	5.29	0.19
Merced	8.05	14.08	0.50
Napa	3.65	6.94	0.25
Orange	855.90	1477.62	52.68
Placer	1.22	2.11	0.08
Sacramento	9.48	23.90	0.85
San Benito	7.54	39.32	1.40
San Bernardino	34.05	52.10	1.86
San Diego	143.20	272.46	9.71
San Francisco	0.86	1.84	0.07
San Joaquin	37.23	54.94	1.96
San Luis Obispo	5.08	13.50	0.48
San Mateo	7.85	22.27	0.79
Santa Barbara	3.85	7.86	0.28
Santa Clara	25.12	49.14	1.75
Santa Cruz	3.19	5.05	0.18
Shasta	16.02	30.95	1.10
Solano	0.68	2.10	0.07
Sonoma	5.27	10.57	0.38
Sutter	0.51	0.99	0.04
Tehama	5.77	16.67	0.59
Tulare	5.67	10.63	0.38
Ventura	5.90	11.15	0.40
Yolo	46.33	66.13	2.36
Yuba	1.91	4.98	0.18
TOTALS	1549.71	2804.94	99.81[b]

[a] Percentages are based upon the upper estimate.
[b] Discrepancy in total percentage is due to rounding.

Table 6.2-2

ESTIMATED EMISSIONS FROM POLYESTER RESIN/FIBERGLASS FABRICATION: DISTRIBUTION BY FEDERAL AIR QUALITY CONTROL REGION (AQCR)

AQCR No.	Name	Estimated Emissions (tons/year) Low	High	Percent of State Total[a]
24	Metropolitan Los Angeles	1158.03	2053.39	73.2
25	North Central Coast	10.73	44.37	1.6
28	Sacramento Valley	81.54	151.20	5.4
29	San Diego	143.20	272.46	9.7
30	San Francisco Bay Area	69.39	138.51	4.9
31	San Joaquin Valley	77.89	123.66	4.4
32	South Central Coast	8.93	21.36	0.8
	TOTALS	1549.71	2804.95	100.0

[a] Based upon upper estimate.

Table 6.2-3

ESTIMATED EMISSIONS FROM POLYESTER RESIN/FIBERGLASS FABRICATION: DISTRIBUTION BY AIR BASIN

Air Basin	Estimated Emissions (tons/year) Low	High	Percent of State Total[a]
Sacramento Valley	80.31	149.09	5.3
Mountain Counties	1.22	2.11	0.1
San Francisco Bay Area	69.39	138.51	4.9
North Central Coast	10.73	44.37	1.6
San Joaquin Valley	77.89	123.66	4.4
South Central Coast	14.83	32.51	1.2
South Coast	1152.14	2042.24	72.8
San Diego	143.20	272.46	9.7
TOTALS	1549.71	2804.95	100.0

[a] Based upon upper estimate.

6.2.2 Distribution of Emissions by Number of Firms

Our results show that the bulk of the styrene emissions from polyester resin/fiberglass fabrication are concentrated among the larger firms. As seen in Figure 6.2-1, about three quarters of the firms in California account for only about 12 percent of the total emissions. On the other hand, only 4 percent of the firms account for 50 percent of the total. In fact one firm in Orange County is estimated to be responsible for 19 percent of the state's emissions from this type of source.

The distribution of emissions by numbers of firms is an important consideration in setting regulatory policy. Since such a high proportion of the firms in the state emit rather small quantities, it may be desirable to establish a minimum uncontrolled emission level, above which a firm would be subject to regulatory attention. Figure 6.2-2 shows the number of firms having emissions greater than or equal to various such levels. It is clear that as the cutoff point decreases below about 30 tons/year, the number of firms potentially subject to regulation rapidly increases. This matter will be discussed further in Chapter 10.

6.2.3 Distribution of Emissions by Product and Production Process

Table 6.2-4 shows our upper estimates of emissions from facilities, according to the types of items manufactured. Emissions from panel plants account for about 30 percent of the state total. As was seen in Chapter 4, these facilities tend to be quite large (See Table 4.3-6). Other products whose manufacture accounts for significant percentages of statewide emissions include boats and bathroom fixtures.

Estimated emissions from the production process combinations identified in our survey are shown in Table 6.2-5. Operations in which resin spraying is used alone or in combination with other processes account for about 47 percent of the state's emissions. Hand layup and continuous lamination processes are also significant emission sources, the former because they have high emission factors and the latter because they are used in some of California's largest polyester resin-using facilities.

6.3 PLACING POLYESTER RESIN/FIBERGLASS EMISSIONS IN PERSPECTIVE

Estimated emissions from polyester resin/fiberglass fabrication in California constitute 0.054 to 0.098 percent of the statewide total organic

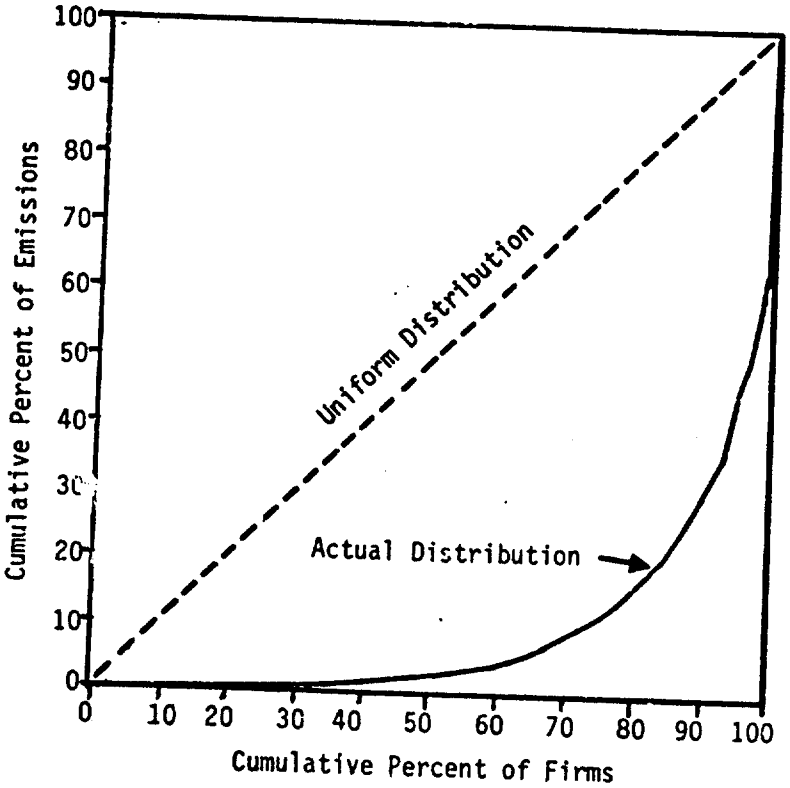

Figure 6.2-1. Lorenz Curve for Distribution of Uncontrolled Emissions From Polyester Resin/Fiberglass Fabrication in California

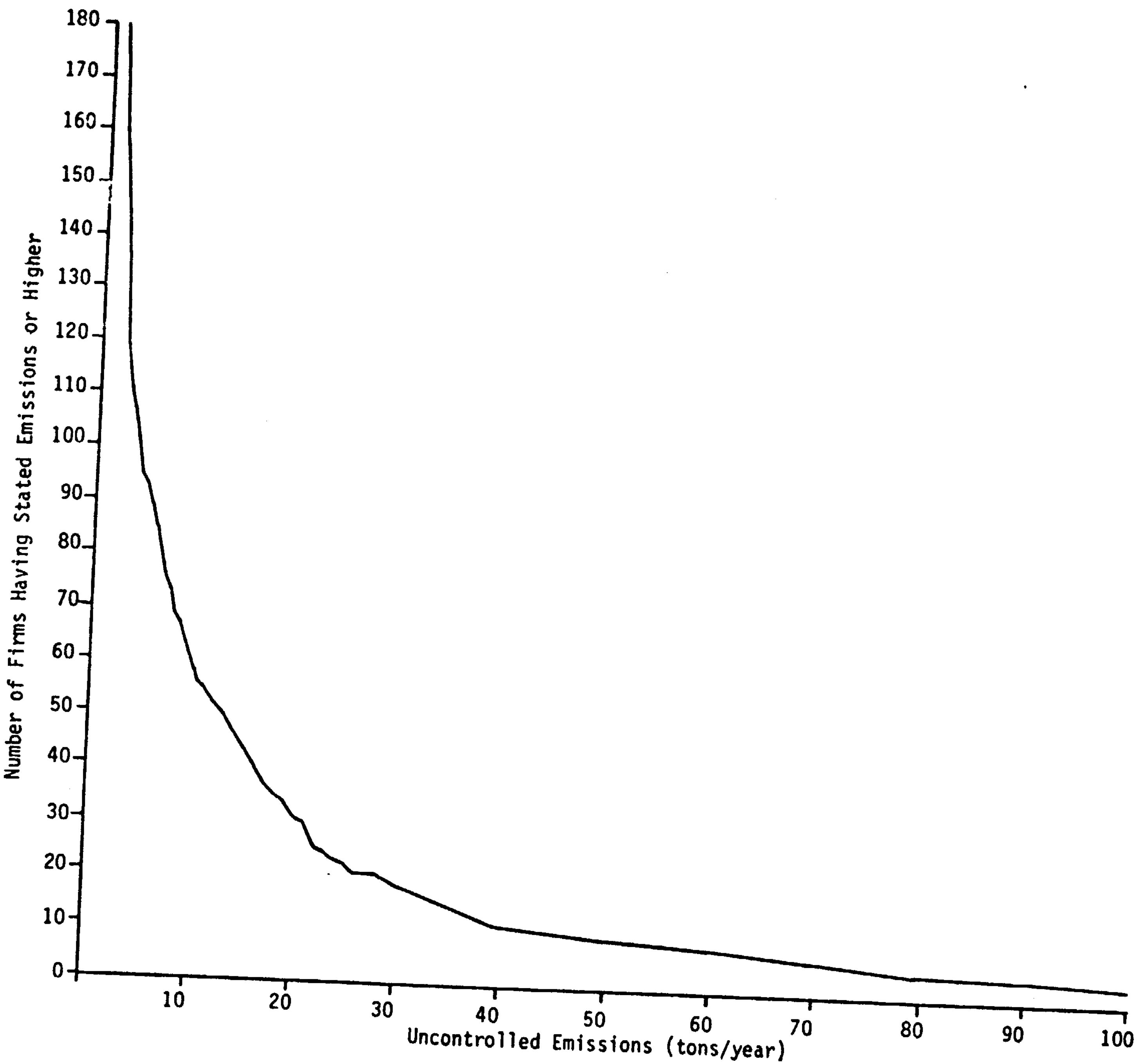

Figure 6.2-2. Distribution of Firms by Uncontrolled Emissions

Table 6.2-4

ESTIMATED EMISSIONS FROM POLYESTER RESIN/FIBERGLASS FABRICATION: DISTRIBUTION BY PRODUCT

Product	Annual Emissions[a] (tons/yr)	Pct. of Total
Boat Building, Repair	629.3	22.4
Synthetic Marble	209.9	7.5
General	71.2	2.5
Tanks, Containers	163.4	5.8
Auto, Aircraft, Truck	68.7	2.4
Spas, Hot Tub	72.1	2.6
Surfboards	7.4	0.3
Panels	846.9	30.2
Bathroom Fixtures[b]	341.6	12.2
Furniture	79.9	2.8
Pipes, Ducts	16.2	0.6
Electronics	17.9	0.6
Antennas, Rods	33.5	1.2
On-site Repairs	4.4	0.2
Swimming Pools	22.0	0.8
Helmets, Sporting Goods	13.2	0.5
Radomes	0.5	<0.1
Not Reported	206.6	7.4
TOTALS	2804.7	100.0

[a] Based upon upper use rate estimate

[b] Does not include fixtures made of synthetic marble

Table 6.2-5

ESTIMATED EMISSIONS FROM POLYESTER RESIN/FIBERGLASS FABRICATION: DISTRIBUTION BY PRODUCTION PROCESS

Process Combination	Estimated Emissions (tons/yr) Low	High	Pct. of Total[a]
Hand layup alone	287.8	635.5	22.7
Hand layup, spray layup	224.3	414.8	14.8
Hand layup, spray layup, bag molding	1.0	2.3	0.1
Hand layup, spray layup, filament winding	13.3	21.9	0.8
Hand layup, spray layup, marble casting	19.1	37.0	1.3
Hand layup, bag molding	14.6	19.6	0.7
Hand layup, filament winding	15.8	22.8	0.8
Hand layup, marble casting	11.8	16.5	0.6
Hand layup, other	1.6	2.8	0.1
Spray layup alone	766.1	1254.8	44.7
Spray layup, bag molding	0.1	0.1	<0.1
Spray layup, filament winding	29.8	42.8	1.5
Spray layup, marble casting	3.0	6.6	0.2
Spray layup, closed molding	1.9	5.0	0.2
Bag molding alone	<0.1	<0.1	<0.1
Continuous lamination alone	89.4	143.8	5.1
Filament winding alone	2.7	3.9	0.1
Pultrusion alone	34.0	123.5	4.4
Marble casting alone	31.6	47.3	1.7
Other	1.8	3.8	0.1
Unknown	0.1	0.1	<0.1
Total	1549.8	2804.9	100.1[b]

[a] Based on upper emission estimate

[b] Discrepancy in total percentage is due to rounding.

gases (TOG) emissions, and 0.075 to 0.13 percent of stationary source TOG emissions as reported in the 1979 Statewide Emission Inventory (CARB, 1981). To really place our emission estimates in perspective, however, it is necessary to compare them with emissions from specific geographical areas. Consider, for example, the South Coast Air Basin (SCAB). According to the Draft 1979 Emissions Inventory (SCAQMD et al., 1981), stationary sources in the SCAB emit 672.02 tons/day of reactive organic gases (ROG). Assuming a 260-day year, our estimate for emissions within the basin would be 4.43 to 7.86 tons/day, or between 0.66 and 1.2 percent of the total. Comparisons with county-specific emissions within the SCAB are as follows:

County	Total ROG (tons/day)	Styrene Emission (tons/day)	Pct. of Total ROG
Los Angeles	466.38	1.01 - 1.97	0.22 - 0.42
Orange	116.93	3.29 - 5.68	2.81 - 4.86
Riverside	36.29	0	0
San Bernardino	53.09	0.13 - 0.20	0.24 - 0.38

Thus polyester resin/fiberglass plants would appear to be relatively important sources of reactive organic gas emissions in Orange County, and relatively minor elsewhere.

Recent emission inventory data were also available for Fresno County (Fresno County APCD, 1981). Stationary sources in the inventory emit 108.08 tons/day of reactive hydrocarbons. Our estimate for styrene emissions from the eight plants we identified in the county was 9.46 to 18.3 tons/year, or 0.036 to 0.070 tons/day. These plants would thus account for about 0.033 to 0.065 percent of reactive hydrocarbon emissions in the county.

It is difficult to compare our emission estimates with those presented in county and regional emission inventories. As was pointed out in Chapter 4, there is no unambiguous source classification code for polyester resin/fiberglass fabrication. In the case of the SCAB, the closest category in which we may compare estimates is "plastics products manufacturing," for which emissions in 1977 were estimated to be 4.37 tons/day. This figure is below our estimate of 4.43 to 7.86 tons/day for styrene emissions, yet it may include emissions from a wide variety of plastics manufacturing processes other than those of concern in this study. As another example, Fresno County appears to place polyester resin/fiberglass fabrication emissions in the category of "surface coatings." The Fresno Air Pollution Control District's estimate of 0.336 tons/year from use of polyester resin is considerably below our range of 9.46 to 18.3 tons/year.

6.4 REFERENCES

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7.0

REVIEW OF EMISSION CONTROL PRACTICES

One of the major objectives of this project was to review all the control techniques that might be applicable to reducing organic vapor emissions from polyester resin/fiberglass fabrication processes. A brief review of the literature, along with discussions with local air pollution control districts and fiberglass manufacturers, resulted in the identification of the following potentially applicable control measures:

- Substitution of new materials and/or processes
- Use of vapor-suppressed polyester resin
- Incineration
- Adsorption
- Absorption
- Condensation

As was reported in Section 4.3.6, our survey of the California polyester resin/fiberglass industry determined that use of vapor-suppressed resin, incineration (at two facilities) and material or process changes were the only control techniques used in the state in 1980. In the vast majority of cases, virtually all the organic vapors released from the polyester resin are emitted to the atmosphere.

Considerable information on organic vapor emission control technology was available in the literature, notably in comprehensive reviews by Cavanaugh (1978), Fogiel (1978) and Taback et al. (1978). Additional information was obtained through further literature review and through contacts with manufacturers of air pollution control equipment. Substitution of new materials and new processes was covered to some extent in Chapter 3; in this chapter (Section 7.1), we consider some modifications to existing processes which could reduce emissions. Section 7.2 contains a review of the benefits and potential drawbacks of using vapor-suppressed resins. Exhaust gas treatment technologies are discussed in Section 7.3 through 7.6. Those techniques which merit further attention are included in the cost analyses presented in Chapter 8.

7.1 CHANGES IN EXISTING PROCESSES

In many cases, organic vapor emissions may be reduced substantially by making changes in product design and/or production process. Before describing a few of these measures, we hasten to note that some changes may have negative effects on other aspects of a plant's operations. For example, they may make certain operations more difficult or time-consuming, or result in changes in product quality. The purpose of this discussion is primarily to identify steps that may be considered as part of an overall emission reduction strategy.

7.1.1 Reducing Resin Use

One very simple way to reduce emissions is to use less polyester resin. This can be accomplished in three ways. First, products can be redesigned to require a lower percentage of resin matrix. Care would have to be taken, of course, to assure that desired oroduct quality is maintained. Second, additional use of fillers and colorants can reduce the need for resin. This approach is particularly applicable to the synthetic marble industry, where filler use is increasing. Using too much filler can lead to surface finish problems (Anon., 1981). Finally, unintentional waste of resin can in some cases be reduced substantially.

An example of the third approach is a change in the way that gel coat is sprayed. Improvements in airless spray guns permit large quantities of gel coat to be applied quite rapidly; thus the production process is accelerated, and more products can be turned out in the same amount of time. However, experiments by Stahlke and Hall (1981) showed that, as the flow rate through a spray gun increases, gun efficiency (defined as the ratio between the amount of gel coat that is sprayed through the gun and the amount of gel coat that actually reacnes the mold) decreases. For example, the efficiency of a gun with an 0.012-inch tip decreases from 94.5 to 71.1 percent when the gel coat flow rate increases from 2.79 to 5.26 lb/min. Resin wastage thus increases from 5.5 percent to 18.9 percent. Stahlke and Hall argue that, in the long run, both operating costs and styrene emissions may be reduced by using spray guns with larger tips and applying gel coat at lower flow rates.

7.1.2 Reducing Monomer Use

Another alternative would be to use resin containing less monomer, provided that desired material properties were not thereby degraded. According to Sneller (1979), "advances in resin formulation through narrowing molecular weight distribution (to preserve chemical resistance and mechanical properties while improving viscosities) have resulted in breakthroughs in commercial, production-oriented resins containing less than 30-percent styrene." A drawback which could present a problem in some cases is that the polyester resin would be more viscous and difficult to mold; indeed, styrene is often added by the user to improve its flow properties. Since the increased surface disruption caused by rollout tends to increase styrene emission potential (Brighton et al., 1979), this alternative could be counterproductive.

7.1.3 Decreasing Gel Time

Our laboratory experiments (see Section 5.3) showed that long-term styrene emissions decreased with decreasing gel time. Thus the use of higher percentages of catalyst could reduce emissions. A drawback of this approach is that it would increase materials costs (for the catalyst). In addition, some processes require a lengthy gel time to enable thorough rollout and other molding operations.

7.2 VAPOR SUPPRESSANTS

For many years, small quantities of paraffin waxes have been added to polyester resins to minimize the diffusion of oxygen (which is a powerful inhibitor of the polymerization reaction) from the atmosphere. Realization that surface films can also reduce the outward diffusion of styrene has led to use of chemical additives, called "vapor suppressants," in the polyester resin/fiberglass industry. Indeed, use of vapor suppressants is the only styrene emission control technique which is used to any significant extent in California.

7.2.1 Composition and Mechanisms of Action

Most vapor suppressants are paraffin waxes, stearates or polymers of proprietary composition (Boenig, 1964). Paraffin waxes used are generally 18- to 40- carbon n-alkanes, along with a small percentage of 2-methyl alkanes and cycloalkanes (Pritchard and Swampillai, 1978). The vapor suppressant content of most laminating resins is from 0.3 to 0.6 percent by weight (Gary, 1980).

According to Sneller (1979), the trend in vapor suppressants is away from aliphatic waxes and toward combinations of new resin formulations and additives.

The mechanism of action of a vapor suppressant is fairly complex. In general, as styrene evaporates from a resin, the concentration of the vapor suppressant increases, causing it to come out of solution. At the same time, the exothermic nature of the cross-linking reaction raises the resin temperature, thereby increasing the solubility of the suppressant. Finally, evaporation of styrene cools the resin surface, making the suppressant less soluble there. Jowett (1979) reports a narrow temperature range for optimum performance of paraffin waxes used in the rubber industry; a similar range may exist for vapor suppressants in polyester resin.

7.2.2 Effectiveness of Vapor Suppressants

Laboratory and field data on the effectiveness of vapor suppressants are quite limited. Results of previous research in this area were reported in Table 5.1-1. Our own laboratory experiments (see Section 5.3) showed that vapor suppressants indeed reduced emissions, at least under the carefully controlled conditions maintained in our test chamber. Unfortunately, it is impossible to use test data to quantify precisely the degree of emission reduction for polyester resin use in general, since actual production processes vary so widely. The effectiveness of vapor suppressants is reduced substantially, for example, in processes requiring lengthy rollout, since the surface barrier is continually disturbed (Pritchard and Swampillai, 1978). While emissions in some field tests were observed to have been cut by 80 percent (Ashland Chemical Company, undated), and our laboratory tests showed a 100 percent reduction, no data are available to substantiate such high effectivity in general industry practice. In our calculation of emissions from the firms identified in our California polyester resin/fiberglass industry survey, we assumed that vapor suppressants reduced styrene emissions by 30 to 50 percent. This range represents the best judgement of a major U.S. vapor-suppressed polyester resin producer, who wished to remain anonymous.

7.2.3 Pros and Cons of Vapor Suppressant Use

While vapor suppressants do reduce organic vapor emissions, they are not without their drawbacks. A frequently voiced complaint about these additives is that the waxy surface film makes it difficult to perform secondary bonding, i.e. addition of layers of resin/solid composites to fully or partially cured surfaces. Potential users' greatest concern seems to be that fiberglass structures might delaminate. According to one resin manufacturer, interlaminar bonding problems occur when resin, glass or mold temperatures are below 18°C (65°F) or when the time between the first and second lamination exceeds 16 hours. High concentrations of vapor suppressant are also believed to result in poor secondary bonding (Duffy, 1979). In order to explore this issue further we contacted several of the vapor suppressant users identified in our survey. Our inquiry was not intended to obtain a statistically significant sample; we wished only to identify actual operating problems and how firms cope with them.

Two major polyester resin users reported having no problems with the use of vapor suppressant. At a bathtub and shower plant, which we toured, no secondary bonding was performed. At the other plant, which manufactures boats, the workers sand the outer layer of semi-cured resin before attempting secondary bonding; this extra operation adds five to ten minutes to the construction time for each boat. This same manufacturer has an on-site apparatus to test boat hulls under dynamic loads. No delamination problems have been encountered.

On the other hand, a large manufacturer of fiberglass containers and furniture recently discontinued using vapor suppressants. We were given three reasons:

- The vapor suppressant did not significantly eliminate styrene emissions when resin is applied with a spray gun;
- The suppressant tended to separate from the resin unless the resin was continually stirred; and
- Sanding to preclude secondary bonding problems was too inconvenient.

Another type of problem was reported by a recreational vehicle parts manufacturer. Although this firm had no trouble with secondary bonding, the suppressant appeared to reduce the opacity of the resin so that "you could see through the final coat." Customer complaints led the company to discontinue using that type of resin.

A report by Daniel P. Boyd and Company (1980) discusses the use of vapor-suppressed or "environmental" resins in Sweden. At present 90 percent of the general purpose laminating resins in that country contain vapor suppressants. Vapor-suppressed gel coats are under development. According to Boyd, delamination problems have largely disappeared since the introduction of the current generation of environmental resins in 1978. Secondary bonding problems have been taken care of in three ways. First, boating industry standards require that no more than 24 hours lapse between applications of resin layers. Second, resins are manufactured under very strict controls, so that users are sure of product uniformity and quality. Finally, some companies use a material called "scanstrip" to improve secondary bonding. The material, which consists of a fiberglass screen is installed in the final coat of resin while the latter is still wet. Later, when it is time to join other fiberglass materials to the original, the strip is peeled away, leaving a clean surface for lamination and obviating the need for sanding.

7.3 INCINERATION

7.3.1 Process Description

The most common method of destroying organic vapors is by incineration. In incineration (or combustion) processes, the organic compounds react exothermically with oxygen to form carbon dioxide, water and, depending upon circumstances, other combustion products. To achieve complete combustion requires an excess of oxygen, a sufficiently high temperature, sufficiently long residence time at this temperature, and a high degree of turbulence to achieve intimate mixing of pollutant and oxygen (Crawford, 1976). Although destruction of organics by flaring and other means is theoretically possible, the most practical device for incinerating relatively dilute concentrations of organic gases is the afterburner. The two main types of afterburner, direct-flame and catalytic, will now be described.

Direct-Flame Afterburners

As seen in Figure 7.3-1, a direct-flame afterburner consists of a burner, a combustion chamber, and control devices. The organic vapor stream is conducted to the burner by either the process exhaust system or a blower. Several burner types have been described by Fogiel (1978). While designs vary, most of them consist of a pipe with orifices for the delivery of natural

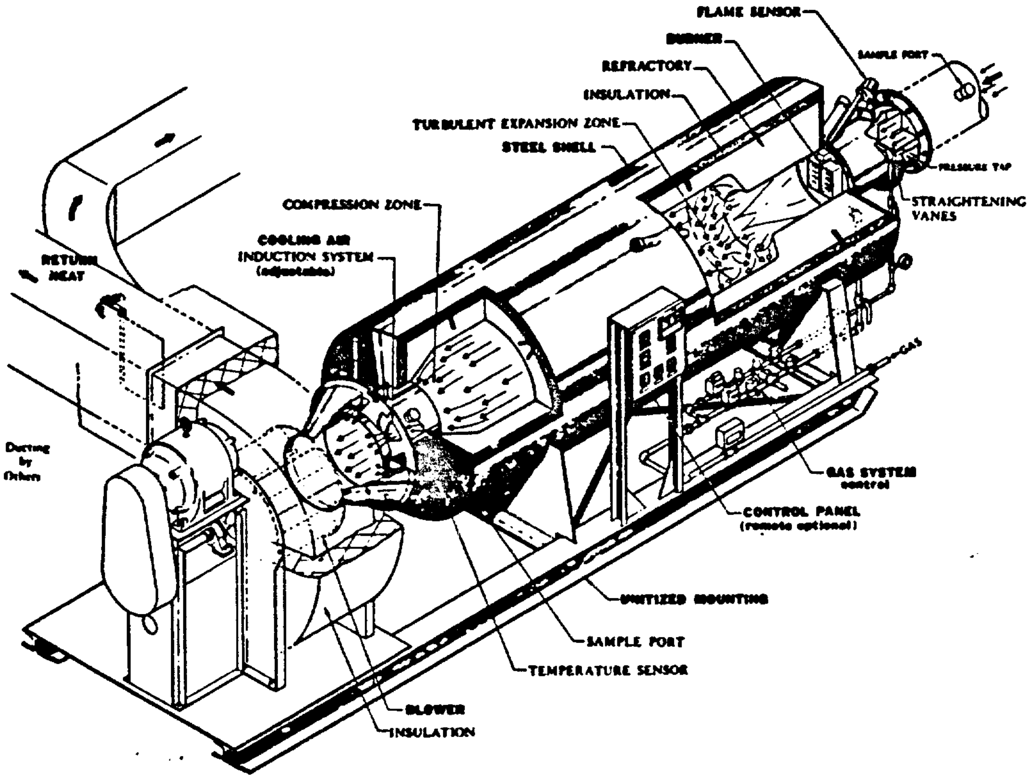

Figure 7.3-1. Direct-Flame Afterburner (Fogiel, 1978).

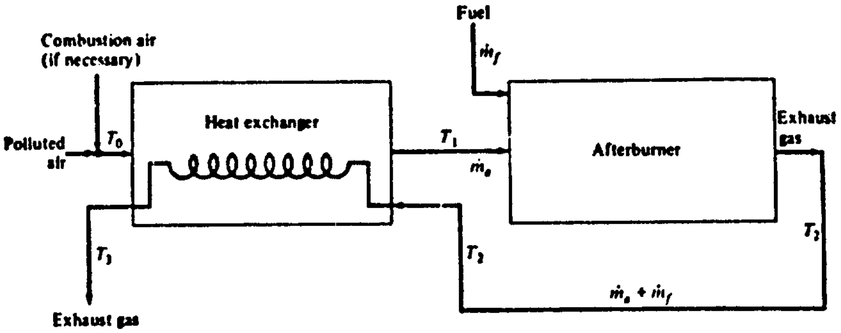

Figure 7.3-2. Schematic of Incineration System With Primary Heat Recovery (Crawford, 1976).

gas and a set of vanes or plates for directing the polluted air stream. Maximum afterburner efficiency results when all the contaminated material passes through the burner. In most cases, the air stream passes through the burner on its way to the combustion chamber. In other designs, multiple gas nozzles are arranged to fire tangentially along the length of the combustion chamber.

The key considerations in incinerator design are the combustion temperature and the pollutant residence time. In order to achieve removal efficiencies of 90 percent or greater, the combustion temperature must be between about 700 and 820°C (1300 and 1500°F) in the case of organic solvents. An adequate residence time is of the order of 0.2 and 0.5 seconds (Crawford, 1976).

While a direct-flame afterburner may be highly efficient in removing pollutants, it consumes a relatively large amount of energy. Significant portions of the heat of combustion can be recovered and re-used, however. In primary heat recovery, an example of which is shown in Figure 7.3-2, the exhaust from the afterburner is passed through a heat exchanger, in which the incoming polluted air stream is pre-heated before it reaches the burner; thus the fuel required to raise the polluted air stream to the desired combustion temperature can be reduced. In secondary heat recovery, the exhaust from the heat exchanger is used as a source of heat to some other process. This type of heat recovery is practical only when the heat-using process is physically near the afterburner and operates on more or less the same time schedule.

Catalytic Afterburners

Fuel for incineration can be saved substantially if the temperature required for complete destruction of the pollutants can be lowered. Construction costs may also be lower since burner materials are subjected to lower thermal stresses than in conventional combustion. Figure 7.3-3 shows a system for accomplishing this. Incoming polluted air is pre-heated in a heat exchanger and then passed through a burner, which raises the gas temperature to between 340 and 590°C (650 and 1100°F). In the catalytic unit, combustion continues at a lower reaction temperature than in a direct-flame afterburner. Catalyst materials include platinum and platinum alloys, copper chromite, copper oxides, manganese, nickel, chromium and cobalt. The catalyst material is coated onto elements such as metal ribbons, ceramic rods, or alumina pellets, which are packed into a bed.

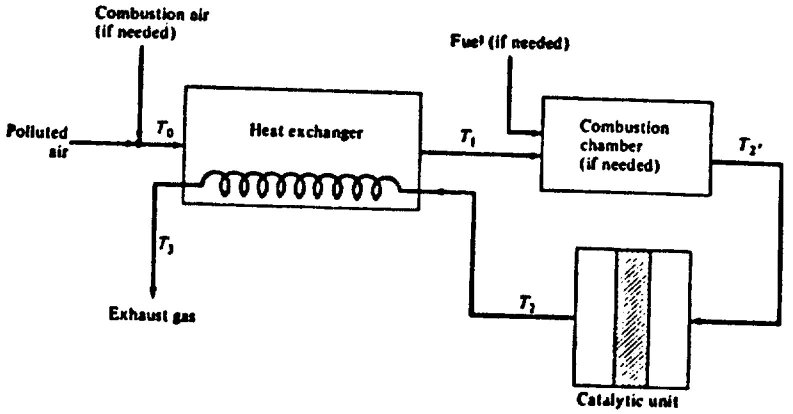

Figure 7.3-3. Schematic of Catalytic Incineration System With Primary Heat Recovery (Crawford, 1976).

While catalytic incineration saves fuel initially, problems may arise if the catalyst becomes contaminated through the buildup of particulate matter and/or chemical reaction with substances in the gas stream. Halogens, sulfur dioxide and nitrogen dioxide are particularly serious catalyst poisons (Hardison and Dowd, 1977). Volatile heavy metals and phosphorus also reduce catalyst efficiency (Thomer and Weiler, 1977). Care must also be taken not to allow temperatures in the catalytic unit to exceed about 650°C (1200°F), as catalyst materials may vaporize at higher temperatures. Catalysts must be periodically replaced. Finally, net fuel savings diminish if one intends to incorporate primary and secondary heat recovery.

7.3.2 Applicability to the Polyester Resin/Fiberglass Industry

Incineration, according to the results of our survey of the industry, is used in two continuous lamination plants in California. Our field tests at one of these (Facility A) showed that the natural gas-fired afterburner removed 98.4 to 98.8 percent of the organic vapors in that portion of the plant exhaust that was treated. At present, none of the heat from the incinerator is being recovered, although the plant management intends to install heat exchange equipment soon. It is not known whether the other plant uses heat recovery. The cost of incineration at these plants is partially offset, since the companies pay a lower emission fee to the local air pollution control district.

In general, incineration is most effective when the pollutant to be treated is at a high concentration and/or has a high heating value. As will be discussed in Chapter 8, the heating value of styrene is negligible compared to the requirement for maintaining a high enough flame temperature to oxidize it; thus an incinerator is in effect combusting natural gas (or other external fuel) and air. This waste of energy can be reduced somewhat by recycling the heat. Many facilities using hand and spray layup have curing ovens, which require heat input. Certain processes, such as continuous lamination and pressure bag molding, usually require some sort of heat input. Steam heating of the interiors of hollow mandrels is used in some filament winding operations.

Weiler and Thomer (1977) suggest a combination of adsorption and incineration when organic concentrations in the exhaust air are low. Organics are removed from the air stream by activated carbon, which is periodically desorbed. The desorbed stream would be at a high organic concentration, so that incineration would require less external fuel.

7.4 ADSORPTION

7.4.1 Process Description

Adsorption is a common technique for removing vapor-phase pollutants from an air stream. Molecules of the gas, which is called the adsorbate, adhere to the surface of a solid material called the adsorbent. Good adsorbents are highly porous and have high surface-to-volume ratios. Both attributes are necessary, as the gas is believed both to attach to the surface (by Van der Waals forces and chemical bonding) and to condense within the pores of the adsorbent. Activated carbon is usually the adsorbent of choice for control of nonpolar gases having molecular weights greater than 45, since it is effective and is relatively inexpensive. The remainder of this discussion will therefore assume that activated carbon (AC) is to be used in controlling styrene emissions.

When the waste gas stream is first applied to the adsorbent, adsorption is rapid and complete; no pollutant appears in the exit stream. After a time characteristic of the pollutant to be removed, the adsorbent, and the temperature, a saturation state is reached. After this "break point," removal efficiency declines rapidly, until the contaminated air stream passes through the adsorption device unchanged. Although a higher saturation level may be achieved by lowering the temperature of the adsorbent, in practical operation the adsorbent must be either disposed of or regenerated.

Adsorbents can be regenerated by heating with air or steam. When steam is used, the effluent gases are routed to a condenser, after which they can be separated by gravity decantation or by distillation. If no pollutant recovery is desired, then the steam and organic vapors may be directly incinerated. Regeneration can take place on site. Alternatively, adsorbent canisters can be removed periodically and regenerated at a central facility.

An example of an on-site regeneration system is described by Bouroff (1981). A chemical plant in Missouri uses activated carbon to collect organic vapors vented from reaction vessels and storage tanks. Among the controlled substances are toluene, methyl methacrylate, epichlorohydrin, and ethyl acetate. Vapors are collected in pairs of canisters containing 68 kg (150 lb) of 4 x 10 mesh BPL vapor-phase carbon. The canisters themselves are vented to manifolds, through which the collected monomers are carried by forced air to a totally enclosed adsorption bed at the rear of the plant. Compounds which do not adsorb readily are disposed of by incineration.

According to Ohmori et al. (1977), adsorption can be improved by using activated carbon fibers rather than granules. Using an experimental spray booth system, they were able to increase equilibrium toluene adsorption three-fold by using cylindrical adsorption elements composed of a nonwoven activated carbon fabric. Pollutant-laden air enters the cylinders radially; clean air exits axially. When the filters are saturated, the top of the cylinders are capped and steam is introduced axially from the bottom; flowing radially outward, the steam picks up the adsorbate and conveys it to a collector. A separate adsorption system (using granular activated carbon) is used to purify the condensed steam.

Kenson (1979) describes a system for regenerating activated carbon and recovering the adsorbed pollutant without the need for steam. A vacuum of 5 torr is applied to the AC bed, which is simultaneously heated. The desorbed compound is condensed in a water-cooled chamber and then collected in a recovery tank for disposal or recycle. According to Kenson, the system has been used to recover methylene chloride from pharmaceutical operations and vinyl chloride monomer from polyvinyl chloride manufacturing. Its advantages are that it requires no steam, has a low energy requirement, eliminates the problem of separating recovered compounds from water, and creates no waste disposal problem.

7.4.2 Applicability to the Polyester Resin/Fiberglass Industry

Styrene Adsorptivity

Figure 7.4-1 shows the relationship between influent styrene concentration, temperature, and capacity of a typical activated carbon (type BPL granular activated carbon, by Calgon Corporation). The 75^{0}F curve would be applicable to most of the California polyester resin/fiberglass industry, since most operations are conducted at "room temperature" or slightly above. (Temperature effects are discussed below.)

Styrene adsorption experiments have been conducted recently in Japan by Tanada and Boki (1979) and Boki et al. (1980). First, the adsorbent capacity of two types of zeolite and two types of activated carbon were tested. Styrene adsorption on the activated carbon was an order of magnitude

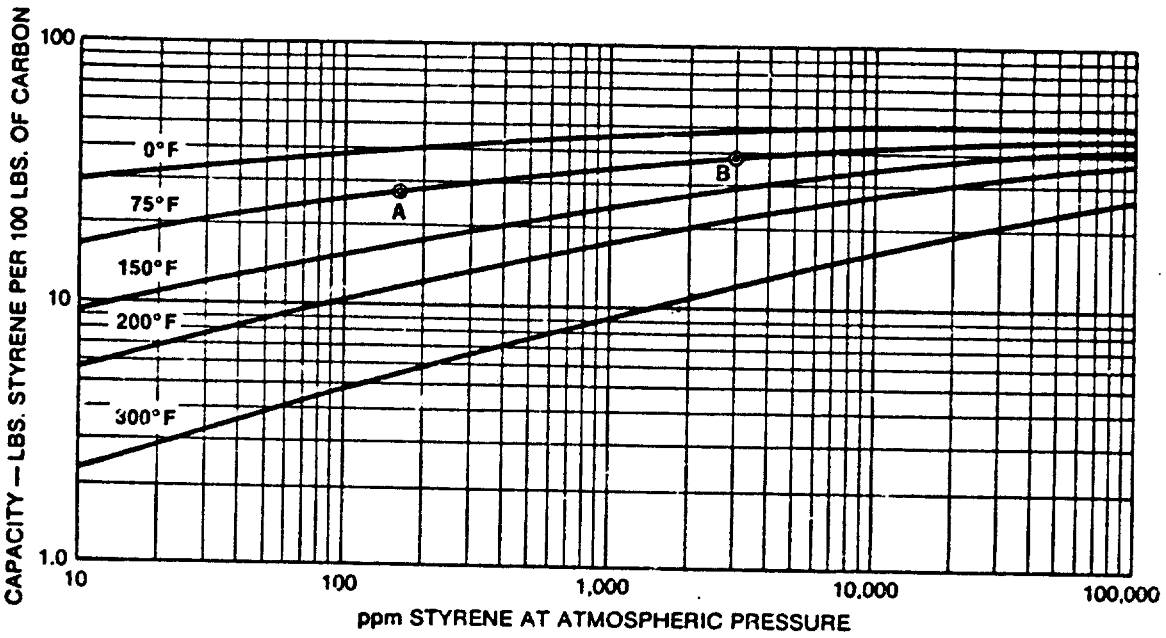

Figure 7.4-1. Styrene Adsorption of BPL Activated Carbon (Calgon Corporation).

higher than on the zeolite. From their data, Tanada and Boki estimated that the effective diameter of a styrene molecule is about 6.8 Å. These molecules are more readily condensed in the micropores of activated carbon (15 or 16Å) than of zeolite (9 to 10 Å). Using a finely-divided activated carbon (200 x 400 mesh) and air having 6000 ppm styrene at 30°C (0.088 psi partial pressure at 86°F), they measured adsorption capacities of 25.3 and 30.9 mass units of styrene per 100 mass units of activated carbon. These values are lower than those predicted by the curves shown in Figure 7.4-1.

In Boki et al.'s experiments, styrene at 30°C, at atmospheric pressure, and at equilibrium concentrations of 50 to 4000 ppmv was adsorbed onto 4 x 16 mesh activated carbon. The adsorbent size range was thus more typical of that used in industry. At equilibrium styrene concentrations of 2000 ppm, the highest observed adsorptive capacity was 32 to 34 mass units of styrene per 100 mass units of activated carbon; at 4000 ppmv styrene, adsorption capacity was 45 percent. These values are consistent with those predicted from the curves shown in Figure 7.4-1. Since the activated carbon particle sizes were comparable, we used Figure 7.4-1 for the cost analyses presented in Chapter 8.

Use of Activated Carbon in the Industry

The only application of adsorption to pollutant control in the polyester resin/fiberglass industry of which we are aware was a system installed at an Owens-Corning Fiberglass facility in Tukwila, Washington. Designed for 24 hour operation, the system consisted of parallel shallow-bed adsorbers containing Pittsburgh Type BPL carbon (Calgon Corporation, Pittsburgh, Pennsylvania). The influent air stream contained 100 ppmv styrene. The adsorbers were regenerated in place by steam stripping. After the steam and styrene were condensed, the styrene was stored for reuse. According to a pollution control equipment manufacturer familiar with the system, the plant was closed after the demand for its specialty product (pipe collars for the Alaska Pipeline) ended. No degeneration of the activated carbon was observed during two years of operation (Lee, 1980).

Potential Operating Problems

Taback et al. (1978) identify several operating problems which may be encountered when using carbon adsorption systems for organic solvent removal; only those applicable to control of monomer emissions from polyester resin/fiberglass fabrication will be mentioned here. The problems may include:

Overheating of Adsorbent. Acetone, which is widely used as a cleanup solvent in fiberglass plants, has a relatively high heat of adsorption. Since the capacity of an adsorbent decreases as its temperature rises, the presence of acetone in the waste gas stream cou. reduce system effectiveness. According to Taback et al., the problem can be avoided by using a wet adsorbent bed and humidifying the inlet air stream; if these actions are taken, the acetone's heat of adsorption can be transformed into heat of vaporization of water, leaving the adsorbent cool.

Polymerization on the Adsorbent. Activated carbon can serve as a catalytic agent for the polymerization of some monomers. If high-molecular weight polymers are produced, then the adsorbent surface can become fouled and regeneration may not be possible. According to a major activated carbon supplier, however, no polymerization of styrene was observed aft 70 adsorption-regeneration cycles in a field test (Calgon, undated). In our own laboratory tests of the activated charcoal traps used in field sampling (see Section 5.2) up to 20 percent of the styrene placed on the traps could not be recovered; whether styrene homopolymerized is unknown. It should be pointed out that small concentrations of polyester backbone components, styrene, catalyst, and promoter are likely to be present in the waste gas stream, so that, in principle at least, cured polyester resin could permanently occupy a portion of the activated carbon's surface. The seriousness of this problem could only be ascertained through laboratory or field tests simulating actual operations.

Clogging by Particulate Matter. Several of the production processes used in polyester resin/fiberglass production generate significant amounts of particulate matter, including glass fibers and cured resin particles. Indeed, many plants have installed electrostatic precipitators, water curtains, and other devices to reduce particulate emissions. If this matter is present in the waste gas stream, it could clog the adsorbent, thereby reducing the latter's effectiveness and increasing the pressure drop through the system. Some type of precleaning of the inlet gas may therefore be necessary, depending upon circumstances.

High Air Stream Temperature. As seen in Figure 7.4-1, the capacity of activated carbon to adsorb styrene drops markedly as the air stream temperature increases. For high-temperature operations, therefore, it may be worthwhile to reduce gas stream temperature by water sprays (which could remove particulate matter at the same time, if necessary) or by cooling coils upstream from the adsorbent device.

7.5 ABSORPTION

7.5.1 Process Description

Absorption is a process by which components of a gas stream are selectively transferred to a liquid solvent. In physical absorption, the gas dissolves in the absorbent, while in chemical absorption, the gas reacts with either the absorbent or reagents dissolved therein. The process has been used to control organic vapors in several types of industrial operations, including surface coating, degreasing, and varnish and resin cooking. According to Treybal (1955), absorption is most efficient under the following conditions:

- The organic vapors are quite soluble in the absorbent;
- The absorbent is relatively nonvolatile;
- The absorbent is inexpensive and readily available;
- The absorbent has low viscosity; and
- The solvent is nontoxic, nonflammable, chemically stable, and has a low freezing point.

Commonly used absorbents for organic vapors include water, mineral oil, nonvolatile hydrocarbon oils, and aqueous solutions of oxidizing agents, sodium carbonate, or sodium hydroxide.

Although spray towers and venturi scrubbers are common absorption devices, the choice of equipment for organic vapor absorption is usually between a packed tower and a plate tower (Cavanaugh, 1978). The purpose of either of these devices is to create a large surface area for gas and liquid to interact.

Packed Towers

A packed tower consists of a vertical cylindrical shell substantially filled with thousands of small objects, called "packing elements," whose surfaces become wetted with solvent and serve as absorption sites.

Elements come in a variety of shapes and sizes, and may be stacked in an orderly way or placed at random in the tower. Random packing elements include gravel, Raschig rings, Berl saddles, and Intalox saddles; stacked elements include Raschig rings, spiral rings, expanded-metal lath, wood grids, and drip-point grids (Crawford, 1976). Random packing has a higher specific surface contact area and a higher gas pressure drop across the bed. Stacked packings have the advantage of a lower pressure drop, but are more expensive to install (Fogiel, 1978).

Figure 7.5-1 is a schematic of a packed tower. Usually the flow through this type of device is countercurrent; i.e., gas is introduced at the bottom, while the absorbent liquid is distributed at the top of the packing. As the solvent trickles down, it picks up solute from the gas stream. Thus at the bottom of the tower the pollutant of interest is highly concentrated in both the gas stream and the solvent, while near the top, solute concentrations in both media are low. While concentration differences, which drive diffusion of the pollutant into the absorbent, may be higher at certain points in other flow arrangements, countercurrent flow results in the highest driving force for the system as a whole.

Plate Towers

A plate tower consists of a number of plates, or trays, nested above each other inside a cylindrical shell. Figure 7.5-2 shows one type of plate tower, in which the trays are fitted with "bubble caps." Absorbent liquid is fed to the tower at the top and at intermediate stages in sufficient quantities that a substantial layer of liquid is maintained on each tray. The gas stream, which is introduced at the bottom of the tower, rises into each tray through perforations or bubble caps. Thus gas-liquid diffusion of pollutant occurs in the trays. In contrast to the continuous contact process occurring in packed towers, diffusion takes place in discrete steps. Since the flow is countercurrent, however, the average diffusive driving force is still relatively high.

7.5.2 Applicability to the Polyester Resin/Fiberglass Industry

Literature on absorption equipment was obtained from six manufacturers, four of which had comments on the applicability of this method to the organic species of interest in this study. One company said that it

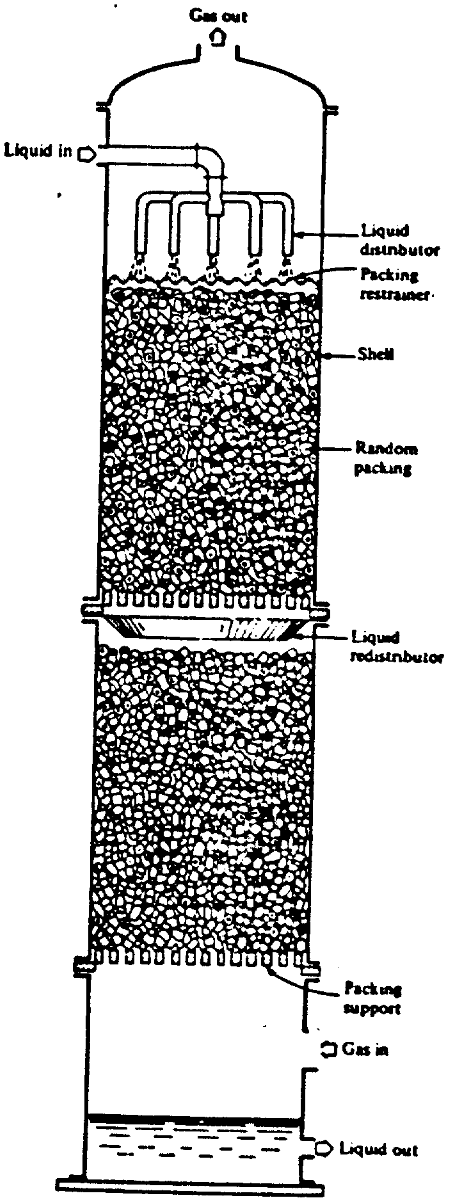

Figure 7.5-1. Packed Tower Absorption Unit (Treybal, 1955).

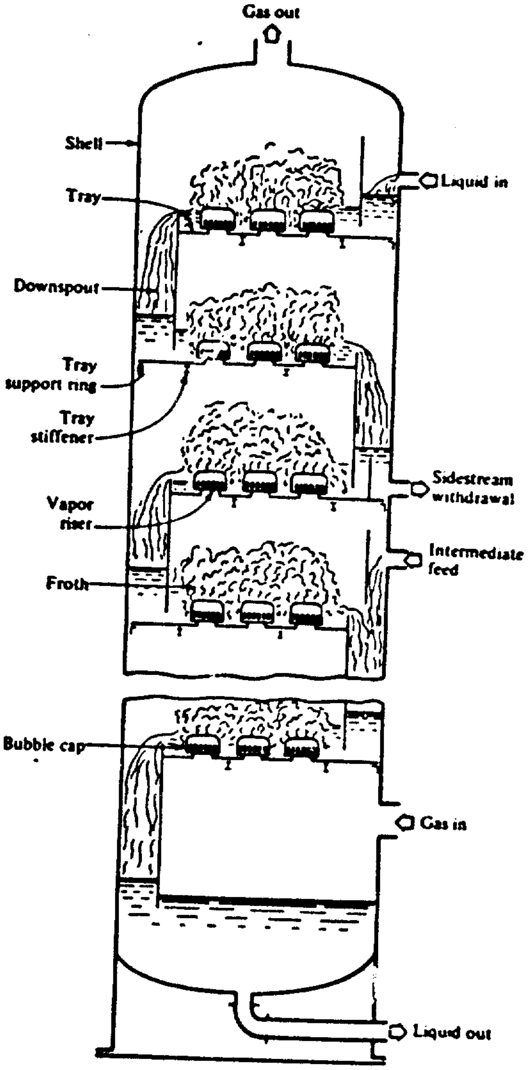

Figure 7.5-2. Bubble-Cap Plate Tower Absorption Unit (Treybal, 1955).

had never used absorption to control styrene vapors (Rowe, 1981). Another company designed a packed tower for control of methyl methacrylate; the absorbent was a dilute caustic solution (Gilbert, 1981). The same firm also installed a scrubber which absorbed styrene incidentally to the main purpose of the device. According to this company, "the absorption of styrene monomer is very limited, and other control techniques are normally used."

Another firm, which manufactures packed bed absorption equipment, recommended against absorption, noting (Cooper, 1981):

> "If we used water as the absorbent, the styrene, being insoluble in the water, would only condense on the packing and in a relatively short time plug the bed. If we used an organic solvent to absorb the styrene, then we will be introducing solvent emissions into the air stream, which may be just as objectionable as the styrene."

Plugging of tower packing was also mentioned by the fourth company (Warren, 1981). Another disadvantage of absorption is the creation of a new problem, i.e. disposal of monomer-laden absorbent. The solvent solution most likely would have to be treated before discharge. If absorbent were to be recycled, then additional equipment would be necessary for removal of the styrene or methyl methacrylate.

Use of absorption to control styrene emissions from fiberglass pipe production has been evaluated in considerable detail by the Fibercast Company of Sand Springs, Oklahoma (Maguire and Currieo, 1978). Dibutyl phthalate (DBP), a common plasticizer, was found to meet the following criteria for an absorbent medium:

- Very low vapor pressure at operating temperature
- Miscible with styrene in all proportions
- Stable, inert, noncorrosive, odorless and nontoxic
- Low viscosity
- Inexpensive
- Must not contaminate recovered styrene

Fibercast built a pilot plant to test the feasiblity of a DBP-based scrubber system. Since it was found that the process efficiency increases almost linearly with decreasing absorbent temperature, the DBP is chilled in a heat exchanger and the styrene-laden air stream is sprayed with cold water before absorbent and absorbate come into contact in a packed tower. Flow is countercurrent. Styrene is separated from the DBP by vacuum distillation. Then the styrene is condensed and stored, and the DBP is recycled. An inhibitor is added to the styrene to prevent spontaneous polymerization.

According to one of the system's designers (Maguire, 1981), a full-scale scrubber has not been built. The main reason for the delay in construction is the high capital cost. Fibercast now estimates that styrene prices would have to rise to 50 to 60 cents/lb before recovered costs (i.e. savings in energy as in purchase of styrene) would balance control costs within an acceptable time limit.

7.6 CONDENSATION

7.6.1 Process Description

In a two-component gaseous mixture, such as styrene in air, condensation occurs when the partial pressure of the condensible component equals that component's vapor pressure. Although condensation may be achieved by increasing the system pressure or by removing heat, only the latter means is commonly used in air pollution control systems.

In surface condensers, the polluted air stream and the cooling fluid do not come into direct contact. Most surface condensers are common shell-and-tube heat exchangers, in which the coolant flows through the tubes and the vapor to be removed condenses on the outer tube surface. The condensed vapor then drains away for storage or disposal. Air-cooled surface condensers consist of finned tubes. The fins expedite heat transfer to the air, while the vapor condenses inside the tubes. In contact condensers, the air stream is sprayed with a chilled or ambient-temperature liquid. The condensed vapor and water mixture must then either be treated or discarded as waste.

Contact condensers are generally less expensive and more efficient in removing organic vapors than are surface condensers. However, their use creates a liquid waste disposal problem, and recovery of pollutants for reuse is far less feasible.

7.6.2 Applicability to the Polyester Resin/Fiberglass Industry

In order for the partial pressure of styrene in a polluted air stream to equal the vapor pressure, the system temperature must be quite low. For example, styrene present at 1000 ppm will condense only at temperatures below -6.7°C (20°F). Thus direct contact condensers would not be practical. Since styrene concentrations in the exhaust streams from most polyester resin/fiberglass fabrication plants are generally below 1000 ppm, use of surface contact condensers would require either refrigeration or pre-concentration of the exhaust stream. Indeed, condensation is frequently used to recover the vapors desorbed from activated carbon units.

Refrigerated surface condenser units are commonly used in dry cleaning and degreasing operations, where solvent concentrations are quite high (e.g. 50 percent), and where the polluted gas mixture is nonflammable. According to Taback et al. (1978), condensation is generally not applicable to surface coating operations, which are similar in their pollutant-emitting characteristics to those of interest in this study.

The use of refrigeration devices was discussed with the manufacturer of a combination refrigeration/heat exchange unit that has been applied to a variety of solvents (United Air Specialists, 1980). This device can be operated economically if heat can be practically returned to the process and the recovered solvent can be reused or sold. Temperatures for styrene recovery would be on the order of -29 to -40°C (-20 to -40°F), and a distillation step would be required to separate the styrene from water vapor condensed from the ambient plant air (Memoring, 1981).

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8.0
ESTIMATION OF ORGANIC VAPOR EMISSION CONTROL COSTS

While most of the emission control techniques described in Chapter 7 are in principle applicable to the California polyester resin/fiberglass industry, their implementation costs vary considerably. Given that the great majority of facilities in the state are rather small and thus quite sensitive to increases in their operating costs, the costs to the industry of implementing various control strategies should be taken into account. In this chapter we provide rough estimates of the costs of installing incineration, adsorption, and condensation equipment in two prototypical facilities. Absorption was not evaluated since it is unlikely to be practical for removing styrene.

8.1 GENERAL APPROACH

8.1.1 Case Study Definition

We have selected as a "typical" polyester resin/fiberglass fabrication facility the tank manufacturing plant at which we performed source tests. This plant uses spray layup and vents all exhaust air through a roof duct equipped witn a fan. Our second case is a hypothetical hand- and spray-layup plant using 1 million lb/yr of laminating resin and using a gas-fired oven to cure its products.

Emission characteristics of the two plants are summarized in Table 8.1-1. Those for Case 1 were actually measured at Facility B (see Section 5.3), while those for Case 2 are based upon the following assumptions:

- 45 percent styrene in resin, 40 percent styrene in gel coat
- Emission factor of 0.15 for lamination, 0.35 for gel coat spraying
- Air flow rate proportional to total resin and gel coat use

Note that the emission factors for Case 2 are, as throughout this study, based upon the amount of cross-linking agent, and not upon the amount of resin or gel coat.

In each case, we have selected equipment to remove 90 percent of the uncontrolled emissions. We have also assumed that each plant operates 8 hours per day, 5 days per week, and 52 weeks per year.

Table 8.1-1
EMISSION CHARACTERISTICS OF PLANTS USED IN COST ESTIMATION EXERCISE

Parameter	Plant 1	Plant 2
Laminating Resin Use (lb/yr)	120,000	1,000,000
Gel Coat Use (lb/yr)	4,800	100,000
Uncontrolled Emissions (lb/hr)	12.0	39.2
Exhaust Air Flow (cfm)	3,200	28,000
Styrene Concentration in Exhaust (ppm)	234	234

8.1.2 Cost Estimation Methodology

It was beyond the scope of this project to develop detailed designs of many alternative control systems. Instead, we relied heavily upon a series of generic pollution control cost analyses performed recently by IT Enviroscience (ITE) for the U.S. Environmental Protection Agency (EPA), Office of Air Quality Planning and Standards, Emission Standards and Engineering Division. (Individual analyses will be cited as necessary.) The purpose of these technology reviews was to support the development of new source performance standards for a wide variety of synthetic organic chemical manufacturing industries.

The capital and operating cost estimates presented in the EPA series were valid as of December, 1979. Fortunately, we were able to disaggregate the estimates, so that the costs of individual components (e.g. labor, electricity, etc.) could be escalated to mid-1981 levels. Table 8.1-2 shows the assumptions used in all our cost estimates. Capital equipment costs were inflated to July 1981 values by means of the Council of Economic Advisers' Producer Price Index for Capital Equipment (CEA, 1981). The interest rate on borrowed capital was assumed to be 18 percent (as opposed to 12 percent in the EPA/ITE analysis). At that rate, and an equipment life of 10 years, the capital recovery factor is 0.223. Unit electricity and natural gas costs were obtained from Southern California Edison Company and Southern California Gas Company, respectively.

Annual net costs were estimated by:

$$C = f \times CC + L + G + E - R$$

where CC is the capital cost of installing new air pollution control equipment, f is a fixed cost factor (defined below), L is the operating labor cost, G is the cost of natural gas (where applicable), E is the electrical cost, and R represents credits in the form of recovered heat or styrene. The fixed cost factor consists of the following components:

$$f = CR + M + T$$

where CR is the capital recovery factor, M is the cost of maintenance labor and materials, and T is the cost of taxes and insurance; these are shown in Table 8.1-2. In all our analyses, f was set to 0.333. Additional assumptions are presented in connection with the individual analyses.

Table 8.1-2
ASSUMPTIONS USED IN ALL COST ANALYSES

Parameter	Value	Units
Operating Time	2080	hr/year
Capital Equipment Cost Escalation (Dec. 1979 to July 1981)	23.0	percent
Interest Rate for Borrowed Capital	18	percent
Life of Equipment	10	years
Operating Labor Rate	7	$/hr
Electricity Cost	0.10	$/kWh
Gas Cost	3.76	$/MMBtu
Maintenance Labor and Materials	(6% of installed capital)	
Taxes, Insurance, etc.	(5% of installed capital)	
Price of Styrene	0.60	$/lb

Finally, it was necessary to define a parameter which could be used to compare the costs of various control technologies. We chose for this the quantity "dollars per pound of styrene removed."

8.2 INCINERATION COSTS

8.2.1 Methods

Our analysis was based upon the generic study by Blackburn (1980), as part of the EPA/ITE series. The combustion system analyzed by Blackburn consists of a combustion chamber, fans, ductwork and stacks. Retrofit costs were not considered. Since some polyester resin/fiberglass fabricating processes can use excess heat from the incinerator exhaust, we included heat exchangers for recovering 30 and 50 percent of the waste heat.

Although we were unable to obtain an exact value for the heat of combustion of styrene, it is safe to assume that it is similar to that of ethyl benzene, i.e. on the order of 18,000 Btu/lb. Given the exhaust flow concentration data presented in Table 8.1-1, we estimate the heating value of the gas to be treated to be about 1.1 Btu/scf, which is quite low. Fortunately, Blackburn has performed generic analyses of capital and operating costs for incinerators which treat gas having 1 to 10 Btu/scf and have temperatures and flame times of 1400^{o}F and 0.5 second, respectively.

Figure 8.2-1 shows the total installed capital cost for an incinerator system having the desired characteristics for our case studies. It should be noted that Blackburn assumes that the waste gas has no oxygen, so that the requirement for combustion air is at a maximum. Since oxygen is probably present in the waste gas from most polyester resin/fiberglass operations, the cost estimates derived from Figure 8.2-1 are probably higher than they would be in practice. Following Blackburn's method, we reduced the size of the combustion chamber by 15 and 23 percent for the alternatives using 30 and 50 percent heat recovery, respectively. Natural gas requirements were also reduced by 36.5 and 58 percent, respectively.

8.2.2 Results

Table 8.2-1 shows the results of our analysis of incineration costs. For both cases, net costs may be reduced substantially by incorporating heat exchangers. Unfortunately, however, relatively few polyester resin/fiberglass facilities in California would be able to use all of the heat recovered; the

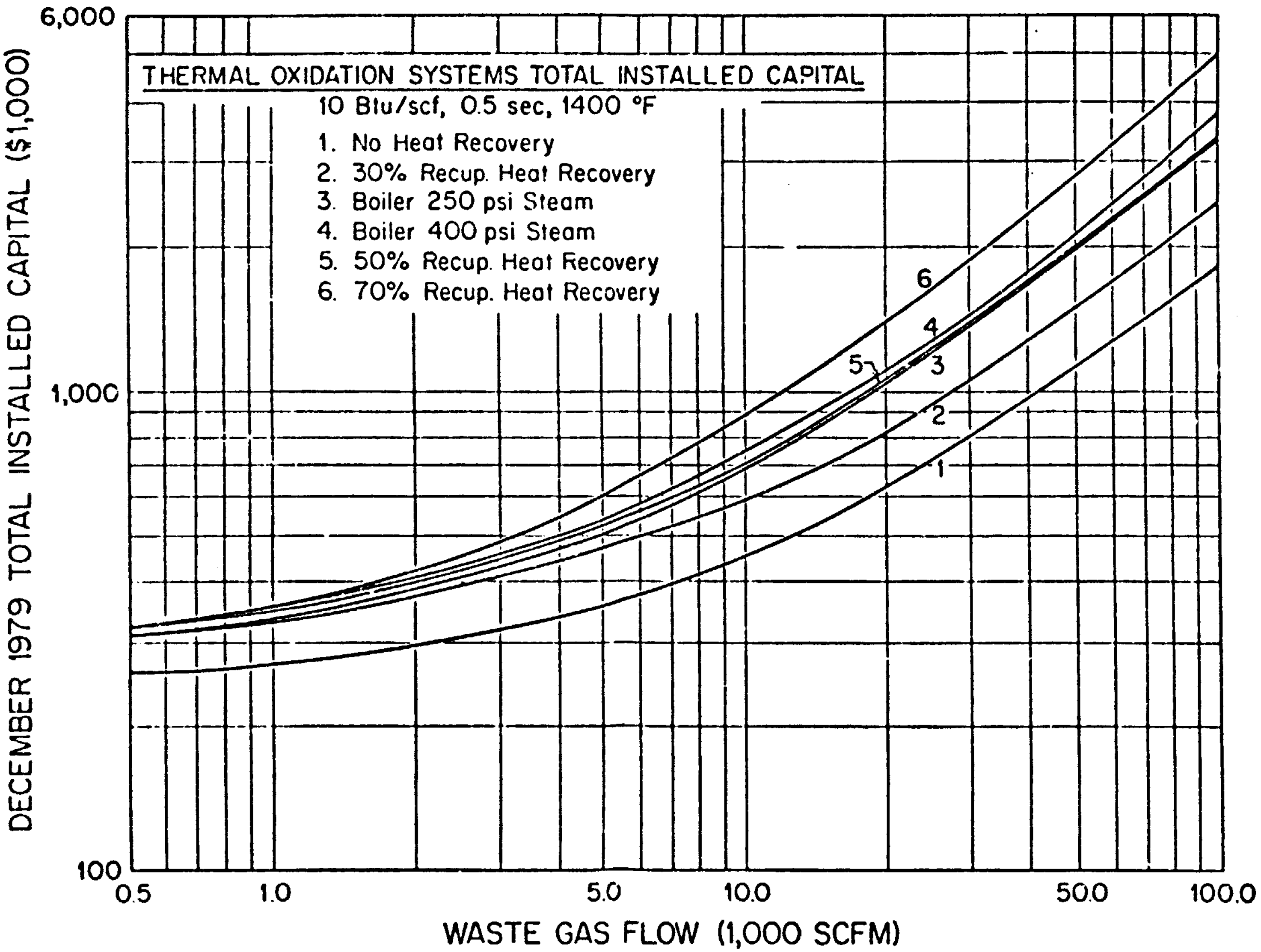

Figure 8.2-1. Total Installed Capital Cost For Thermal Oxidation Systems With Waste-Gas Heat Content = 10 Btu/scf, Residence Time = 0.5 sec, and Combustion Temperature = 1400 °F (Blackburn, 1980).

Table 8.2-1
CAPITAL AND OPERATING COSTS FOR INCINERATION

(Costs in $1000 except where otherwise noted)

Case	Variant	Capital Cost	Annual Operating Costs						Cost per lb Styrene Removed ($)
			Fixed	Labor	Gas	Elec.	Credit	Net	
1	No heat recovery	394.4	131.3	2.0	95.5	1.6	0	230.4	10.3
	30% heat recovery	492.0	163.8	2.0	60.6	1.6	18.2	209.8	9.3
	50% heat recovery	512.9	170.8	2.0	40.1	1.6	20.0	194.5	8.7
2	No heat recovery	952.9	317.3	2.0	834.3	14.4	0	1168.0	15.9
	30% heat recovery	1107.0	368.6	2.0	529.7	14.4	158.9	755.8	10.3
	50% heat recovery	1148.8	382.6	2.0	350.4	14.4	175.2	574.2	7.8

no heat recovery case is therefore most realistic. There is apparently no economy of scale for the two cases analyzed. While fixed costs rise by a factor of about three, operating costs (chiefly those of natural gas) rise by a factor of nine. For the larger facility, the incinerator is essentially wasting a great deal of energy in simply burning natural gas.

8.3 ADSORPTION COSTS

8.3.1 Methods

Activated carbon requirements were determined from Figure 8.3-1, using the 77°F isotherm and assuming a safety factor of 2. The remainder of the analysis followed closely the methodology described by Basdekis and Parmele (1980). Figure 8.3-2 shows the relationship between waste gas flow rate and system capital cost. The following assumptions were made:

- 100 ft/min air flow rate through the bed
- Bed depth of 3 ft
- Steam regeneration
- Replacement of carbon every 5 years

The costs of distillation of condensed styrene and water vapor were not included, although we have subtracted credits for recovered styrene (at 60 cents per pound) from the operating costs. Our estimate of $1.60 /lb for activated carbon was obtained from a major manufacturer (Riley, 1982).

8.3.2 Results

Capital and operating costs for the activated carbon alternative are shown in Table 8.3-1. Costs of cooling water were negligible compared to the other costs. As with incineration, there are evidently no economies of scale when installing an activated carbon system in a larger plant. The main reason is that fixed costs rise rapidly, while variable costs are a small fraction of the total. For both the small and the large plant, the cost per pound of styrene removed would decrease considerably if the facility were used for more than eight hours per day.

8.4 CONDENSATION COSTS

8.4.1 Methods

Our analysis of capital and operating costs for condensation followed the method outlined by Erikson (1980), despite the author's caveat

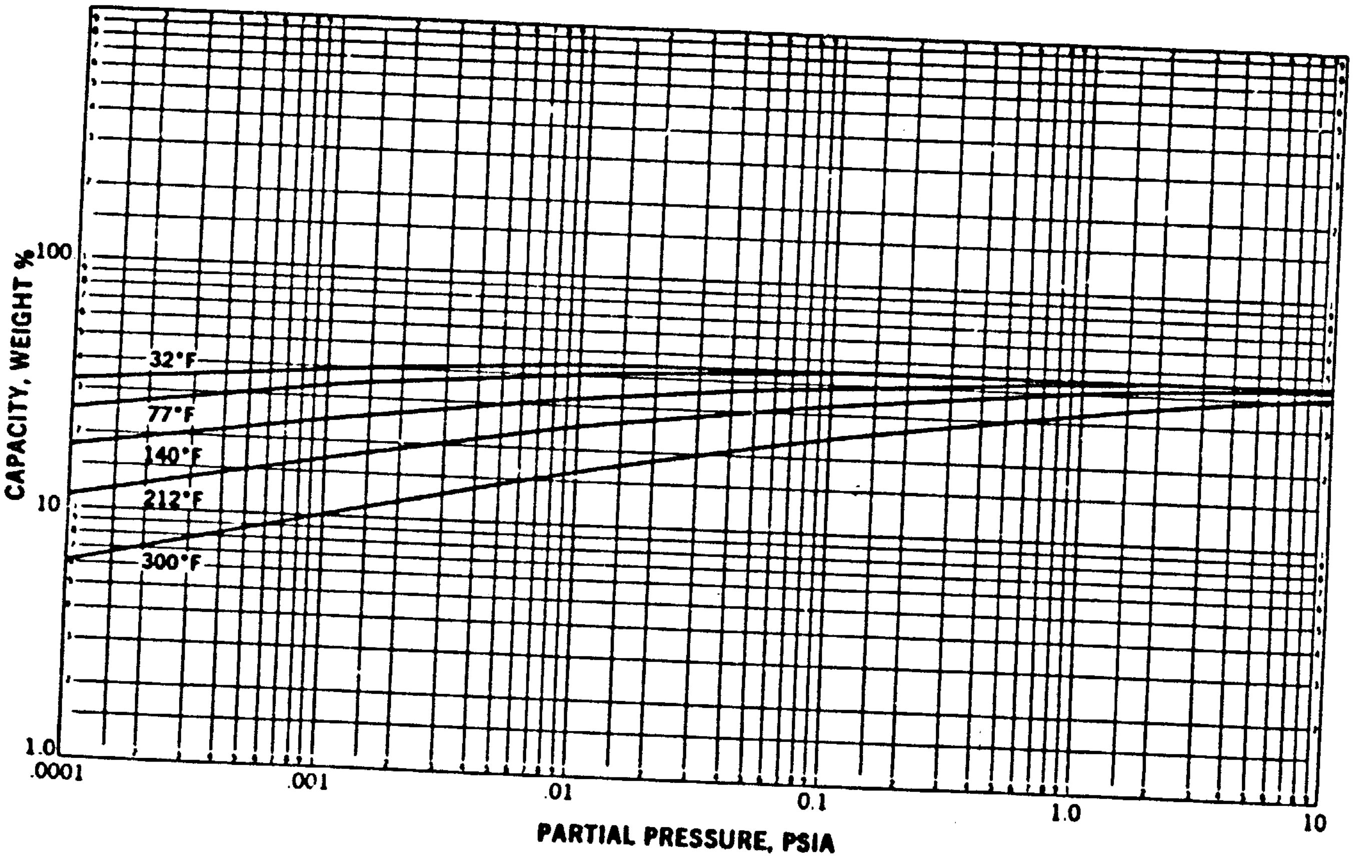

Figure 8.3-1. Styrene Adsorption on BPL Activated Carbon (Calgon Corporation).

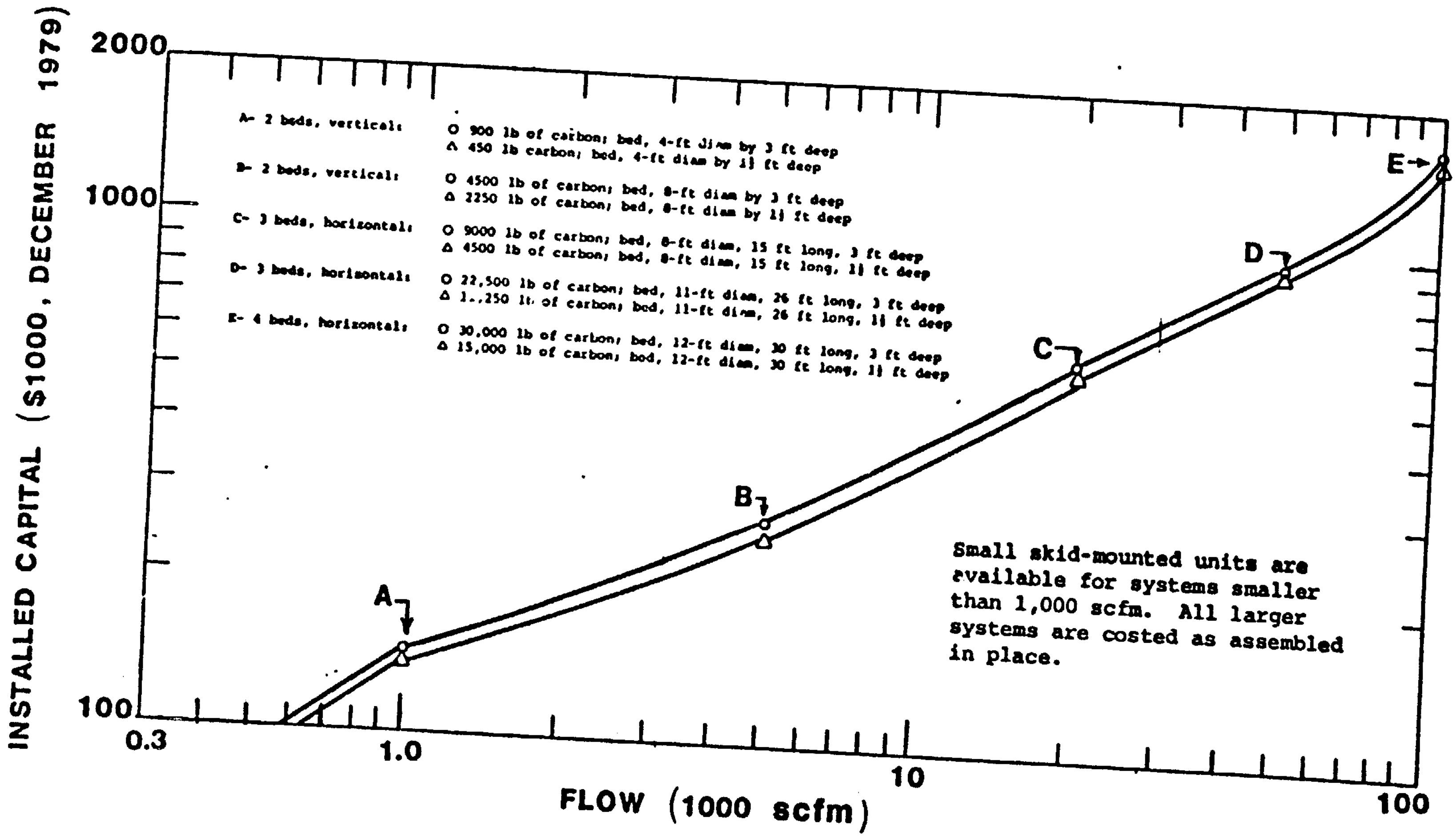

Figure 8.3-2. Installed Capital Cost of Carbon Adsorption Systems (Basdekis and Parmele, 1980).

Table 8.3-1

CAPITAL AND OPERATING COSTS FOR ADSORPTION

(Costs in $1000 except where otherwise noted)

Case	Variant	Capital Cost	Annual Operating Costs						Cost per lb Styrene Removed ($)
			Fixed	Carbon	Steam	Elec.	Credit	Net	
1	No styrene recovery	275.9	91.9	1.8	0.1	2.5	0	96.3	4.3
	50% styrene recovery	275.9	91.9	1.8	0.1	2.5	7.5	88.8	4.0
	70% styrene recovery	275.9	91.9	1.8	0.2	2.5	10.4	85.9	3.9
2	No styrene recovery	907.3	302.1	16.1	0.7	21.8	0	340.7	4.6
	50% styrene recovery	907.3	302.1	16.1	0.7	21.8	24.5	216.2	4.3
	70% styrene recovery	907.3	302.1	16.1	1.4	21.8	34.2	306.5	4.2

that the application of condensers on streams with less than 0.5 percent of volatile organic carbon would be very limited. (In our case, the waste gas stream contains 0.0224 percent styrene.) Capital costs were obtained from Figure 8.4-1. Since the air flow in our case studies exceeds the range shown in the figure, we assumed that multiple condenser units would be used. Although, as was reported in Chapter 7, the gas stream would have to reach -40 °F for complete condensation, data provided by Erikson indicate that a system could operate efficiently at 10°F; this assumption was used in the calculations. (A check on the sensitivity of total cost to this assumption showed that reducing the temperature to -40°F would increase total annual costs by about 3 percent.)

8.4.2 Results

The results of our analysis of condensation costs are shown in Table 8.4-1. As with carbon adsorption, fixed costs represent a major fraction of the total. Costs per pound of styrene removed appear to be intermediate between those of incineration and carbon adsorption. Of the three alternatives, this one is the most likely to actually provide a credit in the form of recovered styrene. The price of styrene would have to rise considerably, however, for this credit to offset the annual cost significantly.

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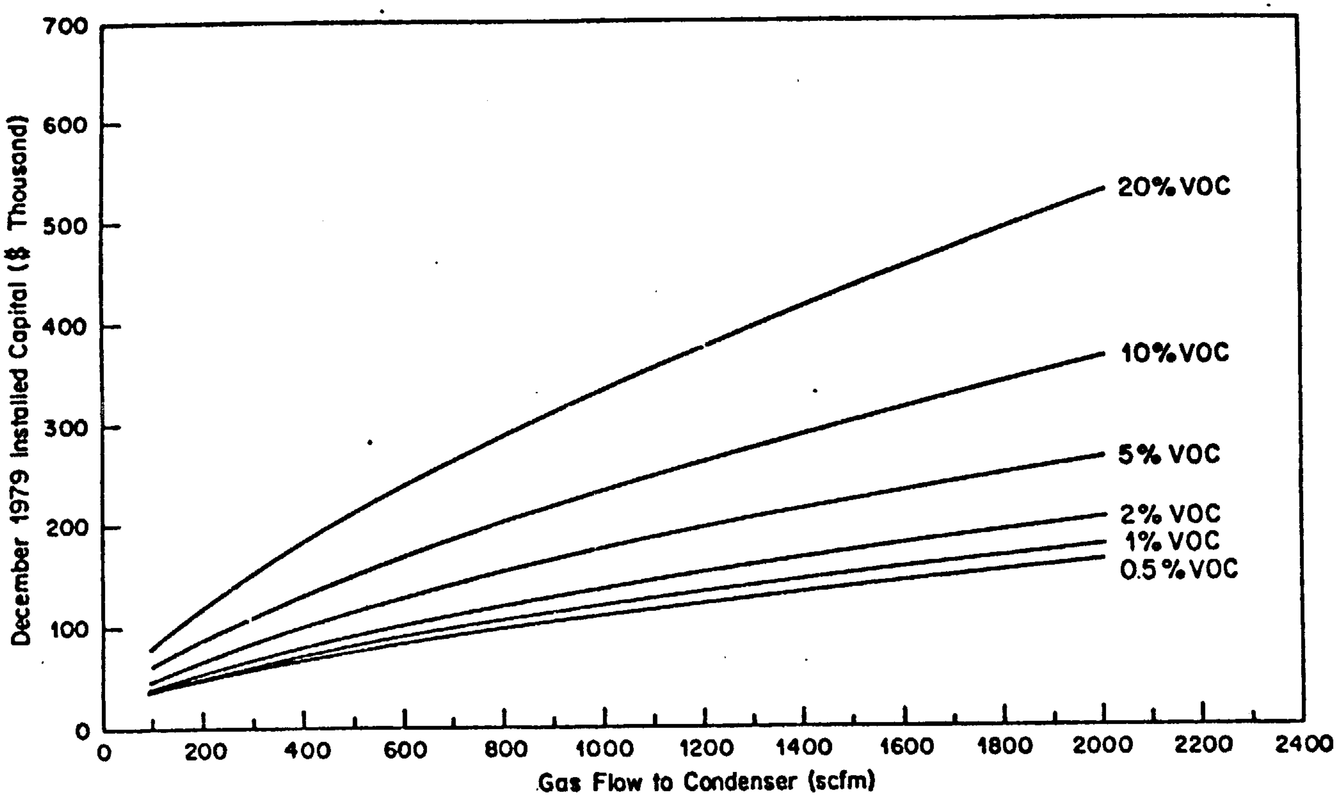

Figure 8.4-1. Installed Capital Cost vs Flow Rate for Complete Condenser System With Volatile Organic Carbon (VOC) Removal Efficiency of 80 Percent (Erikson, 1980).

Table 8.4-1

CAPITAL AND OPERATING COSTS FOR CONDENSATION

Case	Variant	Capital	Annual Operating Costs ($1000) Fixed	Labor	Elec.	Credit	Net	Cost per lb Styrene Removed ($)
1	No styrene recovery	430.5	143.4	14.6	6.7	0	164.7	7.3
	Styrene at 40¢/lb	430.5	143.4	14.6	6.7	9.0	155.7	6.9
	Styrene at 60¢/lb	430.5	143.4	14.6	6.7	13.5	151.2	6.7
2	No styrene recovery	3,444.4	1,146.9	14.6	58.4	0	1219.9	15.0
	Styrene at 40¢/lb	3,444.4	1,146.9	14.6	58.4	32.6	1187.3	14.6
	Styrene at 60¢/ib	3,444.4	1,146.9	14.6	58.4	48.9	1171.0	14.4

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9.0

MATERIAL PROPERTY TESTS

9.1 INTRODUCTION

In our discussion of vapor suppressants in Chapter 7, we noted that a chief concern of those who are considering using vapor-suppressed polyester resins was that products would delaminate, especially in places where secondary bonding is used. Deterioration in product quality is thus one potential "side effect" of using vapor suppressants for emission control. One of the objectives of this project was to measure this deterioration.

Numerous standardized methods for testing the physical properties of plastics composites are available (Bultman, 1978). Since our project resources for testing were quite limited, we decided to focus upon interlaminar shear strength as an indicator of possible effects of using vapor-suppressed resins. Following the recommendations of McKenna (1975), who has conducted a thorough review of interlaminar effects in reinforced plastics, we chose the short beam shear test, which is described below. It should be noted that no attempt was made to determine minimum, maximum or "typical" values of interlaminar shear strength for polyester resin/glass composites. Instead, it was felt that the most useful approach would be to fabricate all test specimens in the same way, varying only the presence or absence of vapor suppressant.

9.2 METHODS

9.2.1 Preparation of Test Laminates

Our original plan was to test several pairs of laminates, each pair consisting of one made with a vapor-suppressed resin and one without a suppressant. The two resins in each pair of laminates were to be from the same manufacturer. Unfortunately, our requests for resin samples from major manufacturers were subject to lengthy delays, and we decided to proceed with those resins on hand by June, 1981. Table 9.2-1 summarizes the resin types used for the tests. Resins A and D are similar in all of their properties, except that A contains a vapor suppressant and D does not. Resin B does not contain a vapor suppressant; however, according to the manufacturer, it is supposed to emit less styrene since (1) it has a low monomer content (35 to 37 percent) and (2) it has a special "proprietary formulation" (Cremaschi, 1981).

Table 9.2-1

CHARACTERISTICS OF LAMINATES USED FOR MATERIALS TESTS

Laminate Code	Resin Manufacturer	Type	Vapor Suppressant	Fabrication
A	Owens-Corning	HE4-101	Yes	One-stage
B	Owens-corning	HE4-101	Yes	Two-stage
C	Reichhold	90-550	No[a]	One-stage
D	Owens-Corning	E-480-1	no	One-stage
E	Koppers	82-73	No	One-stage

[a] Claimed to be a low-vapor-emitting resin (see test).

All test laminates were prepared by Andreas Fibercraft Company of North Hollywood, California. They consist of alternating layers of resin, 10-ounce glass cloth and 10-ounce glass mat, built up to a final thickness of 0.5 inch. The ratio of resin to glass was 60:40 by weight. All laminates were laid up by hand and cured at room temperature. In order to test effects on secondary bonding, Laminate B was fabricated to half its final thickness, allowed to cure for 24 hours, and then completed. At least four months elapsed between fabrication and testing.

Test specimens 0.5 x 0.5 inch in cross section and 6 inches in length were cut from noncontiguous sections of each laminate. Later, the specimens were precision milled by Prime-Mover Products Company (Torrance, California) so that their cross-sectional dimensions varied by less than 0.001 inch along their entire lengths.

9.2.2 Physical Test Methods

Material tests were conducted on 21 October 1981 at Magnaflux-Peabody Testing Laboratory in the City of Commerce, California. The following discussion of procedures is based upon an internal memorandum by the SAI test supervisor (Osofsky, 1981).

Interlaminar Shear Strength

Test specimens were designed to conform with ANSI/ASTM D 2344-76, "Standard Test Method for Apparent Interlaminar Shear Strength of Parallel Fiber Composites by Short-Beam Method," a copy of which is provided in Appendix C. In this test, a short beam having a square cross section is mounted on two supports, and force is applied by a loading nose positioned exactly midway between the supports.

Figure 9.2-1 shows the standard test setup. Horizontal shearing stress (lb/in^2) is defined as:

$$S_H = \frac{VQ}{Ib} \qquad (9\text{-}1)$$

where V = vertical shear force (lb), Q = statical moment of the area (in^3), I = moment of inertia (in^4), and b = width of the beams (in).

Figure 9.2-1. Standard Test Setup for Interlaminar Shear Strength Tests (Beam Has Failed in Tension).

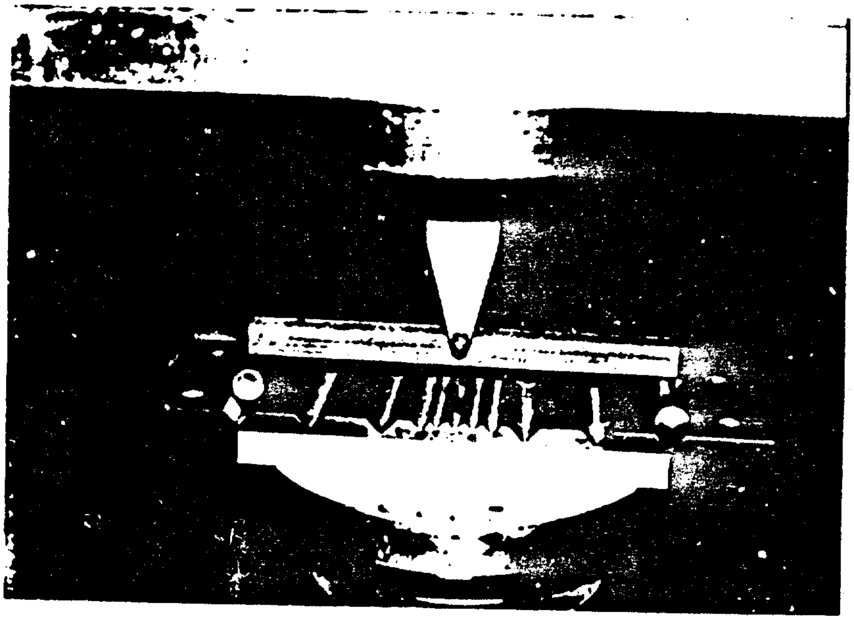

Figure 9.2-2. Standard Test Setup for Bending Tests

For a rectangular beam,

$$I = \frac{bd^3}{12} \qquad (9\text{-}2)$$

$$Q = \frac{bd^2}{8} \qquad (9\text{-}3)$$

where d is the specimen thickness. For a simple beam, V = P/2, where P is the breaking load (lb). Substituting these values of Q, I and V into Equation 9-1, we obtain

$$S_H = \frac{3P}{4bd} \qquad (9\text{-}4)$$

The ASTM method recommends test span/thickness and beam length/thickness ratios of 5 and 7, respectively, for the type of composites we tested. Since our beam widths varied from 0.392 to 0.461 inch, the span length (i.e. the distance between the test supports) should have been 1.96 to 2.31 inches. When the first specimen was tested in this manner, it failed in tension along its lower edge. In order to obtain meaningful shear data, we shortened the test span to 1.00 inch. This reduced the bending moment, which loads the lower outer fibers of the beam in tension. The bending moment is calculated as PL/4, where P is as defined above and L is the test span (in). By reducing L, we reduced the potential for a tensile failure while leaving the shear stress unchanged for a given load. It was observed, nevertheless, that many failures apparently occurred in tension even with the shortened beam.

Bending Tests

Because shear tests may be inconclusive in determining the differences among specimens, a non-destructive bending test was also performed. The test is outlined in Method 1, Procedure A of ASTM D 790-71, "Standard Methods of Test for Flexural Properties of Plastics," a copy of which is included in Appendix C. Figure 9.2-2 shows a test specimen mounted between 6-inch centers on 0.25-inch diameter dowels. A load is applied to a central 0.125-inch diameter dowel at a speed of 0.05 inches per second. Deflection as a function of load is plotted on a strip chart recorder. The tangent modulus of elasticity in bending, E_B (lb/in^2), is defined as follows:

$$E_B = \frac{L^3 m}{4bd^3} \qquad (9\text{-}5)$$

where L, b, and d are as defined above and m is the slope of the tangent to the initial straight-line portion of the load deflection curve (lb/inch). By setting L equal to 6 inches, we obtain:

$$E_B = \frac{54m}{bd^3} \qquad (9\text{-}6)$$

9.3 RESULTS

9.3.1 Interlaminar Shear Strength Tests

Shear strength tests were performed on six specimens from each of the five laminates. Test specimen dimensions, failure strengths, and apparent failure modes are shown in Table 9.3-1. Nine of the specimens failed in tension. It may be significant that the laminate with the highest percentage of failures in tension rather than in shear was the one fabricated in two stages (Laminate B). Table 9.3-2 summarizes the observed maximum applied force at failure and the apparent shear stress for those specimens which failed in shear.

Mean interlaminar shear strengths of the laminates were compared by paired t-tests, the results of which are shown in Table 9.3-3. Given the low variances, it is not surprising that differences in means are significant at the 95-percent confidence level in all cases except for A vs C. In order of decreasing shear strength, the laminates may be ranked as follows:

Laminate	Characteristic
E	No vapor suppressant
B	Vapor suppressant/two-stage fabrication
A,C	Vapor suppressant (A), special formulation (C)
D	No vapor suppressant

The only "head-to-head" comparison of vapor-suppressed and non-suppressed resins was that between Laminates A and D. In that case, the laminate made with the suppressed resin had a 9-percent higher shear strength than did the one made with its non-suppressed counterpart. There was, however, no significant difference in mean interlaminar shear strength between the groups of laminates made with vapor suppressed and non-suppressed resins. This result is the same whether the laminate fabricated from the "specially formulated" resin (C) is included with the suppressed or non-suppressed group. It is interesting to note that the laminate made in two stages (B) was about 8

Table 9.3-1

INTERLAMINAR SHEAR STRENGTH TEST CONDITIONS

Specimen Number	Specimen depth, d inches			Specimen width, b inches			Theoretical Shear Span, inches	Maximum Force, P lbs	Apparent Failure Mode
	Min.	Max.	Average	Min.	Max.	Average			
A-1	.449	.454	.452	.451	.461	.456	2.26	620	Tensile
A-2	.441	.453	.447	.456	.462	.459	2.24	570	Tensile
A-3	.450	.456	.453	.458	.463	.461	2.27	1425	Shear
A-4	.455	.455	.455	.460	.460	.460	2.28	1490	"
A-5	.447	.453	.450	.460	.463	.461	2.25	1430	"
A-6	.447	.454	.450	.454	.462	.458	2.25	1490	"
B-1	.402	.409	.405	.405	.408	.406	2.03	1210	Tensile
B-2	.405	.407	.406	.398	.406	.402	2.03	1150	"
B-3	.406	.409	.407	.405	.407	.406	2.03	1245	"
B-4	.402	.408	.405	.407	.409	.408	2.03	1170	"
B-5	.400	.406	.403	.403	.407	.405	2.02	1255	Shear
B-6	.405	.408	.406	.405	.407	.406	2.03	1230	"
C-1	.390	.396	.393	.397	.397	.397	1.97	1150	Shear
C-2	389	.395	.392	.394	.398	.396	1.96	1060	"
C-3	.393	.397	.395	.390	.397	.393	1.98	1140	"
C-4	.385	.393	.389	.394	.397	.395	1.95	1075	"
C-5	.390	.396	.393	.396	.398	.397	1.97	1040	"
C-6	.388	.396	.392	.390	.398	.394	1.96	1060	"
D-1	.399	.402	.400	.400	.402	.401	2.00	1040	Shear
D-2	.403	.406	.404	.400	.401	.400	2.02	1060	"
D-3	.401	.403	.402	.400	.400	.400	2.01	970	"
D-4	.404	.404	.404	.400	.401	.400	2.02	1055	"
D-5	.403	.404	.403	.400	.402	.401	2.02	1005	Tensile
D-6	.396	.402	.399	.356	.401	.398	2.00	1045	Shear
E-1	.450	.452	.451	.450	.452	.451	2.26	1835	Shear
E-2	.453	.454	.453	.450	.452	.451	2.27	1945	"
E-3	.452	.454	.453	.444	.452	.448	2.27	1785	Tensile
E-4	.454	.458	.456	.447	.452	.449	2.28	1780	"
E-5	.449	.452	.450	.453	.453	.453	2.25	1800	Shear
E-6	.450	.454	.452	.452	.453	.452	2.26	1850	"

Table 9.3-2

INTERLAMINAR SHEAR STRENGTH TEST RESULTS

Laminate	Maximum Force (lb) Mean	Std.Dev	Apparent Shear Stress (lb/in^2) Mean	Std. Dev.	No. Failing in Shear
A	1459	36.1	5262	142.3	4
B	1243	17.7	5682	120.9	2
C	1088	46.0	5258	216.2	6
D	1034	36.6	4827	171.7	5
E	1858	62.0	6830	219.5	4

Table 9.3-3

COMPARISON OF INTERLAMINAR SHEAR STRENGTHS AMONG RESIN TYPES AND LAMINATE FABRICATION METHODS

Laminate	Laminate B	Laminate C	Laminate D	Laminate E
A	A$\overset{*}{<}$B t = -3.533 d.f. = 4	A>C t = 0.0323 d.f. = 8	A$\overset{*}{>}$D t = 4.058 d.f. = 7	A$\overset{*}{<}$E t = -11.988 d.f. = 6
B	x	B$\overset{*}{>}$C t = 2.553 d.f. = 6	B$\overset{*}{>}$D t = 6.277 d.f. = 5	B$\overset{*}{<}$E t = -6.645 d.f. = 4
C	x	x	C$\overset{*}{>}$D t = 3.601 d.f. = 9	C$\overset{*}{<}$E t = -11.200 d.f. = 8
D	x	x	x	D$\overset{*}{<}$E t = -15.420 d.f. = 7

* Means are significantly different ($p<0.05$).

percent stronger than the one-stage laminate made from the identical resin.

9.3.2 Bending Tests

Results of the bending tests are shown in Table 9.3-4. The pattern of flexibility among laminates is different from that of interlaminar shear strength. In this case, Laminate C, which was made from the "specially formulated" resin had the greatest stiffness. In order of decreasing stiffness, the ranking of laminates was:

Laminate	Characteristic
C	Special formulation
E	No vapor suppressant
B	Vapor suppressant/two-stage fabrication
A,D	Vapor suppressant (A), No vapor suppressant (D)

Laminates A and D are ranked the same, since there was no significant difference between their bending moduli. Since the resin used for these laminates differed only in whether it had a vapor suppressant, the use of vapor suppressant apparently did not affect the flexibility of the laminates. On the other hand, constructing Laminate B in two stages appears to have increased its stiffness, since its bending modulus is significantly higher than that of Laminate A, which was made from the same resin. Correlation between bending modulus and interlaminar shear strength was rather low ($r = 0.482$).

9.4 DISCUSSION

It is not surprising that an appreciable fraction (9 of 30) of the test laminates failed in tension, rather than in shear. Indeed, McKenna (1975) points out that, while ASTM D 2344-76 is the only accepted standard for interlaminar shear testing, the values obtained are "apparent." This is due to the fact that the shear stress distribution through the composite is not constant. Mixed mode failures can occur if the composite flexural strength/interlaminar shear strength ratio is too low.

From these limited tests, it does not appear that the use of vapor suppressant degrades interlaminar shear strength significantly. In the one case for which laminates varied only in their vapor suppressant content (A vs

Table 9.3-4
BENDING TEST RESULTS

Specimen Number	Deflection, @ 200 lbs. L inches	Width, b inches	Depth, d inches	Modulus of Elasticity, psi	Mean Modulus of Elasticity	Standard Deviation psi
A-1	4.62	.456	.452	55,500	55,500	1100
A-2	4.66	.459	.447	56,500		
A-3	4.72	.461	.453	53,400		
A-4	4.47	.460	.455	55,800		
A-5	4.61	.461	.450	55,800		
A-6	4.64	.458	.450	55,800		
B-1	6.93	.406	.405	57,800	57,400	900
B-2	6.99	.402	.406	57,400		
B-3	6.77	.406	.407	58,300		
B-4	7.07	.408	.405	56,600		
B-5	7.00	.405	.403	58,200		
B-6	7.07	.406	.406	56,200		
C-1	6.21	.397	.393	72,200	71,900	2600
C-2	6.40	.396	.392	70,700		
C-3	5.81	.393	.395	76,700		
C-4	6.70	.395	.389	69,300		
C-5	6.40	.397	.393	70,000		
C-6	6.30	.394	.392	72,200		
D-1	7.63	.401	.400	55,200	53,600	2000
D-2	7.48	.400	.404	54,700		
D-3	8.30	.400	.402	50,100		
D-4	7.60	.400	.404	53,900		
D-5	7.82	.401	.403	52,600		
D-6	7.75	.398	.399	55,100		
E-1	3.87	.451	.451	67,500	67,800	1600
E-2	3.74	.451	.453	68,900		
E-3	3.86	.440	.453	67,200		
E-4	3.80	.449	.456	66,800		
E-5	3.72	.453	.450	70,300		
E-6	3.92	.452	.452	66,000		

D), the laminate made with a vapor suppressed resin was actually slightly stronger in shear. No degradation of secondary bonding strength was apparent either. Finally, no conclusions may be reached about the effect of vapor suppressants on bending properties.

That our test results show no clear adverse effects of vapor suppressant use on the two material properties considered should not be interpreted as a blanket endorsement of this means of emission control. A manufacturer who is interested in using vapor-suppressed resins should perform these and other pertinent tests on laminates made to the same specifications and by the same processes as the ultimate product.

9.5 REFERENCES

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McKenna, G.B. 1975. "Interlaminar effects in fiber-reinforced plastics-a review," Polymer plastics technology and engineering 5(1): 23-53.

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10.0
DEVELOPMENT OF CONTROL STRATEGIES

Our final objective in this project was to postulate alternative strategies for controlling organic vapor emissions from California's polyester resin/fiberglass industry. The following discussion is equally applicable whether control strategies are being considered at the state or at the local level.

10.1 SCOPE OF REGULATORY ATTENTION

It is clear from the results of our emission inventory survey that a relatively small number of sources are responsible for the bulk of the emissions from polyester resin/fiberglass fabrication in California. As was reported in Chapter 6, about 4 percent of the firms account for about half of the industry's organic vapor emissions. Furthermore, several of the larger emission sources were not identified in local air pollution control district emission inventories. Given the limited resources of regulatory agencies, it would probably be most cost-effective to focus attention upon these large sources, rather than to worry about controlling fractions of tons per year of emissions from the myriad of small fabricators. Table 10.1-1 shows in which counties the state's largest sources in this industry are located, and the number of firms corresponding to various threshold levels of regulatory concern. For example, if one were interested only in those sources emitting over 25 tons per year, then 25 plants (almost half of which are in Orange County) would be affected.

10.2 CONTROL STRATEGY ALTERNATIVES

On the basis of our findings in this study, we have identified three broad approaches to controlling organic vapor emissions from the California polyester resin/fiberglass industry. Their pros and cons will be outlined here.

10.2.1 Absolute Limits on Emissions

In this alternative, maximum hourly, daily, or annual limits on emissions would be set for all firms, regardless of size or production process. The means of achieving the desired level of emissions would be up to each firm. Unless the maximum emission level were set rather low, this approach would affect only the largest firms in the state. It is likely that

Table 10.1-1

LOCATION OF FIRMS HAVING UNCONTROLLED EMISSIONS[a] EXCEEDING VARIOUS LEVELS OF POSSIBLE REGULATORY INTEREST

County	Cutoff Point (tons) 10	15	20	25
Contra Costa	1	1	0	0
Fresno	1	0	0	0
Kern	1	1	1	0
Los Angeles	15	12	9	8
Merced	1	0	0	0
Orange	26	21	16	12
Sacramento	1	0	0	0
San Benito	1	1	1	1
San Bernardino	1	1	1	1
San Diego	4	3	2	1
San Joaquin	1	1	1	1
San Luis Obispo	1	0	0	0
San Mateo	1	1	0	0
Shasta	1	1	0	0
Sonoma	1	0	0	0
Tehama	1	1	0	0
Yolo	1	1	1	1
Totals	59	45	32	25

[a] Count based upon upper emission estimates.

some sort of exhaust gas treatment would have to be retrofitted in existing plants, at considerable expense to the owenrs. It could be difficult for the very large plants to expand their operations.

10.2.2 Percentage Removal-Based Standards

In this regulatory approach, all firms (or all firms whose emission would otherwise exceed a certain level) would have to apply whatever means necessary to reduce their emissions by a stated percentage. This is the approach taken, for example, in the federal New Source Performance Standards for sulfur removal from coal. The burden placed on smaller firms could be unreasonably heavy, since the only way some of these could reduce their already small emissions would be to install expensive control equipement or change their production processes radically. Larger firms might have less trouble with this approach than with one based upon absolute emission limits. However, the net reduction in emissions from the industry might be lower than if absolute emission standards were used.

10.2.3 Technology-Based Standards

Finally, as is already done under new source review provisions of local district regulations, polyester resin/fiberglass fabricators would have to apply "best available control technology" (BACT) to reduce emission from their operations. Given the variability among firms, even among those using the same production processes, no simple definition of BACT is feasible. Rather, control technology would have to be matched to each particular case. Our comments on the control technologies described in Chapter 7 and 8 are as follows.

Changes in Process, Type of Resin, Fabrication Protocols, Etc.

In the long run, the most cost-effective means for reducing emission from the large number of plants would be to use lower-monomer resins, change from open to closed molding, reduce rollout time, improve housekeeping practices and make other changes not requiring treatment of exhaust gases. In some cases, these emission reduction could be achieved at essentially zero cost. However, process changes in a plant having a large capital investment in assembly line-type equipment, such as is associated with filament winding or pultrusion, would be extremely costly. Furthermore, product quality could suffer from substitution of lower-monomer resins.

Use of Vapor Suppressed Resins

Vapor-suppressed resins could prove highly cost-effective in many cases, especially where secondary bonding requirements are minimal. Before these resins were used it should be demonstrated for each particular case that product quality would not be degraded. Blanket requirements for use of vapor suppressants are not recommended.

Incineration

The fact that incineration is presently being used to reduce emissions from two large continuous lamination plants in California demonstrates its practicality. Our cost analysis, however, showed this to be the most expensive of the three "end of pipe" treatment technologies evaluated. Furthermore, there is no economy of scale in using incineration, and if natural gas prices are decontrolled, operating costs could rise considerably. On the other hand, costs could be reduced by treating a more concentrated waste gas stream and/or treating less exhaust air.

Adsorption

Activated carbon adsorption was the least expensive of the three control technologies evaluated in Chapter 8. Its main disadvantage is that even if recovery of styrene proves feasible, the process creates a liquid waste disposal problem. Further research in this area is warranted. Vacuum stripping of the spent carbon may improve the chances of recovering styrene in economical quantities.

Absorption

Scrubbing of styrene from exhaust air does not appear to be feasible at this time.

Condensation

While condensation is in principle feasible, it is not normally applied to waste streams having organic vapor concentrations as low as those from polyester resin/fiberglass fabrication. However, this removal technique could be used in conjunction with vacuum-stripped activated carbon, since styrene concentrations in the desorption stream could be increased considerably.

APPENDIX A

QUESTIONNAIRE SENT TO LOCAL AIR POLLUTION CONTROL DISTRICTS

Dear Sir:

Science Applications, Inc. (SAI) is under contract to the Research Division of the California State Air Resources Board (ARB) to investigate techniques to control organic gas emissions from operations where polyester resin is used in California. The objectives of our research are (1) to estimate emissions (principally styrene) by type of operation and by county and (2) to survey present and developing control technology. We are particularly interested in control strategies which minimize the financial burden upon small businesses.

In order to obtain basic information on polyester resin use, styrene emissions, and control technology in California, we have conducted a survey of approximately 600 firms, of which 160 used the fabrication processes of interest in this study. At this writing, it appears that there are no polyester resin users in your jurisdiction. In order that our emissions inventory be as complete and accurate as possible, we would like to know if you are aware of any such firms in your district. Typical manufactured products include boats, showers and tubs, storage tanks, fiberglass panels and artificial marble. Typical processes include hand and spray layup, pultrusion, matched metal molding, continuous lamination and filament winding. We are <u>not</u> interested in firms which use polyester resin beads in injection molding.

Please return the attached form in the enclosed stamped, self-addressed envelope by January 15, 1981. The form should be returned even if there are no polyester users in your district.

The ARB research contract monitor for this project is Mr. Joseph Pantalone, whose telephone number is (916) 445-8699. Our contract number is A9-120-30. If you have any questions please contact me at (213) 553-2705.

Thank you very much for your cooperation.

Sincerely,

SCIENCE APPLICATIONS, INC.

Michael B. Rogozen, D.Env.
Principal Investigator
ARB/Polyester Resin-Fiberglass Project

Science Applications, Inc. 1801 Avenue ars, Suite 1205, Los Angeles, CA 90067 (213) 553-2705
Other SAI Offices: Albuquerque, Atlanta, Chicago, Dayton, Denver, Hunt ngeles, Oak Ridge, San Diego, San Francisco, Tucson, and Washington D C

SCIENCE APPLICATIONS, INC.

POLYESTER RESIN EMISSIONS INVENTORY
AIR POLLUTION CONTROL DISTRICT SURVEY

Name of District ______________________________

Person to Contact ______________________________ Telephone ( ) ________________

(Check if Applicable) There are no polyester resin users in this jurisdiction _________.

Please furnish whatever information is readily available.

Name of Firm	Address	Telephone No.

APPENDIX B

ANALYTICAL METHODS

B.1 CALIBRATION OF THE ORGANIC VAPOR ANALYZER

We used a Foxboro Instruments Model OVA 128 organic vapor analyzer (OVA) in all the field tests. The OVA was calibrated the day before each two-day test period. A 100 ng/L calibration sample was prepared by injecting the appropriate amount of liquid styrene into a clean 20-L glass carboy and shaking the carboy vigorously for 3 to 5 minutes.

A 100-ml bubble flow meter was used to calibrate the flow through the activated charcoal trap connected in series with the OVA, with and without additional tubing. Connections between the traps and the 0.125-inch (i.d.) metal tubing were made with tygon tubing. Sampling flow rates varied from day to day, but were the same with and without the extension tubing.

B.2 CHARCOAL EXTRACTION PROCEDURES

The following procedure was used to extract styrene from the activated charcoal traps used in the field:

1. Charcoal traps are opened and the entire contents are transferred to a 15 ml glass culture tube.
2. 3 ml of reagent grade carbon disulfide are added to the culture tube and the culture tube is placed in a Burrell Model #75 wrist action shaker for 1/2 hour.
3. Using a syringe, the CS_2 is withdrawn and transferred to a 10 ml micro-KD distillation flask column.
4. 0.5 ml of CS_2 is added back to the culture tube to rinse the charcoal and this fraction is then transferred to the micro-KD flask. (No shaking for the 1 ml rinse).
5. 3 ml of CS_2 is now added back to the culture tube and the tube is placed in the wrist action shaker. This procedure is repeated for a total of 3 times.
6. After the final rinse, the micro-KD flask with condenser is placed in a water bath and gently heated to evaporate off the CS_2.

7. The flask is evaporated down to contain approximately 0.5 ml.

8. Using a 1 ml syringe, the remaining sample is removed from the micro KD flask and, using CS_2, is brought back to a PIV (pre injection volume) of exactly 1 ml and transferred to a septum vial for GC injection.

B.3 INSTRUMENT CONDITIONS

Instrument:	HP 5730A Gas Chromatograph
Column:	8 ft x 2 mm ID (1/4" OD) glass, packed column (160/80 Carbopack/10% SP 1000)
Column temp.:	200^{0} C
Temp. program:	Isothermal
Injection:	2 µL
Standard:	90.6 ng/µL styrene

B.4 CHARCOAL EXTRACTION EFFICIENCY RUNS

Following each return from field sampling three blank charcoal tubes were loaded with 1, 2 and 3 µL of pure styrene, respectively, to be extracted at the same time as the actual samples. These samples determined the actual extraction efficiency. One blank sample was also run for each set of data.

B.5 CALCULATION OF INTEGRATED AVERAGE STYRENE CONCENTRATION BY PLANIMETRY

Because the concentration of styrene in two of the three facilities we tested varied from minute to minute, dependence upon grab samples would have led to inaccurate emission estimates. We therefore devised a method to estimate integrated average concentrations for each test run. The output of the OVA was connected to a strip chart recorder, which provided a continuous trace of the instantaneous OVA readings. The area under the trace is proportional to the mass of styrene emitted during the sampling interval. As was described in Section 5.2.2, the proportionality between chart area and styrene mass emissions was determined by collecting air samples on charcoal, analyzing them, and computing the area under the trace corresponding to each charcoal sampling interval.

To facilitate area measurement, the OVA recorder trace was cut into several sections. Figure 5.2-6 for example, shows the first three sections of the trace recorded during our second visit to Facility B. We then used a

Keuffel and Esser compensating planimeter to measure the area under each trace section. Table B.5-1 shows the analysis of the Facility B trace. The planimeter reading at the end of the trace is subtracted from the reading at the start; the difference is equal to the number of chart "units." As noted above, the chart units are related to styrene mass by our calibration procedure. (See Section 5.2.2.) Each trace section was measured at least three times. The mean areas of all the sections were added to get the total chart area.

The chart area was multiplied by the styrene mass/chart area ratio (determined by the charcoal trap calibration) to get total mass emissions from each run. For example in one run at Facility B,

$$\text{Mass emitted} = (55\ \mu g/\text{unit})\ (2157\ \text{units}) = 118635\ \mu g$$

Finally, integrated average styrene concentrations were calculated by dividing the mass emission by the product sampling air flow rate and the sampling time:

$$\text{Concentration} = \frac{118635\ \mu g}{(0.9\ L/\text{min})(145\ \text{min})} = 909\ \mu g/L$$

Table B.5-1

PLANIMETRIC MEASUREMENTS OF OVA RECORDER CHART, FACILITY B, SECOND VISIT

Chart Section	Trace No.	Planimeter Reading Start	Planimeter Reading Stop	Area ("Units")	Mean of Three Traces ("Units")
1	1	3658	3745	87	85
	2	2745	3828	83	
	3	3828	3914	86	
2	1	3691	4119	428	429
	2	4119	4347	428	
	3	4547	4978	431	
3	1	4318	4848	530	528
	2	4848	5375	527	
	3	5375	5903	528	
4	1	0669	1096	427	423
	2	1096	1517	421	
	3	1517	1937	420	
5	1	1775	2061	286	287
	2	2061	2348	287	
	3	2348	2636	288	
6	1	3000	3329	329	328
	2	3329	3657	328	
	3	3657	3985	328	
7	1	4135	4211	76	77
	2	4211	4288	77	
	3	4288	4367	79	
		Total Chart Area		2157	

APPENDIX C

MATERIALS TEST SPECIFICATIONS

Standard Test Method for
APPARENT INTERLAMINAR SHEAR STRENGTH OF PARALLEL FIBER COMPOSITES BY SHORT-BEAM METHOD[1]

This Standard is issued under the fixed designation D 2344; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

This method has been approved for use by agencies of the Department of Defense and for listing in the DoD Index of Specifications and Standards.

$^{\epsilon}$ Note—The title was changed editorially in July 1979.

1. Scope

1.1 This method covers the determination of the apparent interlaminar shear strength of parallel fiber reinforced plastics. The specimen is a short beam in the form of segments cut from a ring-type specimen or a short beam cut from a flat laminate up to 6.4 mm (0.25 in.) in thickness. The method is applicable to all types of parallel fiber reinforced samples.

2. Applicable Documents

2.1 *ASTM Standards:*

D618 Conditioning Plastics and Electrical Insulating Materials for Testing[2]

D2991 Recommended Practice for Testing Stress-Relaxation of Plastics[2]

E 4 Load Verification of Testing Machines[3]

E 18 Tests for Rockwell Hardness and Rockwell Superficial Hardness of Metallic Materials[4]

3. Summary of Method

3.1 The horizontal shear test specimen (Figs. 1 and 3) is center-loaded as shown in Figs. 2 and 4. The specimen ends rest on two supports that allow lateral motion, the load being applied by means of a loading nose directly centered on the midpoint of the test specimen.

4. Significance

4.1 Shear strength determined by this method is useful for quality control and specification purposes. It is also applicable for research and development programs concerned with interply strength. The apparent shear strength obtained in this method can not be used as a design criteria, but can be utilized for comparative testing of composite materials, if all failures are in horizontal shear.

4.2 The method is not limited to specimens with the sizes shown (Note 1) but is limited to specified span length-to-depth ratios. This ratio is recommended to be 5 when the specimen is reinforced with filaments having a Young's modulus of less than 100 × 10^9 Pa (14.5 × 10^6 psi) and 4 when the specimen is reinforced with filaments above 100 × 10^9 Pa (14.5 × 10^6 psi). See Table 1 for ratios for several typical reinforcements.

Note 1—The test method is also applicable to thicker specimens, especially where plies are thick (for example, ply, thicknesses of 1.3 mm (0.05 in.) are sometimes seen in cloth reinforcements; it is only necessary to scale the fixture in proportion to the thickness).

5. Apparatus

5.1 *Testing Machine*, properly calibrated, which can be operated at constant rate of crosshead motion, and in which the error in the load measuring system shall not exceed ±

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[1] This method is under the jurisdiction of ASTM Committee D-30 on High Modulus Fibers and Their Composites.

Current edition approved Jan. 30, 1976. Published March 1976. Originally published as D 2344 - 65 T. Last previous edition D 2344 - 72.

[2] *Annual Book of ASTM Standards*, Part 35

[3] *Annual Book of ASTM Standards*, Parts 10, 14, 32, 35, and 41

[4] *Annual Book of ASTM Standards*, Part 10

1 percent. The load-indicating mechanism shall be essentially free of inertia lag at the crosshead rate used. Inertia lag may not exceed 1 percent of the measured load. The accuracy of the testing machine shall be verified in accordance with Method E 4.

5.2 *Loading Nose and Supports*, as shown in Figs. 2 and 4. The loading nose shall be a 6.35-mm (0.250-in.) diameter dowel pin with a hardness of 60 to 62 HRC, as specified in Methods E 18, and shall have a finely gound surface free of indentation and burrs with all sharp edges relieved.

5.3 *Micrometers*, suitable ball-type, reading to at least 0.025 mm (0.001 in.) for measuring the width, thickness, and length of the test specimen.

6. Test Specimen

6.1 The rings used in this test method shall be fabricated in accordance with Recommended Practice D 2291. The dimensions of the rings shall conform to the Type C specimens as described in Recommended Practice D 2291. Shear test specimens cut from the rings shall conform to the dimensions and notes specified in Fig. 1.

NOTE 2—The flat specimens shall be molded by any suitable laminating means, such as press, bag, or autoclave molding.

6.2 *Number of Specimens*—The number of test specimens is optional. However a minimum of ten specimens is required to obtain a satisfactory average for one ring or laminate.

7. Conditioning

7.1 Condition the test specimen and test in a room or enclosed space maintained at 23 ± 1 C (73.4 ± 1.8 F) and 50 ± 10 percent relative humidity in accordance with Procedure A of Methods D 618. Record any deviation from the above conditions.

7.2 If it is desired to test the effect of boiling water on the shear strength, place the specimens in boiling distilled water for a prescribed period of time; then remove and place in distilled water at 23 ± 1 C (73.4 ± 1.8 F) for a minimum of 15 min. Wipe the specimens dry and test at the standard conditions given in 7.1.

8. Speed of Testing

8.1 Test the specimen at a rate of crosshead movement 1.3 mm (0.05 in.)/min.

9. Procedure

9.1 Before conditioning or testing, measure the thickness and width of each specimen to the nearest 0.025 mm (0.001 in.) at midpoint.

9.2 Place the test specimen in the test fixture as shown in Figs. 2 or 4. Align the specimen so that its midpoint is centered and its long axis is perpendicular to the cylindrical axis or under the loading nose. Push the side supports into the span previously determined (depending on the modulus of the material being tested). Suggested span-to-depth ratios are given in Table 1.

9.3 Apply the load to the specimen at the specified crosshead rate. Record the load to break specimen (maximum load on load-indicating mechanism). Often when testing laminates that are made with the high modulus fibers, specimens do not always fail in shear, especially when the incorrect span-to-depth ratio is chosen. It is therefore very important to record the type of break that occurs (shear or tensile). Also record the position of the shear plane (for example, left, right, center, or complete delamination across specimen).

10. Retests

10.1 Values for properties at break shall not be calculated for any specimen that breaks at some obvious, fortuitous flaw, unless such flaws constitute a variable being studied. Retests shall be made for any specimen on which values are not calculated. If a specimen in the shear test failed in a manner other than horizontal shear, the value shall be discarded and retest shall be made.

11. Calculations

11.1 Calculate the apparent shear strength as follows:

$$S_H = 0.75\, P_B/bd$$

where:

S_H = shear strength, N/m^2 (or psi),
P_B = breaking load, N (or lbf),
b = width of specimen, m (or in.), and
d = thickness of specimen, m (or in.).

11.2 *Arithmetic Mean for Each Series of Tests*—Calculate the arithmetic mean of all values obtained to three significant figures and report as the "average value."

11.3 *Standard Deviation*—Calculate the standard deviation (estimated) as follows and report to two significant figures:

$$s = \sqrt{(\Sigma X^2 - n(\bar{X}))^2/(n - 1)}$$

where:

s = estimated standard deviation,
X = value of a single observation,
n = number of observations, and
$\bar{X}$ = arithmetic mean of the set observations.

12. Report

12.1 The report shall include the following:

12.1.1 Complete identification of the material tested, including type, source form, principal dimensions, and previous history.

12.1.2 Fabrication procedure,

12.1.3 Thickness and width of the specimen,

12.1.4 Conditioning procedure used,

12.1.5 Atmospheric conditions in the test room,

12.1.6 Number of specimens tested,

12.1.7 Rate of crossl ead motion,

12.1.8 Span length,

12.1.9 Length of specimen,

12.1.10 Type of failure,

12.1.11 Apparent horizontal shear strength of each specimen, and average,

12.1.12 Standard deviation,

12.1.13 Location of failure,

12.1.14 Average resin content, by weight,

12.1.15 Void content, by volume, and

12.1.16 Date of test.

TABLE 1 Recommended Ratios of Thickness to Span Length and to Specimen Length

	Span/ Thickness	Length/ Thickness
Woven cloth reinforcement	5	7
Continuous glass filaments	5	7
Silica fibers (continuous)	4	6
Graphite yarn	4	6
Carbon yarn	5	7
Boron filaments	4	6
Steel wire	5	7

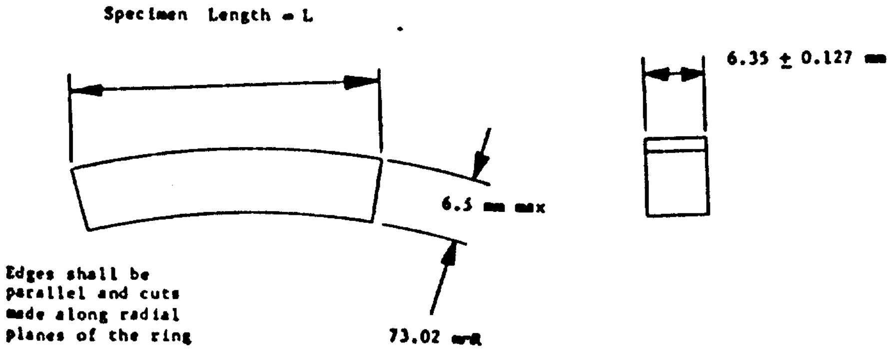

FIG. 1 Horizontal Shear Test Specimen (Ring Specimen).

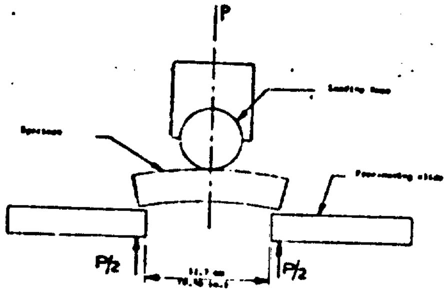

FIG. 2 Horizontal Shear Load Diagram (Ring Specimen).

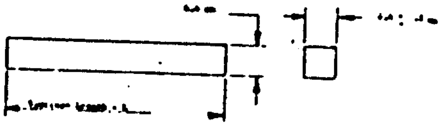

FIG. 3 Shear Test Specimen (Flat Laminate).

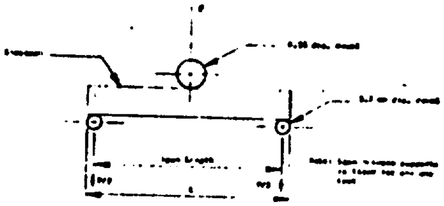

FIG. 4 Horizontal Shear Load Diagram (Flat Laminate).

Standard Method of Test for

FLEXURAL PROPERTIES OF PLASTICS[1]

ASTM Designation: D 790 - 66

This Standard of the American Society for Testing and Materials is issued under the fixed designation D 790; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision.

NOTE.—Editorial correction to units of *m* in Eq 5 was made in September, 1966.

1. Scope

1.1 This method covers the determination of flexural properties of plastics and electrical insulating materials in the form of rectangular bars molded directly or cut from sheets, plates, or molded shapes. The method is generally applicable to rigid and semirigid materials; however, flexural strength cannot be determined for those materials that do not break or that do not fail in the outer fibers. Two procedures are described, as follows:

1.1.1 *Procedure A* is designed principally for materials that break at comparatively small deflections.

1.1.2 *Procedure B* is designed particularly for those materials that undergo large deflections during testing.

1.2 Comparative tests may be run according to either procedure, provided that procedure is found satisfactory for the material being tested. All specification tests, however, must be run according to procedure A, unless otherwise stated in the material specifications.

2. Summary of Method

2.1 A bar of rectangular cross section is tested in flexure as a simple beam, the bar resting on two supports and the load applied by means of a loading nose midway between the supports. The specimen is deflected until rupture occurs, or until the maximum fiber strain (see 11.7) of 5 per cent is reached, whichever occurs first.

3. Significance

3.1 Flexural properties determined by this method are especially useful for quality control and specification purposes. Reproducibility between specimens is approximately ±5 per cent for homogeneous materials tested under comparable conditions. However, flexural properties may vary with specimen thickness, temperature, atmospheric conditions, and the differences in rate of straining specified in Procedures A and B (see also Note 7).

4. Apparatus

4.1 *Testing Machine*—A properly calibrated testing machine which can be operated at constant rates of crosshead

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[1] Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-20 on Plastics, and is the direct responsibility of Subcommittee I on Mechanical Properties. A list of committee members may be found in the ASTM Year Book.

Current edition accepted March 31, 1966. Originally issued 1944. Replaces D 790 - 63.

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motion over the range indicated,
which the error in the load-mea
system shall not exceed ±1 per
It shall be equipped with a defl
measuring device. The stiffness
testing machine shall be such th
total elastic deformation of the
does not exceed 1 per cent of th
deflection of the test specimen
test, or appropriate corrections sh
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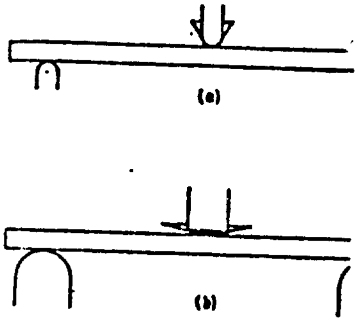
shall be essentially free from iner



(*a*) Minimum radius = 3.2 mm (⅛ i
(*b*) Maximum radius supports = 1½
specimen depth, maximum radius loadi
= 4 times specimen depth (minimum le
chord defining arc in contact with the
men = 2 times specimen depth).

FIG. 1—Allowable Range of Loading N
Support Radii for Specimen 6.4 mm (¼ in.

at the crosshead rate used. The acc
of the testing machine shall be
in accordance with ASTM Method
Verification of Testing Machines.[2]

4.2 *Loading Nose and Supports*
loading nose and supports shall
cylindrical surfaces. In order to
excessive indentation, or comp
failure, that is, nonrecoverable de
tion or compressive failure due to
concentration directly under the l
nose, the radius of nose and su
shall be at least 3.2 mm (⅛ in.)
specimens. For specimens 3.2 mm

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differences in rate of
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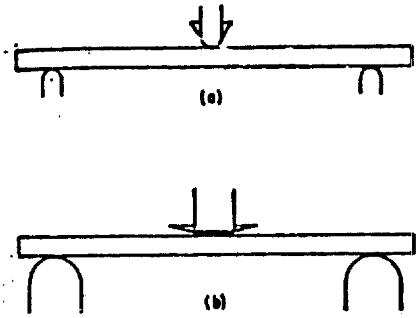
motion over the range indicated, and in which the error in the load-measuring system shall not exceed ±1 per cent. It shall be equipped with a deflection-measuring device. The stiffness of the testing machine shall be such that the total elastic deformation of the system does not exceed 1 per cent of the total deflection of the test specimen during test, or appropriate corrections shall be made. The load-indicating mechanism shall be essentially free from inertia lag at the crosshead rate used. The accuracy of the testing machine shall be verified in accordance with ASTM Methods E 4, Verification of Testing Machines.[2]



(a) Minimum radius = 3.2 mm (⅛ in.).
(b) Maximum radius supports = 1½ times specimen depth, maximum radius loading nose = 4 times specimen depth (minimum length of chord defining arc in contact with the specimen = 2 times specimen depth).

FIG. 1—Allowable Range of Loading Nose and Support Radii for Specimen 6.4 mm (¼ in.) Thick.

4.2 *Loading Nose and Supports*—The loading nose and supports shall have cylindrical surfaces. In order to avoid excessive indentation, or compressive failure, that is, nonrecoverable deformation or compressive failure due to stress concentration directly under the loading nose, the radius of nose and supports shall be at least 3.2 mm (⅛ in.) for all specimens. For specimens 3.2 mm (⅛ in.) in thickness or greater, the radius of the supports may be up to 1½ times the specimen depth, and the radius of the loading nose may be up to 4 times the specimen depth, and shall be this large if significant indentation or compressive failure occurs. The chord defining the arc of the loading nose in contact with the specimen shall be sufficiently large to prevent contact of the specimen with the sides of the nose. A minimum chord length of twice the specimen depth shall be used where possible (Fig. 1).

5. Test Specimens

5.1 The specimens may be cut from sheets, plates, or molded shapes, or may be molded to the desired finished dimensions (Note 1).

NOTE 1—Any necessary polishing of specimens shall be done only in the lengthwise direction of the specimen.

5.2 *Sheet Materials (Except Laminated Thermosetting Materials and Certain Materials Used for Electrical Insulation, Including Vulcanized Fiber and Glass Bonded Mica):*

5.2.1 *For Materials 1.6 mm (1/16 in.) or Greater in Thickness*—For flatwise tests, the depth of the specimen shall be the thickness of the material. For edgewise tests, the width of the specimen shall be the thickness of the sheet and the depth shall not exceed the width (Notes 2 and 3). For all tests, the span shall be 16 (tolerance +4 or −2) times the depth of the beam. Specimen width shall not exceed one fourth of the span for specimens greater than 3.2 mm (⅛ in.) in thickness. Specimens 3.2 mm (⅛ in.) or less in thickness shall be 12.7 mm (½ in.) in width. The specimen shall be long enough to allow for overhanging on each end of at least 10 per cent of the span, but in no case less than 6.4 mm (¼ in.) on each end. Overhang shall be suffi-

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[2] Appears in this publication.

TABLE 1—SUGGESTED DIMENSIONS FOR TEST SPECIMENS OF 5.3 AND 5.5 (NOTE 6).

Nominal Specimen Thickness, mm (in.)	Width of Specimen, mm (in.)	Span-to-Depth Ratio								
		16 to 1			32 to 1			40 to 1		
		Length of Specimen, mm (in.)	Span, mm (in.)	Rate of Cross-head Motion (Procedure A), mm (in.)/min[a]	Length of Specimen, mm (in.)	Span, mm (in.)	Rate of Cross-head Motion (Procedure A), mm (in.)/min[a]	Length of Specimen, mm (in.)	Span, mm (in.)	Rate of Cross-head Motion (Procedure A) mm (in.)/min[a]
0.8(1/32)	25(1)	50(2)	16(5/8)[b]	0.5(0.02)	50(2)	25(1)	1.3(0.05)	60(2¼)	30(1¼)	2.0(0.08)
1.6(1/16)	25(1)	50(2)	25(1)	0.8(0.03)	80(3)	50(2)	2.8(0.11)	90(3½)	60(2½)	4.3(0.17)
2.4(3/32)	25(1)	60(2½)	40(1½)	1.0(0.04)	100(4)	80(3)	4.1(0.16)	120(4¾)	95(3¾)	6.4(0.25)
3.2(1/8)	25(1)	80(3)	50(2)	1.3(0.05)	130(5)	100(4)	5.3(0.21)	180(7)	130(5)	8.4(0.33)
4.8(3/16)	13(½)	100(4)	80(3)	2.0(0.08)	191(7½)	150(6)	8.1(0.32)	240(9½)	191(7½)	12.7(0.50)
6.4(1/4)	13(½)	130(5)	100(4)	2.6(0.11)	250(10)	200(8)	10.9(0.43)	330(13)	250(10)	17.0(0.67)
9.6(3/8)	13(½)	191(7½)	150(6)	4.1(0.16)	380(15)	300(12)	16.3(0.64)	480(19)	380(15)	25.4(1.00)
12.7(1/2)	13(½)	250(10)	200(8)	5.3(0.21)	495(19½)	410(16)	21.6(0.85)	640(25)	510(20)	34.0(1.34)
19.1(3/4)	19(¾)	380(15)	300(12)	8.1(0.32)	740(29)	610(24)	32.5(1.28)	940(37)	760(30)	50.8(2.00)
25.4(1)	25(1)	495(19½)	410(16)	10.9(0.43)	990(39)	810(32)	43.4(1.71)	1240(49)	1020(40)	67.8(2.67)

[a] Rates indicated are for Procedure A where strain rate is 0.01 mm/mm min (0.01 in./in. min). To obtain speeds for Procedure B where strain rate is 0.10 mm/mm min (0.10 in./in. min), multiply these values by 10. Procedure A is to be used for all specification purposes unless otherwise stated in specifications. See 8.3 for the method of calculation.

[b] This span-to-depth ratio is greater than 16 to 1 in order to give clearance between moving head and specimen support.

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cient to prevent the speci ping through the supports

NOTE 2—Whenever possibl surfaces of the sheet shall be ever, where machine limitati possible to follow the above unaltered sheet, both surfaces to the desired dimensions and t specimens with reference to t shall be noted. The values obta with machined surfaces may obtained on specimens with Consequently, any specificat properties on the thicker sh whether the original surfaces or not.

NOTE 3—Edgewise tests a for sheets that are so thin tha ing these requirements canno men depth exceeds the wid occur.

5.2.2 *For Materials Le (1/16 in.) in Thickness*— shall be 50.8 mm (2 in.) l (½ in.) wide, tested flatwi (1-in.) span (Notes 4 and

NOTE 4—The formulas for in this method for calculating that the width is small in c span. Therefore, they do not these dimensions.

NOTE 5—Where machine that specimens of these di measured, wider specimens both, may be used, provided is at least 14 to 1. All dimen in the report (see also Note

5.3 *Laminated Ther rials and Sheet and Pla for Electrical Insulation canized Fiber and Glas* Specimens shall be test with Table 1. For pape base grades over 25.4 nominal thickness, th be machined on both su ness of 25.4 mm (1 in and nylon-base grade 12.7 mm (½ in.) in t shall be machined on l thickness of 12.7 mm (

5.4 *Molding Materi*

cient to prevent the specimen from slipping through the supports.

NOTE 2—Whenever possible, the original surfaces of the sheet shall be unaltered. However, where machine limitations make it impossible to follow the above criterion on the unaltered sheet, both surfaces shall be machined to the desired dimensions and the location of the specimens with reference to the total thickness shall be noted. The values obtained on specimens with machined surfaces may differ from those obtained on specimens with original surfaces. Consequently, any specifications for flexural properties on the thicker sheets must state whether the original surfaces are to be retained or not.

NOTE 3—Edgewise tests are not applicable for sheets that are so thin that specimens meeting these requirements cannot be cut. If specimen depth exceeds the width, buckling may occur.

5.2.2 *For Materials Less than 1.6 mm ($\frac{1}{16}$ in.) in Thickness*—The specimen shall be 50.8 mm (2 in.) long by 12.7 mm ($\frac{1}{2}$ in.) wide, tested flatwise on a 25.4-mm (1-in.) span (Notes 4 and 5).

NOTE 4—The formulas for simple beams used in this method for calculating results presuppose that the width is small in comparison with the span. Therefore, they do not apply rigorously to these dimensions.

NOTE 5—Where machine sensitivity is such that specimens of these dimensions cannot be measured, wider specimens or shorter spans, or both, may be used, provided span-to-depth ratio is at least 14 to 1. All dimensions must be stated in the report (see also Note 4).

5.3 *Laminated Thermosetting Materials and Sheet and Plate Materials Used for Electrical Insulation, Including Vulcanized Fiber and Glass-Bonded Mica*—Specimens shall be tested in accordance with Table 1. For paper-base and fabric-base grades over 25.4 mm (1 in.) in nominal thickness, the specimens shall be machined on both surfaces to a thickness of 25.4 mm (1 in.). For glass-base and nylon-base grades, specimens over 12.7 mm ($\frac{1}{2}$ in.) in nominal thickness shall be machined on both surfaces to a thickness of 12.7 mm ($\frac{1}{2}$ in.).

5.4 *Molding Materials (Including Phenolics, Polyesters, and Molding Materials Used for Electrical Insulation)*—The recommended specimen for molding materials is 127 by 12.7 by 6.4 mm (5 by $\frac{1}{2}$ by $\frac{1}{4}$ in.) tested flatwise on a 102-mm (4-in.) span.

5.5 *High-Strength Reinforced Plastic Composites for Structural and Semistructural Applications, Including Highly Orthotropic Laminates*—Specimens shall be tested in accordance with Table 1 or as described below. For flatwise tests, the depth of the specimen shall be the thickness of the laminate and the depth shall not exceed the width (Notes 2 and 3). Specimen width shall not exceed one fourth of the support span for specimens greater than 3.2 mm ($\frac{1}{8}$ in.) in thickness. Specimens 3.2 mm ($\frac{1}{8}$ in.) or less in thickness shall be at least 12.7 mm ($\frac{1}{2}$ in.) in width. The specimen shall be long enough to allow for overhanging on each end of at least 10 per cent of the support span. Overhang shall be sufficient to prevent the specimen from slipping through the supports. For all tests the support span shall be a minimum of 16 and a maximum of 40 times the depth of the specimen (Note 6). The support span shall have a numerical value chosen so that the failures occur in the outer fibers of the specimens, due only to the bending moment. When laminate materials have low compression strength perpendicular to the laminations, they shall be loaded with a large-radius loading nose (up to maximum of 4 times specimen thickness) to prevent premature damage to the outer fibers. Three recommended span-to-depth ratios are 16, 32, and 40 to 1.

NOTE 6—As a general rule, span-to-depth ratios of 16 to 1 are satisfactory when the ratio of tensile strength to shear strength is less than 8 to 1, but the span-to-depth ratio must be increased for composite laminates having relatively low shear strength in the plane of the laminate and relatively high tensile strength parallel to the span.

6. Number of Test Specimens

6.1 At least five specimens shall be tested for each sample in the case of isotropic materials or molded specimens.

6.2 For each sample of anisotropic material in sheet form, at least five specimens shall be tested for each condition. Recommended conditions are flatwise and edgewise tests on specimens cut in lengthwise and crosswise directions of the sheet. For purposes of this test, "lengthwise" shall designate the principal axis of anisotropy, and shall be interpreted to mean the direction of the sheet known to be the stronger in flexure. "Crosswise" shall be the sheet direction known to be the weaker in flexure, and shall be at 90 deg to the lengthwise direction.

7. Conditioning

7.1 Unless otherwise indicated in material specifications, all test specimens shall be conditioned in accordance with Procedure A of ASTM Methods D 618, Conditioning Plastics and Electrical Insulating Materials for Testing,[2] and tests shall be conducted in the Standard Laboratory Atmosphere as defined in the same methods.

8. Procedure A

8.1 Use an untested specimen for each measurement. Measure the width and thickness of the specimen to the nearest 0.03 mm (0.001 in.) at the center of the span. For specimens less than 2.54 mm (0.100 in.) in thickness, measure the thickness to the nearest 0.003 mm (0.0001 in.).

8.2 Determine the span to be used as described in 5. Test Specimens. After the span is set, measure the actual span length to the nearest 1 per cent.

8.3 If Table 1 is used, set the machine for the specified rate of crosshead motion, or as near as possible to it. If Table 1 is not used, calculate the rate of crosshead motion as follows and set the machine for that calculated rate, or as near as possible to it:

$$N = \frac{ZL^2}{6d} \qquad (1)$$

where:

N = rate of crosshead motion, mm (or in.)/min,

L = span, mm (or in.),

d = depth of beam, mm (or in.), and

Z = rate of straining of the outer fiber, mm/mm min (or in./in. min). Z shall equal 0.01.

8.4 Align the loading nose and supports so that the axes of the cylindrical surfaces are parallel and the loading nose is midway between the supports. This parallelism may be checked by means of a plate with parallel grooves into which the loading nose and supports will fit when properly aligned. Center the specimen on the supports, with the long axis of the specimen perpendicular to the loading nose and supports.

8.5 Apply the load to the specimen at the specified crosshead rate, and take simultaneous load - deflection data. Measure deflection either by a gage under the specimen in contact with it at the center of the span, the gage being mounted stationary relative to the specimen support, or by measurement of the motion of the loading nose relative to the supports. In either case, make appropriate corrections for indentation in the specimens and deflections in the weighing system of the machine. Load - deflection curves may be plotted to determine the flexural yield strength, secant or tangent modulus of elasticity, and the total work measured by the area under the load - deflection cruve.

8.6 Terminate the test if the maximum strain in the outer fiber has reached

0.05 mm/mm (in./in.) (tes The deflection at which t str may be calculated by letting r mm/mm (or in./in.) as follows

$$D = \frac{rL^2}{6d} \cdots\cdots$$

where:

D = deflection, mm (or in.),

r = strain, mm/mm (or in./i

L = span, mm (or in.), and

d = depth of beam, mm (c

NOTE 7—For some materials strain rate provided under Proce induce the specimen to yield or rup within the required 5 per cent stra

NOTE 8—Beyond 5 per cent s is not applicable, and some other as ASTM Method D 638, Test Properties of Plastics,[3] should be us

9. Procedure B

9.1 Use an untested specim measurement.

9.2 Testing conditions sh tical to those described in 8 A, except that the rate of the outer fiber shall be 0.1 min (in./in. min).

10. Retests

10.1 Values for properties shall not be calculated for a that breaks at some obviou flaw, unless such flaws const able being studied. Retests for any specimens on whi not calculated.

11. Properties and Calculat

11.1 *Maximum Fiber Str* beam of homogeneous, el is tested in flexure as a supported at two points a the midpoint, the maxim the outer fiber occurs at r stress may be calculated f

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er has reached

0.05 mm/mm (in./in.) (Notes 7 and 8). The deflection at which this strain occurs may be calculated by letting r equal 0.05 mm/mm (or in./in.) as follows:

$$D = \frac{rL^2}{6d} \quad \ldots\ldots\ldots\ldots (2)$$

where:

D = deflection, mm (or in.),
r = strain, mm/mm (or in./in.),
L = span, mm (or in.), and
d = depth of beam, mm (or in.)

NOTE 7—For some materials the increase in strain rate provided under Procedure B may induce the specimen to yield or rupture, or both, within the required 5 per cent strain limit.

NOTE 8—Beyond 5 per cent strain, this test is not applicable, and some other method, such as ASTM Method D 638, Test for Tensile Properties of Plastics,[6] should be used.

9. Procedure B

9.1 Use an untested specimen for each measurement.

9.2 Testing conditions shall be identical to those described in 8. Procedure A, except that the rate of straining of the outer fiber shall be 0.10 mm/mm min (in./in. min).

10. Retests

10.1 Values for properties at rupture shall not be calculated for any specimen that breaks at some obvious, fortuitous flaw, unless such flaws constitute a variable being studied. Retests shall be made for any specimens on which values are not calculated.

11. Properties and Calculations

11.1 *Maximum Fiber Stress*—When a beam of homogeneous, elastic material is tested in flexure as a simple beam supported at two points and loaded at the midpoint, the maximum stress in the outer fiber occurs at midspan. This stress may be calculated for any point on the load - deflection curve by the following equation (Notes 9 and 10):

$$S = \frac{3PL}{2bd^2} \quad \ldots\ldots\ldots\ldots (3)$$

where:

S = stress in the outer fiber at mid-span, kg/cm² (or psi),
P = load at a given point on the load - deflection curve, kg (or lb),
L = span, cm (or in.),
b = width of beam tested, cm (or in.), and
d = depth of beam tested, cm (or in.).

NOTE 9—Equation 3 applies strictly to materials for which the stress is linearly proportional to strain up to the point of rupture and for which the strains are small. Since this is not always the case, a slight error will be introduced in the use of this equation. The equation will, however, be valid for comparison data and specification values up to maximum fiber strains of 5 per cent for specimens tested by the procedures herein described.

NOTE 10—The above calculation is not valid if the specimen is slipping between the supports.

11.2 *Maximum Fiber Stress for Beams Tested at Large Spans*—If span-to-depth ratios greater than 16 to 1 are used so that large deflections occur, the maximum fiber stress of a simple beam can be reasonably approximated with the following equation (Note 11):

$$S = \frac{3PL}{2bd^2}\left[1 + 6\left(\frac{D}{L}\right)^2 - 4\left(\frac{d}{L}\right)\left(\frac{D}{L}\right)\right] \quad (3a)$$

where S, P, L, b, and d are the same as for Eq 3 and D is the deflection of the centerline of the specimen at midspan with relation to the supports.

NOTE 11—When large span-to-depth ratios are used, significant end forces are developed which affect the moment in a simply supported beam. An approximate correction factor is given in Eq 3a to correct for this end force in large span-to-depth ratio beams where relatively large deflections exist.

11.3 *Flexural Strength (Modulus of Rupture)*—The flexural strength is equal to the maximum stress in the outer fiber at the moment of break. It is calculated in accordance with Eqs 3 and 3a by letting P equal the load at the moment of break. If the material does not break, this part of the test is not applicable. In this case, it is suggested that yield strength, if applicable, be calculated, and that the corresponding strain be reported also (see 11.4, 11.6, and 11.7).

11.4 *Flexural Yield Strength*—Some materials that do not break at outer fiber strains up to 5 per cent may give load-deflection curves that show a point, Y, at which the load does not increase with an increase in deflection. In such cases, the flexural yield strength may be calculated in accordance with Eqs 3 and 3a by letting P equal the load at point Y.

11.5 *Flexural Offset Yield Strength*—Offset yield strength is the stress at which the stress-strain curve deviates by a given strain (offset) from the tangent to the initial straight-line portion of the stress-strain curve. The value of the offset must be given whenever this property is calculated (Note 12).

NOTE 12—This value may differ from Flexural Yield Strength defined in 11.4. Both methods of calculation are described in the Appendix to Method D 638.[8]

11.6 *Stress at a Given Strain*—The maximum fiber stress at any given strain may be calculated in accordance with Eqs 3 and 3a by letting P equal the load read from the load-deflection curve at the deflection corresponding to the desired strain.

11.7 *Maximum Strain*—The maximum strain in the outer fiber also occurs at midspan, and may be calculated as follows:

$$r = \frac{6Dd}{L^2} \qquad (4)$$

where:

r = maximum strain in the outer fiber, mm/mm (or in./in.),
D = maximum deflection of the center of the beam, mm (or in.),
L = span, mm (or in.), and
d = depth, mm (or in.).

11.8 *Modulus of Elasticity:*

11.8.1 *Tangent Modulus of Elasticity*—The tangent modulus of elasticity, often called "modulus of elasticity," is the ratio, within the elastic limit of stress to corresponding strain and shall be expressed in kilograms per square centimeter (or pounds per square inch). It is calculated by drawing a tangent to the steepest initial straight-line portion of the load-deformation curve and using Eq 5.

$$E_B = \frac{L^3 m}{4bd^3} \qquad (5)$$

where:

E_B = modulus of elasticity in bending, kg/cm^2 (or psi),
L = span, cm (or in.),
b = width of beam tested, cm (or in.),
d = depth of beam tested, cm (or in.), and
m = slope of the tangent to the initial straightline portion of the load-deflection curve, kg/cm (or lb/in.) of deflection.

11.8.2 *Secant Modulus of Elasticity*—The secant modulus of elasticity is the ratio of stress to corresponding strain at any given point on the stress-strain curve, or the slope of the straight line that joins the origin and the selected point on the actual stress-strain curve. It shall be expressed in kilograms per square centimeter (or pounds per square inch). The selected point is generally chosen at a specified stress or strain. It is calculated in accordance with Eq 5 by letting m equal the slope of the secant on the load-deflection curve.

11.9 *Arithmetic Mean*—For each series

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of tests, the arithmetic
obtained shall be calcul
nificant figures and
"average value" for the
erty in question.

11.10 *Standard Devia*
ard deviation (estimate
lated as follows and re
nificant figures:

$$s = \sqrt{\frac{\Sigma X^2}{n}}$$

where:

s = estimated stand
X = value of single ob
n = number of obser
$\bar{X}$ = arithmetic mean
servations.

12. Report

12.1 The report
following:

12.1.1 Complete id
material tested, inclu
manufacturer's code
cipal dimensions, and

12.1.2 Direction of
ing specimens,

ıum strain in the outer fiber,
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mm (or in.).
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modulus of elasticity, often
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s per square inch). It is
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straight-line portion of
ormation curve and using

$$E_B = \frac{L^3 m}{4bd^3} \qquad (5)$$

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ine portion of the load-
n curve, kg/cm (or lb/in.)
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Modulus of Elasticity—
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ual stress-strain curve.
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ied point is generally
ified stress or strain. It
ccordance with Eq 5 by
the slope of the secant
ection curve.
c Mean—For each series

of tests, the arithmetic mean of all values obtained shall be calculated to three significant figures and reported as the "average value" for the particular property in question.

11.10 *Standard Deviation*—The standard deviation (estimated) shall be calculated as follows and reported to two significant figures:

$$s = \sqrt{\frac{\Sigma X^2 - n\bar{X}^2}{n - 1}}$$

where:

s = estimated standard deviation,
X = value of single observation,
n = number of observations, and
$\bar{X}$ = arithmetic mean of the set of observations.

12. Report

12.1 The report shall include the following:

12.1.1 Complete identification of the material tested, including type, source, manufacturer's code number, form, principal dimensions, and previous history,

12.1.2 Direction of cutting and loading specimens,

12.1.3 Conditioning procedure,

12.1.4 Depth and width of the specimen,

12.1.5 Span length,

12.1.6 Span-to-depth ratio,

12.1.7 Radius of supports and loading nose,

12.1.8 Rate of crosshead motion in millimeters (or inches) per minute,

12.1.9 Maximum strain in the outer fiber of the specimen,

12.1.10 Flexural strength (if applicable), average value and standard deviation,

12.1.11 Tangent or secant modulus of elasticity in bending, average value and standard deviation,

12.1.12 Flexural yield strength (if desired), average value and standard deviation,

12.1.13 Flexural offset yield strength (if desired), with offset or strain used, average value and standard deviation,

12.1.14 Stress at a given strain (if desired), with strain used, average value and standard deviation, and

12.1.15 Procedure used.

END

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