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EXECUTIVE SUMMARY

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

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1.0

INTRODUCTION

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 emission from this industry.

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:

1.2.1 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.

1.2.2 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 emission 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 for resins containing vapor suppressant additives.

Emission factors derived from the literature review and our field measurements were used in conjunction with industry survey data to estimate organic vapor emissions in California.

1.2.3 Review of Control Technology

Organic vapor emissions from polyester resin/fiberglass fabrication processes may be reduced by process changes, use of vapor-suppresed 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. Various general approaches for controlling emissions from this industry were identified and discussed.

2.0

FINDINGS AND CONCLUSIONS

2.1 SURVEY OF POLYESTER RESIN USERS IN CALIFORNIA

2.1.1 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.

2.1.2 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).

2.1.3 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.

2.2.3 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.

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.

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.

(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.

2.2.4 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.

2.2.5 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.

(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 0.16 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.

2.3 ESTIMATED ORGANIC VAPOR EMISSIONS IN CALIFORNIA

2.3.1 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.

2.3.2 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.

2.3.3 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.

2.3.4 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.

2.4 REVIEW OF EMISSION CONTROL TECHNOLOGY

2.4.1 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.

2.4.2 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.

2.4.3 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.

2.4.4 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.

2.4.5 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.

2.4.6 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.

2.4.7 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.

2.5 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.

2.6 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.

3.0
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.

(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.