

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.

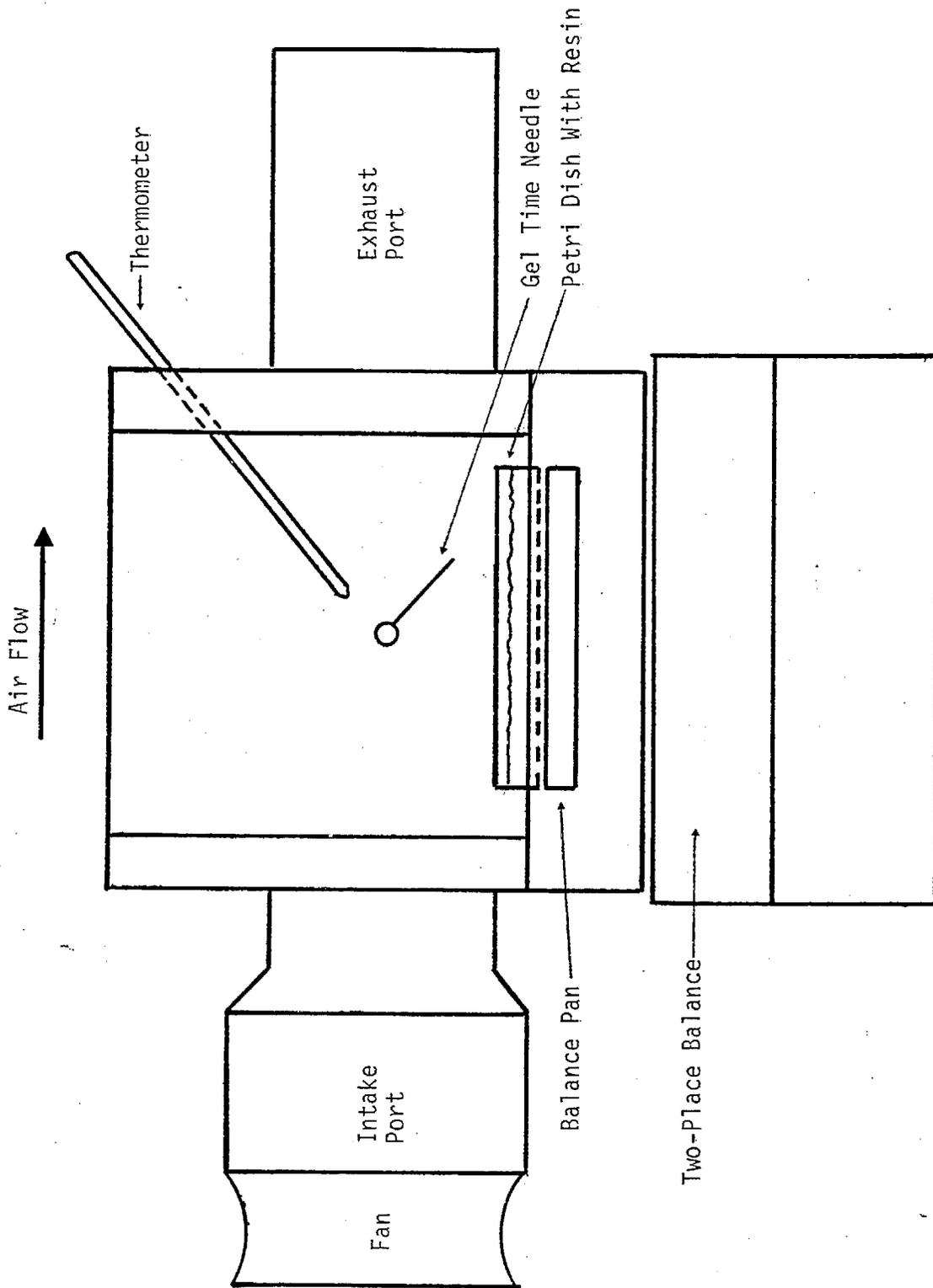


Figure 5.3-1. Resin Evaporation Test Apparatus (Scale: 1" = 2")

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 m³/s (38 cfm). Temperature was measured at the exhaust port with a 0 to 50°C 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 manufacture 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 (°C)	Relative Humidity (Pct)	Pct. MEKPC	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 = $100 \times \frac{\text{MEKP added}}{\text{Mass resin before addition}}$

^d Pct. Weight Loss = $100 \times \frac{(\text{Resin} + \text{MEKP})_{t=t} - (\text{Resin} + \text{MEKP})_{t=0}}{(\text{Resin} + \text{MEKP})_{t=0}}$

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:

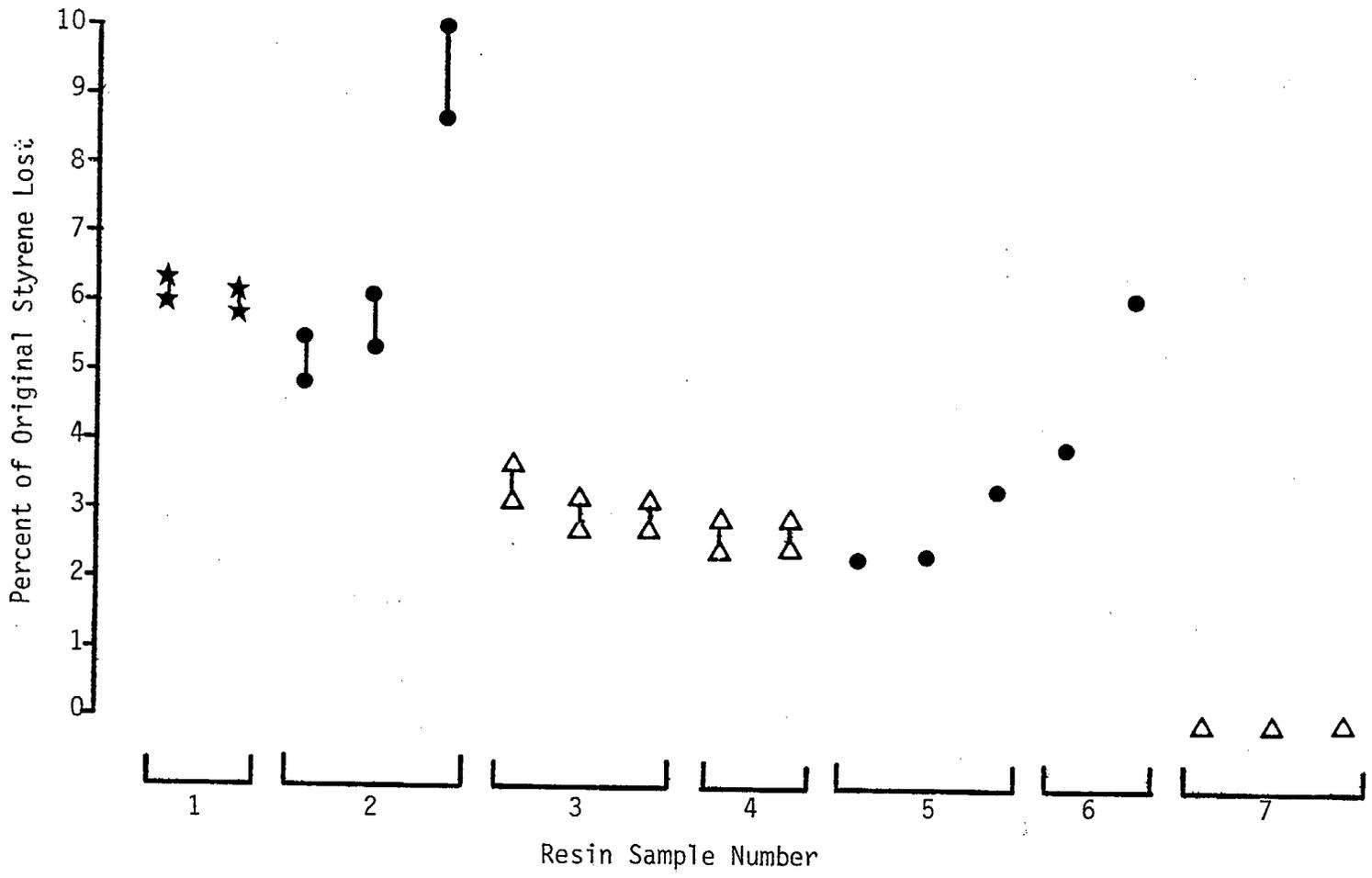
$$\text{Weight Loss Pct.} = 100 \times \frac{\text{Weight Loss}}{\text{Wt. of resin before catalyst} + \text{Wt. of Catalyst}}$$

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,



Key to Symbols
 ● Normal resin
 △ Vapor-suppressed resin
 ★ "Special" resin (see text)

Figure 5.3-2. Cumulative Weight Loss at 60 Minutes

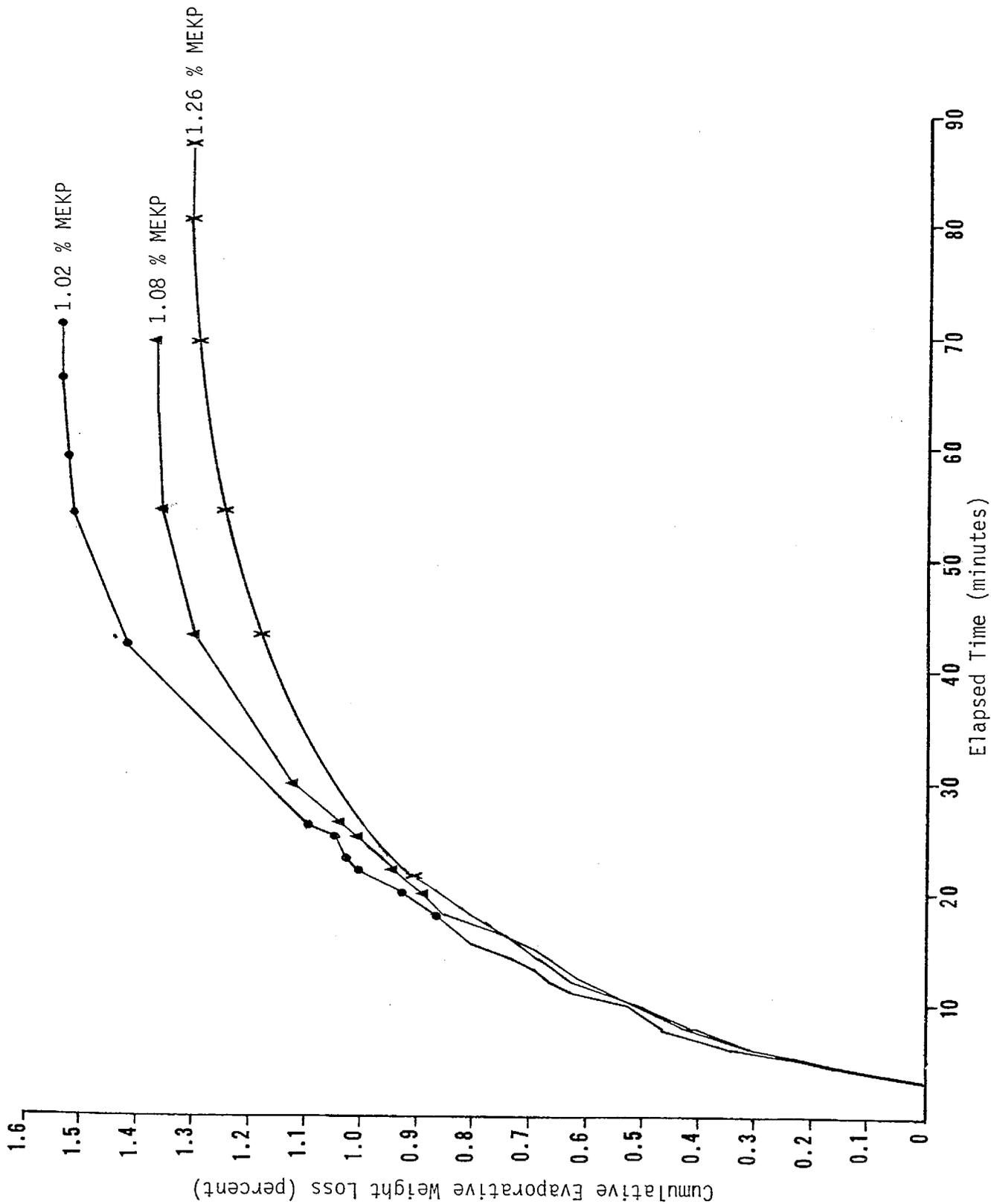


Figure 5.3-3. Weight Loss vs Time for a Vapor-Suppressed Resin

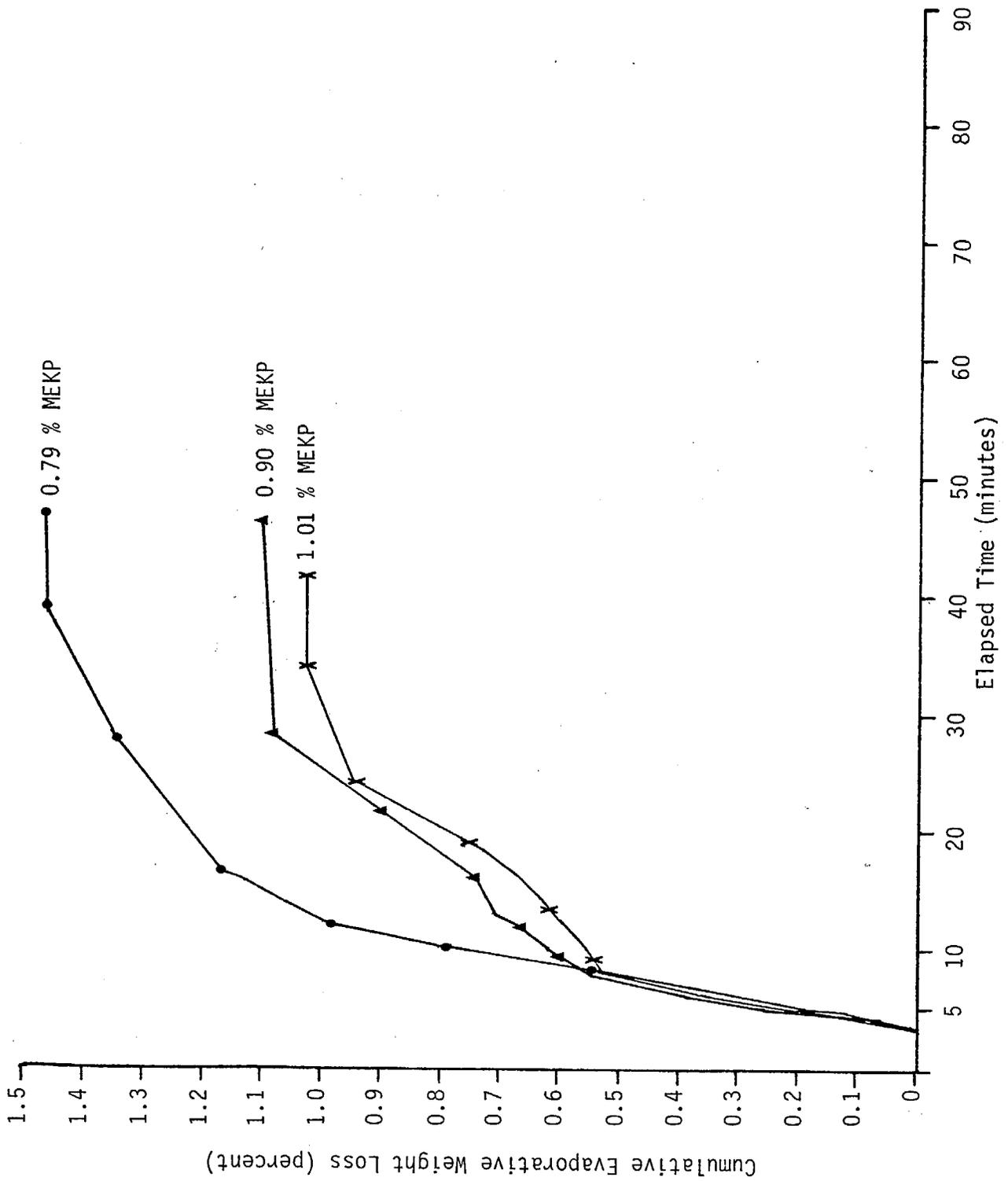


Figure 5.3-4. Weight Loss vs Time for a Normal Resin

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

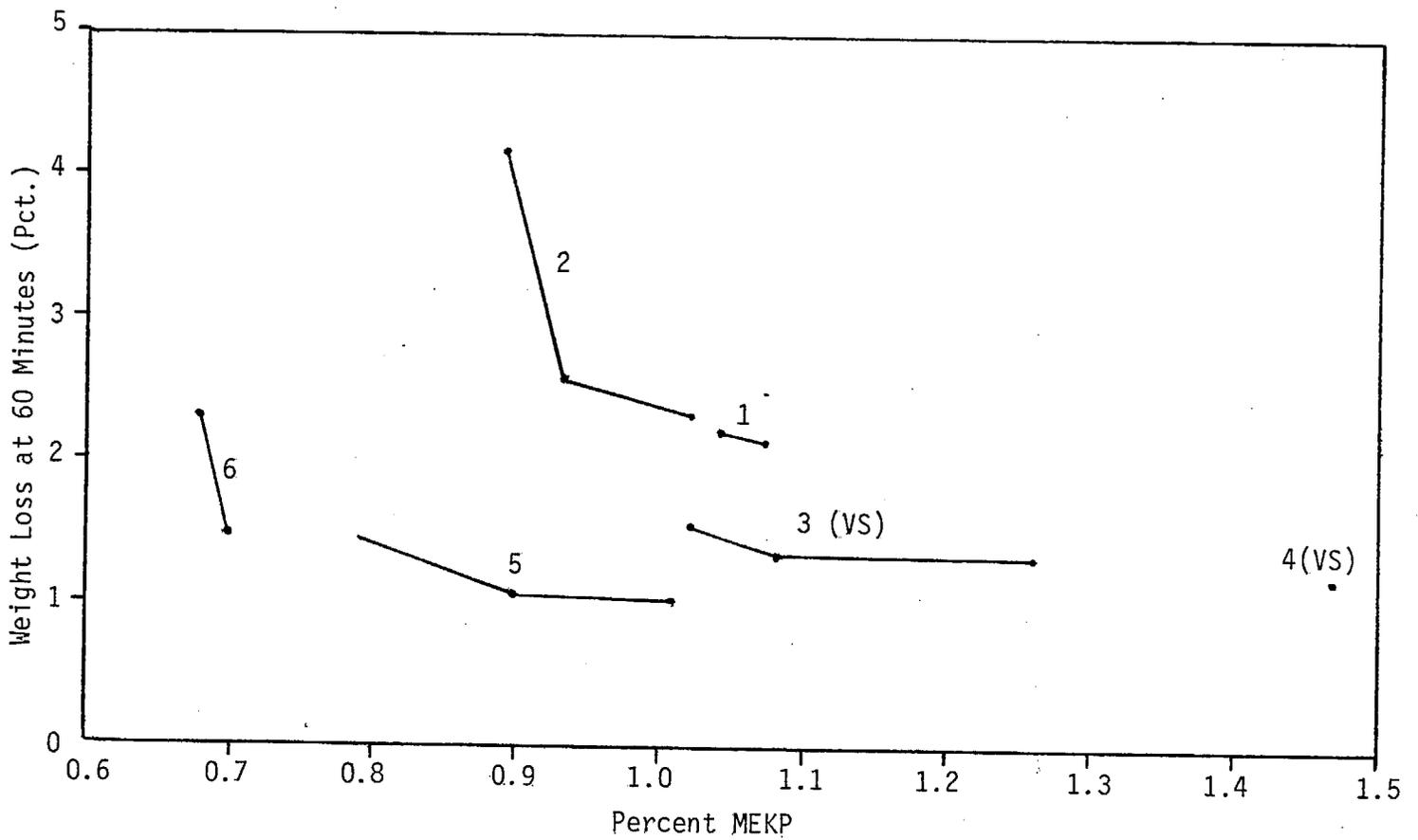


Figure 5.3-5. Resin Weight Loss After 60 Minutes, as a Function of Catalyst Percentage

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

Ashland Chemical Company. (Undated). "Styrene suppressed polyester resins." Brochure, Resins and Plastics Division, Columbus, Ohio.

Balestrieri, S. 1978. "Determination of volatile organic emission losses in styrene polymer resin application." Office memorandum to M. Felstein, Bay Area Air Quality Management District, San Francisco, California (15 May 1978).

Berryman, K. 1978. "Emission tests of gel coat and resin." Shasta County Air Pollution Control District, Redding, California, Internal Memorandum.

DeBoisblanc, W., Chief of New Source Review, Bay Area Air Quality Management District, San Francisco, California. Personal communication (23 July 1980).

Duffy, M.J. (Undated). "Styrene emissions: how effective are suppressed polyester resins." Ashland Chemical Company, Dublin, Ohio.

Macknight, R.J. 1981. "Information on reporting of annual air pollution emissions." Form letter, South Coast Air Quality Management District, El Monte, California (1 January 1981).

Pritchard, G. and G.J. Swampillai. 1978. "Styrene loss during the fabrication of glass reinforced polyester products," Soc. Adv. Mater. Proc. Engrg. 14(1): 15-19.

Reinhardt, David, Owens Corning Fiberglass Corporation, Granville, Ohio. Personal communication (9 April 1981).

Schmitz H.J. 1968. Report about styrene evaporation in the polyester styrene using industry. Internal memorandum, Metropolitan Dade County Department of Environmental Resources Management, Miami, Florida.

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:

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

It should be noted that all emission factors are based upon the quantity of styrene (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:

$$\begin{aligned} \text{Daily emissions} &= (4 \text{ tons/yr}) (1/260 \text{ days/yr}) (1/.75) (2000 \text{ lb/ton}) \\ &= 41 \text{ lb/day} \end{aligned}$$

$$\text{Hourly emissions} = (41 \text{ lb/day}) / (8 \text{ hr/day}) = 5.1 \text{ lb/hr.}$$

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		Gel Coat Emission Factor	
	Low	High	Low	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

^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)		Pct. of State ^a
	Low	High	
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	0.03
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)		Percent of State Total ^a
		Low	High	
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)		Percent of State Total ^a
	Low	High	
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

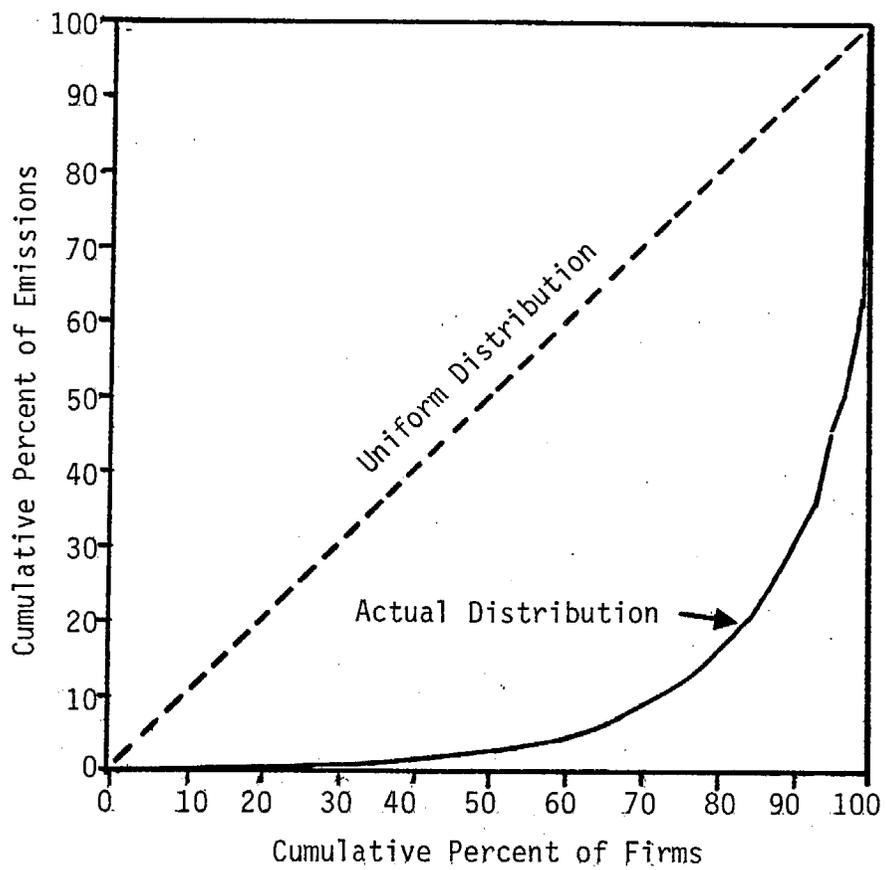


Figure 6.2-1. Lorenz Curve for Distribution of Uncontrolled Emissions From Polyester Resin/Fiberglass Fabrication in California

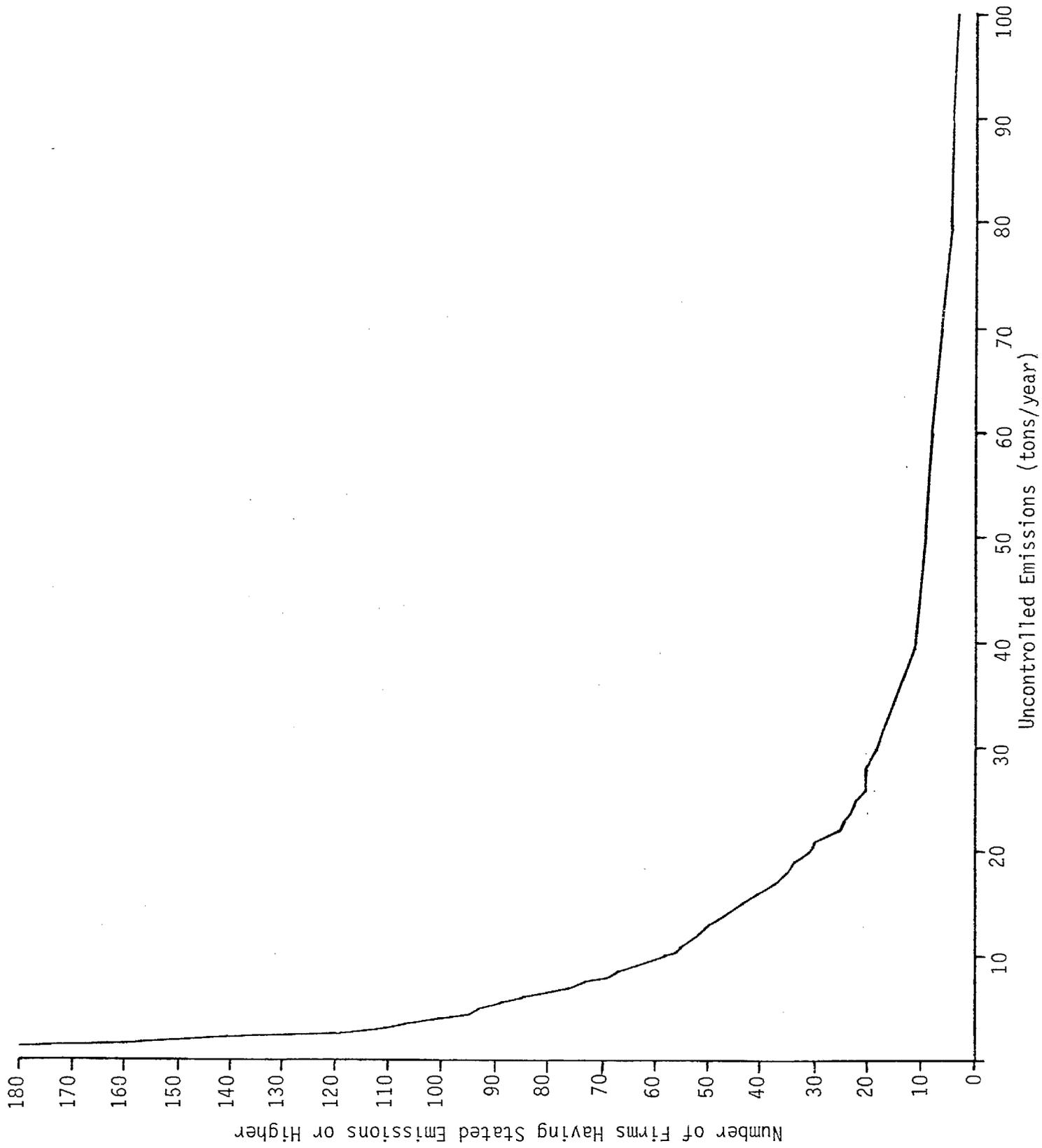


Figure 6.2-2. Distribution of Firms by Uncontrolled Emissions

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

^aBased upon upper use rate estimate

^bDoes 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)		Pct. of Total ^a
	Low	High	
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

^aBased on upper emission estimate

^bDiscrepancy 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:

<u>County</u>	<u>Total ROG (tons/day)</u>	<u>Styrene Emission (tons/day)</u>	<u>Pct. of Total ROG</u>
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

California Air Resources Board. 1981. Emission Data System, 1979 Statewide emissions by process by activity, Sacramento, California.

Fresno County Air Pollution Control District. 1981. 1979 Emissions inventory of reactive hydrocarbons, nitrogen oxides, and carbon monoxide (Revised September 15, 1981).

South Coast Air Quality Management District, Southern California Association of Governments, and California Air Resources Board. 1981. Draft 1979 emissions inventory: South Coast Air Basin, Working Paper No. 1, 1982 AQMP Revision, El Monte, California.

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 product 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 reaches 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 was 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

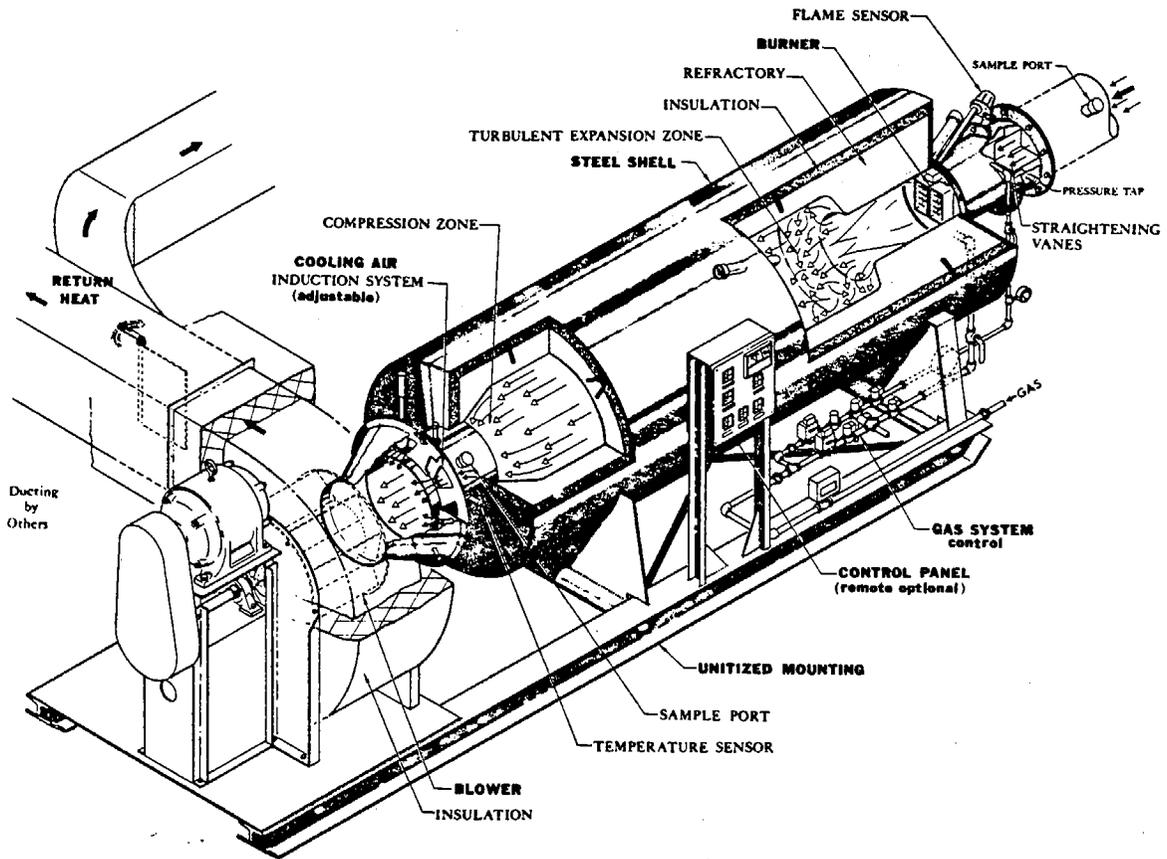


Figure 7.3-1. Direct-Flame Afterburner (Fogiel, 1978).

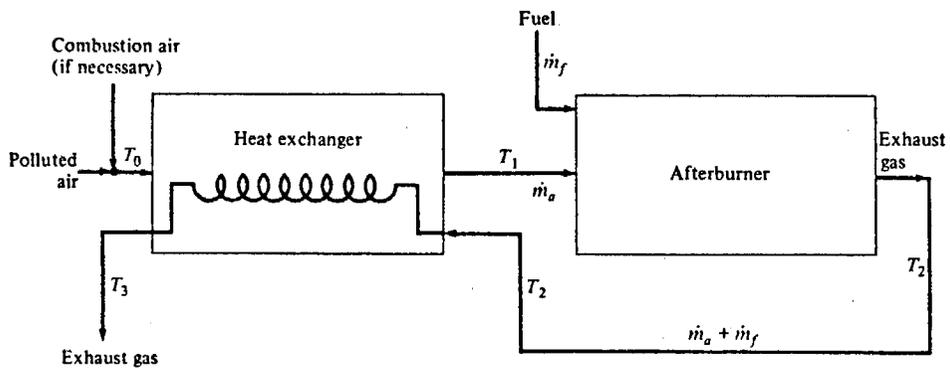


Figure 7.3-2. Schematic of Incineration System With Primary Heat Recovery (Crawford, 1976).

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.

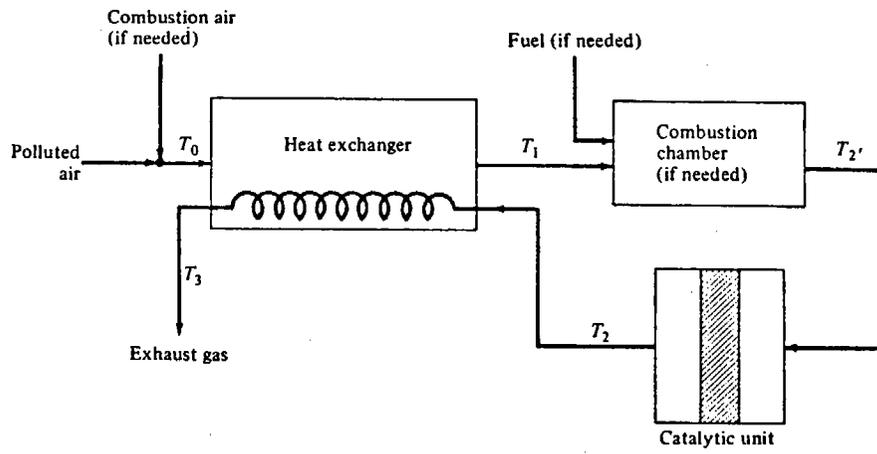


Figure 7.3-3. Schematic of Catalytic Incineration System With Primary Heat Recovery (Crawford, 1976).

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 75⁰F 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

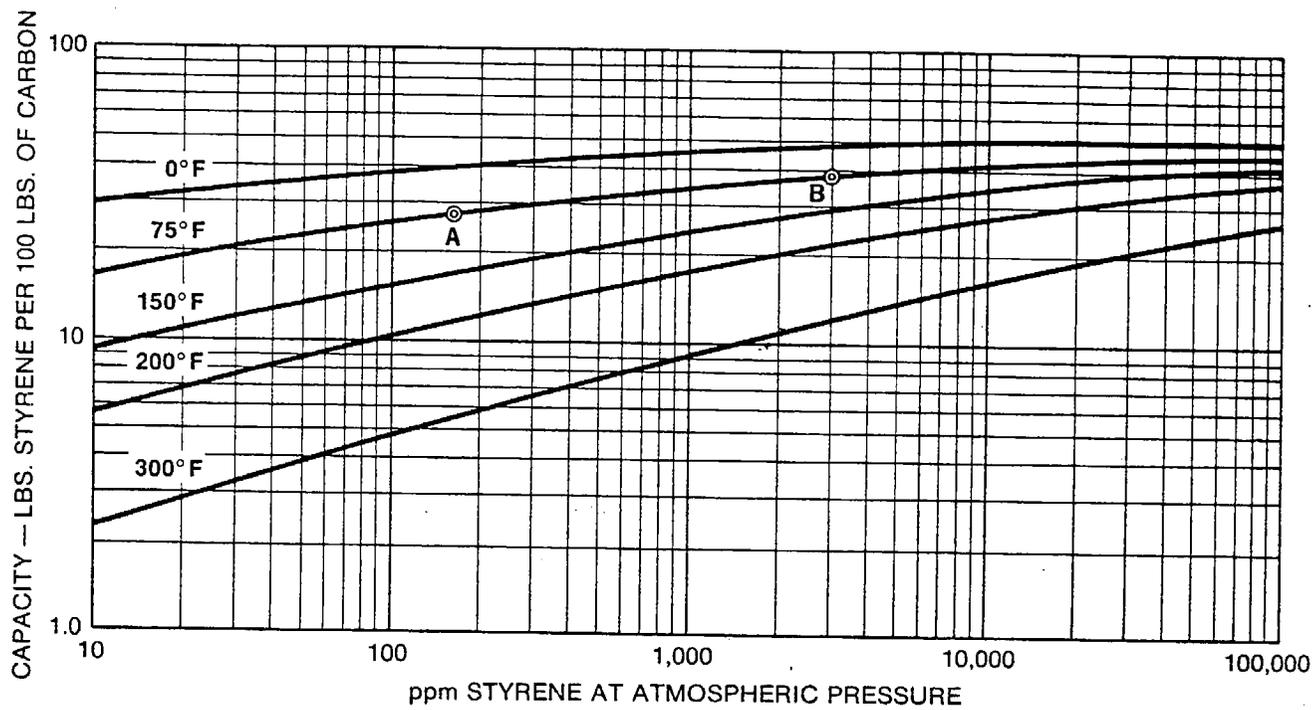


Figure 7.4-1. Styrene Adsorption of BPL Activated Carbon (Calgon Corporation).

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 16 Å) 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 could 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 after 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

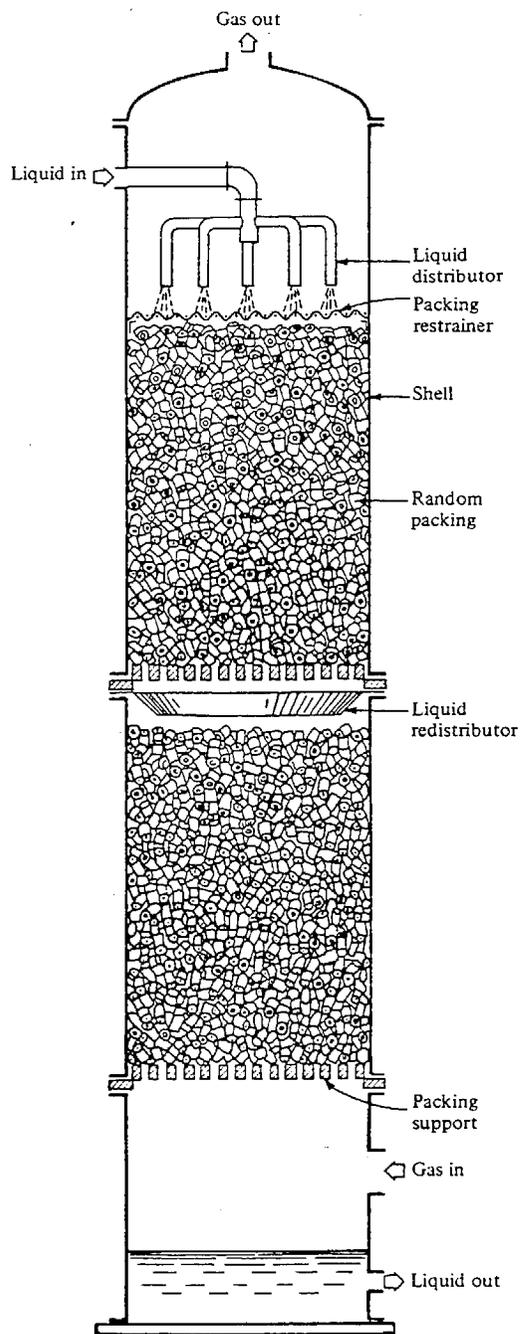


Figure 7.5-1. Packed Tower Absorption Unit (Treybal, 1955).

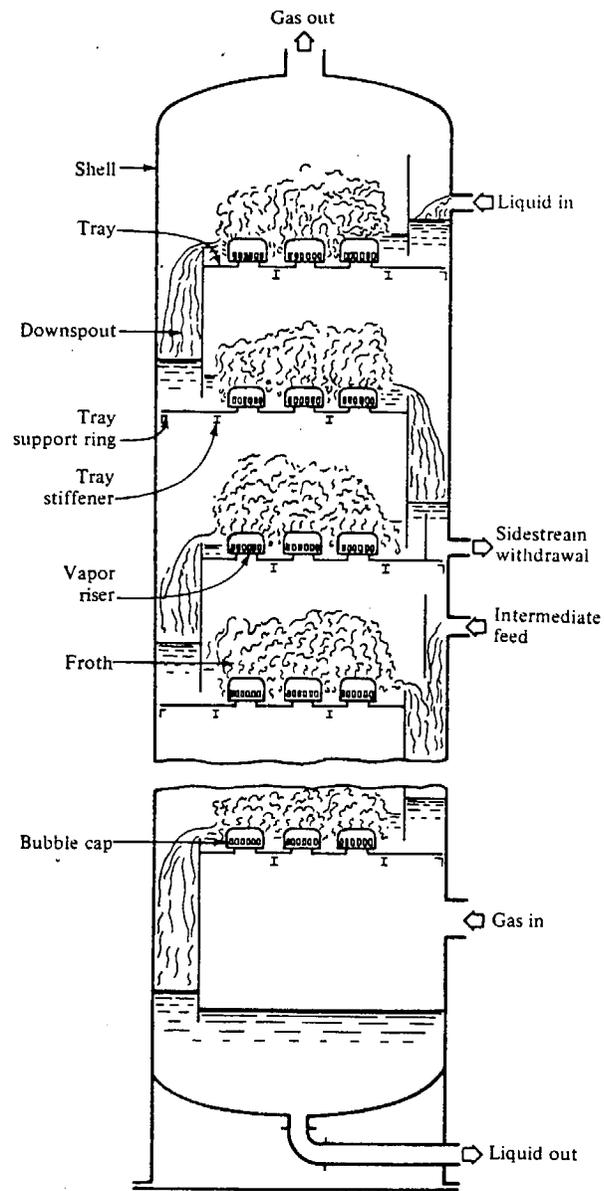


Figure 7.5-2. Bubble-Cap Plate Tower Absorption Unit (Treybal, 1955).

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 feasibility 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).

7.7 REFERENCES

- Anon. 1981. "Improved composites to spur growth of reinforced plastics," Chemical and Engineering News 59(24):28-30.
- Ashland Chemical Company (undated). "Styrene suppressed polyester resins." Brochure, Resins and Plastics Division, Columbus, Ohio.
- Boenig, H.V. 1964. Unsaturated polyesters. Elsevier, Amsterdam. (Cited in Brighton et al. 1979).
- Boki, K., S. Tanada and T. Kita. 1980. "Adsorption of styrene monomer on activated carbon," Bulletin of Environmental Contamination and Toxicology 24(2): 185-189.
- Bouroff, P.P. 1981. "Carbon filters adsorb odorous vapors," Pollution Engineering 13(2):25
- Brighton, C.A., G. Pritchard and G.A. Skinner. 1979. Styrene polymers: technology and environmental aspects. Applied Science Publishers, Ltd., London, 284p.

Calgon Corporation. (Undated). "Controlling styrene emissions with granular activated carbon." Brochure 23-57, Activated Carbon Division.

Cavanaugh, E.C. et al. 1978. Control techniques for volatile organic emissions from stationary sources. Prepared by Radian Corporation for U.S. Environmental Protection Agency, Office of Air and Waste Management, Research Triangle Park, North Carolina, EPA-450/2-78-022.

Cooper, David, Maurice A. Knight Company, Akron, Ohio. Personal communication (19 May 1981).

Crawford, M. 1976. Air pollution control theory. McGraw-Hill Book Company, New York.

Daniel P. Boyd and Company. 1980. An investigation to observe the best available technology applied in Sweden to reduce employee exposure to styrene. Prepared for the Reinforced Plastics/Composites Institute.

Duffy, M.J. (undated). "Styrene emissions: how effective are suppressed polyester resins?" Ashland Chemical Company, Dublin, Ohio.

Fogiel, M. (ed.) 1978. Modern pollution control technology. Vol. I. Air pollution control. Research and Education Association, New York.

Gary, Oris, Manager, Technical Service, Plastics, Reichhold Chemicals, Inc. Azusa, California. Personal communication (22 June 1980).

Gilbert, W.J., Croll-Reynolds Company, Inc., Westfield, New Jersey. Personal communication (1 June 1981).

Hardison, L.C. and E.J. Dowd. 1977. "Emissions control via fluidized bed oxidation," Chemical Engineering Progress 73(8):31-35.

Jowett, F. 1979. "The protection of rubber by petroleum waxes," Elastomerics (September):48-53.

Kenson, R.E. 1979. "Carbon adsorption of hydrocarbon emissions using vacuum stripping," Pollution Engineering 11(7): 38-40.

Lee, Don, Executive Vice-President, Gerber Industries, Los Angeles, California. Personal communication (31 July 1980).

Maguire, Keith, Fibercast Company, Sand Springs, Oklahoma. Personal communication (26 February 1980).

Maguire, K.D. and R.A. Curreio. 1978. "Control of styrene monomer emissions by countercurrent absorption." Presented at 33rd Annual Technical Conference, Reinforced Plastics/Composites Institute, The Society of the Plastics Industry, Inc., Section 23-D.

Memoring, Larry, United Air Specialists, Inc., Cincinnati, Ohio. Personal communication (23 February 1981).

Ohmori, S., Y. Fujii et al. 1977. "Waste gas treatment for spray booth by making use of activated carbon fiber," Proceedings of the 4th International Clean Air Congress, Tokyo, Japan, 16-20 May 1977, pp. 767-770.

Pritchard, G. and G.J. Swampillai. 1978. "Styrene loss during the fabrication of glass reinforced polyester products," Soc. Adv. Mater. Proc. Engrg. 14(1):15-19.

Rowe, Stuart B., Sales Representative, Buffalo Forge Company, Santa Fe Springs, California. Personal communication (6 July 1981).

Sneller, J. 1979. "Cost efficiency is bonus in BP resins developed to cut styrene emissions," Modern Plastics 56(12):38-41.

Stahlke, N.P. and C.V. Hall. 1981. "Optimizing efficiency of gel coating with airless spray equipment," Modern Plastics 58(1):86-87.

Taback, H.J., T.W. Sonnichsen et al. 1978. Control of hydrocarbon emissions from stationary sources in the California South Coast Air Basin, Vol. I. Prepared by KVB, Inc. for California Air Resources Board, KVB 5804-714.

Tanada, S. and K. Boki. 1979. "Adsorption of various kinds of offensive odor substances on activated carbon and zeolite," Bulletin of Environmental Contamination and Toxicology 23(4/5):524-530.

Thomer, K.W. and G.G. Weiler. 1977. "Afterburning, a process for cleaning the exhaust air from painting plants," Proceedings of the 4th International Clean Air Congress, Tokyo, Japan, 16-29 May 1977, pp. 759-761.

Treybal, R.E. 1955. Mass-transfer operations. McGraw-Hill Book Company, Inc., New York.

United Air Specialists, Inc. 1980. "Kon-den-solverTM regenerative condensing systems for solvent vapor recovery." Brochure KDS-100-380, Cincinnati, Ohio.

Warren, Mr., Sales Representative, Ametek, Schutte and Koerting Division, Los Alamitos, California. Personal communication (6 July 1981).

Weiler, G.G. and K.W. Thomer. 1977. "Possibilities for emission reduction in painting plants," Proceedings of the 4th International Clean Air congress, Tokyo, Japan, 16-20 May 1977, pp. 762-766.

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 with 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	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^oF 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

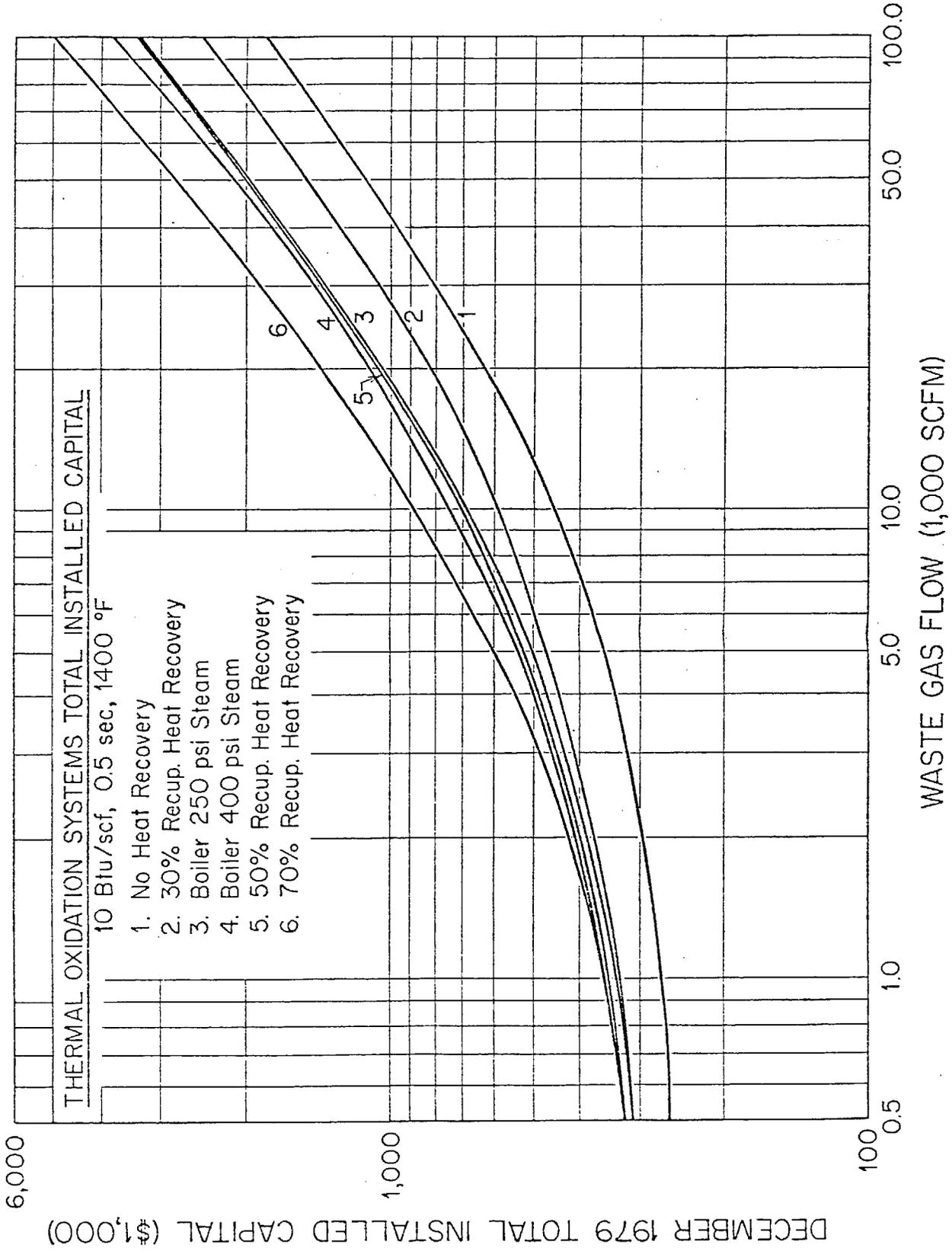


Figure 8.2-1. Total Installed Capital Cost For Thermal Oxidation Systems With Waste-Gas Heat Content = 10 Btu/scf, Residence Time = 0.5 sec, and Combustion Temperature = 1400-°F (Blackburn, 1980).

Table 8.2-1

CAPITAL AND OPERATING COSTS FOR INCINERATION

(Costs in \$1000 except where otherwise noted)

Case	Variant	Capital Cost	Annual Operating Costs					Credit Net	Cost per lb Styrene Removed (\$)
			Fixed	Labor	Gas	Elec.			
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 77⁰F 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

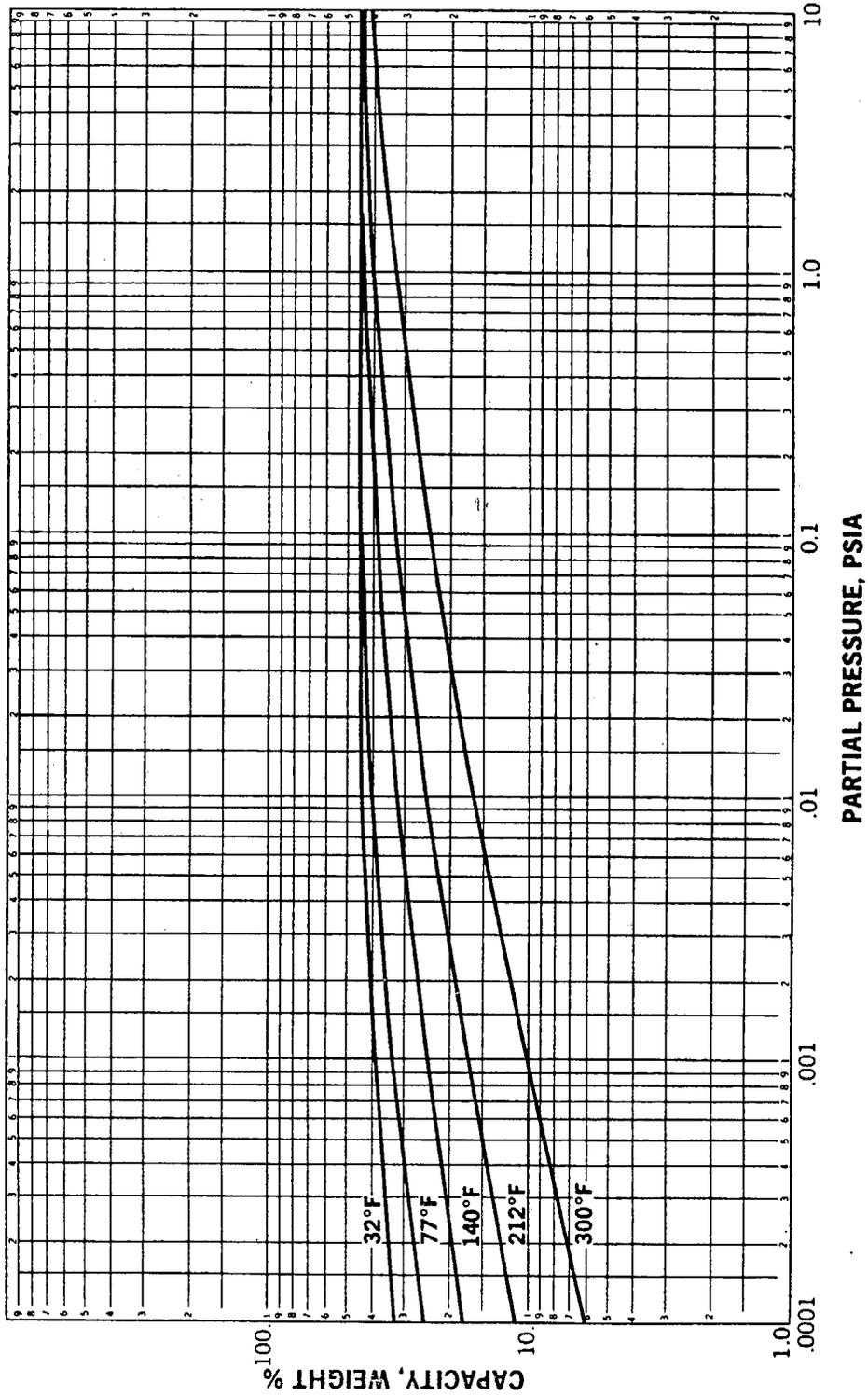


Figure 8.3-1. Styrene Adsorption on BPL Activated Carbon (Calgon Corporation).

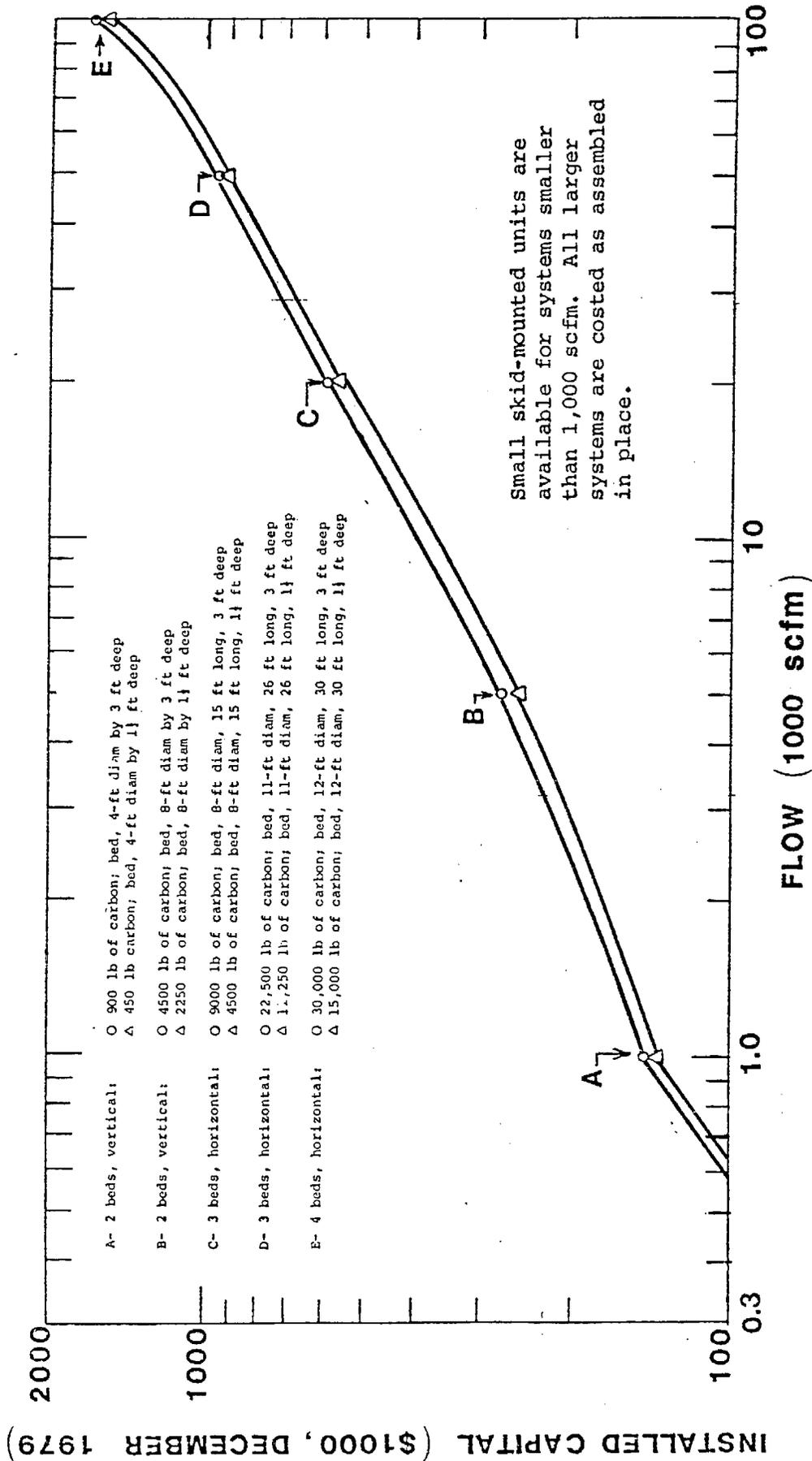


Figure 8.3-2. Installed Capital Cost of Carbon Adsorption Systems (Basdekis and Parmele, 1980).

Table 8.3-1
CAPITAL AND OPERATING COSTS FOR ADSORPTION

(Costs in \$1000 except where otherwise noted)

Case	Variant	Capital Cost	Annual Operating Costs				Credit	Net	Cost per lb Styrene Removed (\$)
			Fixed	Carbon	Steam	Elec.			
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.

8.5 REFERENCES

Basdekis, H.S. and C.S. Parmele. 1980. "Control device evaluation: carbon adsorption," in Organic chemical manufacturing. Vol. 5: Adsorption, condensation, and absorption devices. Prepared by IT Enviroscience for U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Emission Standards and Engineering Division, Research Triangle Park, North Carolina, EPA-450/3-80-027.

Blackburn, J.W. 1980. "Control device evaluation: thermal oxidation," In Organic chemical manufacturing. Vol. 4: combustion control devices. Prepared by IT Enviroscience for U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Emission Standards and Engineering Division, Research Triangle Park, North Carolina, EPA-450/3-80-026.

Calgon Corporation. (Undated). "Controlling styrene emissions with granular activated carbon." Brochure 23-57, Activated Carbon Division.

Council of Economic Advisers. 1981. Economic indicators, August 1981, Prepared for the Joint Economic Committee, 97th Congress, 1st Session, p.22.

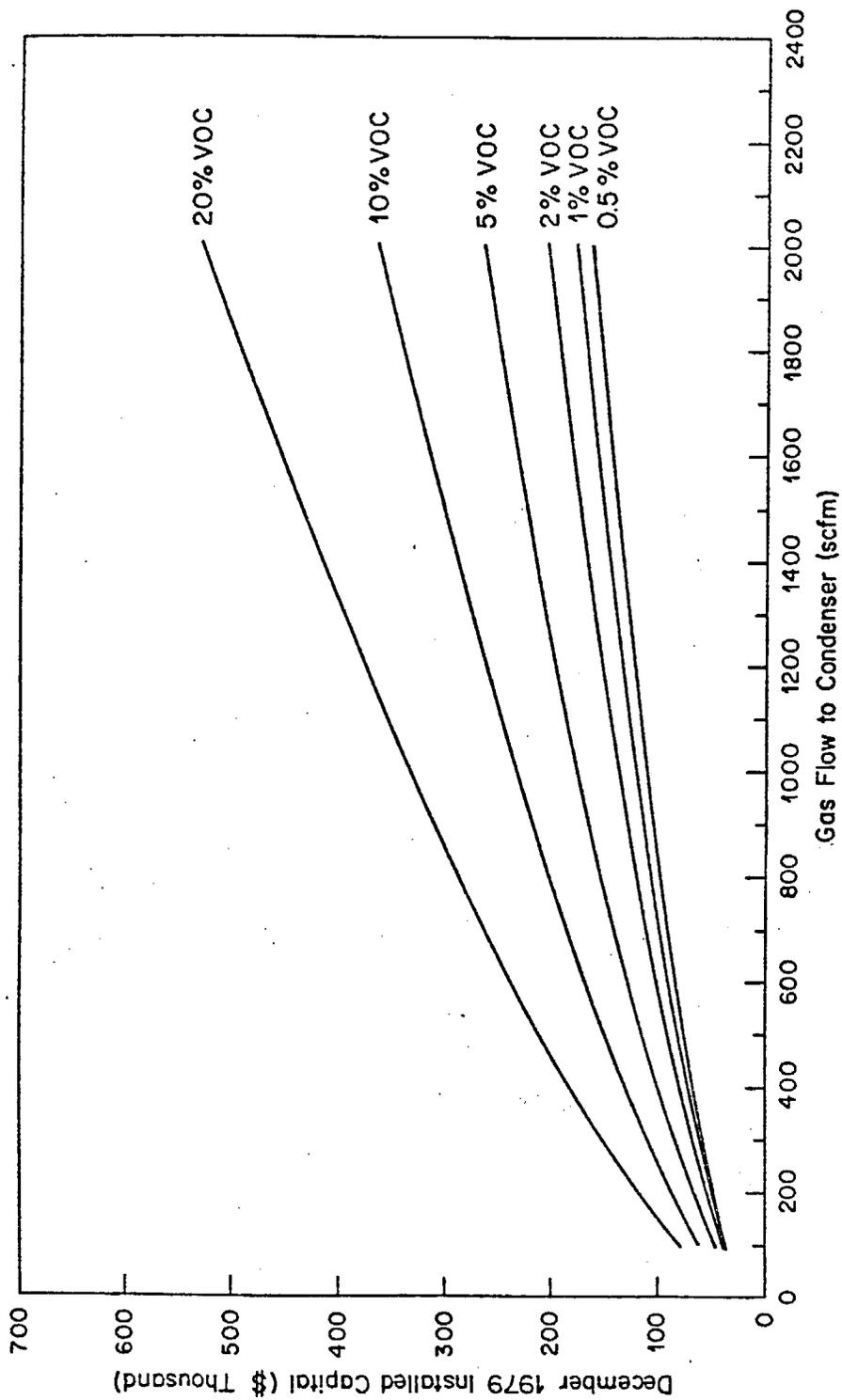


Figure 8.4-1. Installed Capital Cost vs Flow Rate for Complete Condenser System With Volatile Organic Carbon (VOC) Removal Efficiency of 80 Percent (Erikson, 1980).

Table 8.4-1
CAPITAL AND OPERATING COSTS FOR CONDENSATION

Case	Variant	Capital	Annual Operating Costs (\$1000)				Credit	Net	Cost per lb Styrene Removed (\$)
			Fixed	Labor	Elec.				
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¢/lb	3,444.4	1,146.9	14.6	58.4	48.9	1171.0	14.4	

Erikson, D.G. 1980. "Control device evaluation: condensation," in Organic chemical manufacturing Vol. 5: Adsorption, condensation and absorption devices. Prepared by IT Envirosience for U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Emission Standards and Engineering Division, Research Triangle Park, North Carolina, EPA-450/3-80-027.

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:

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

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).

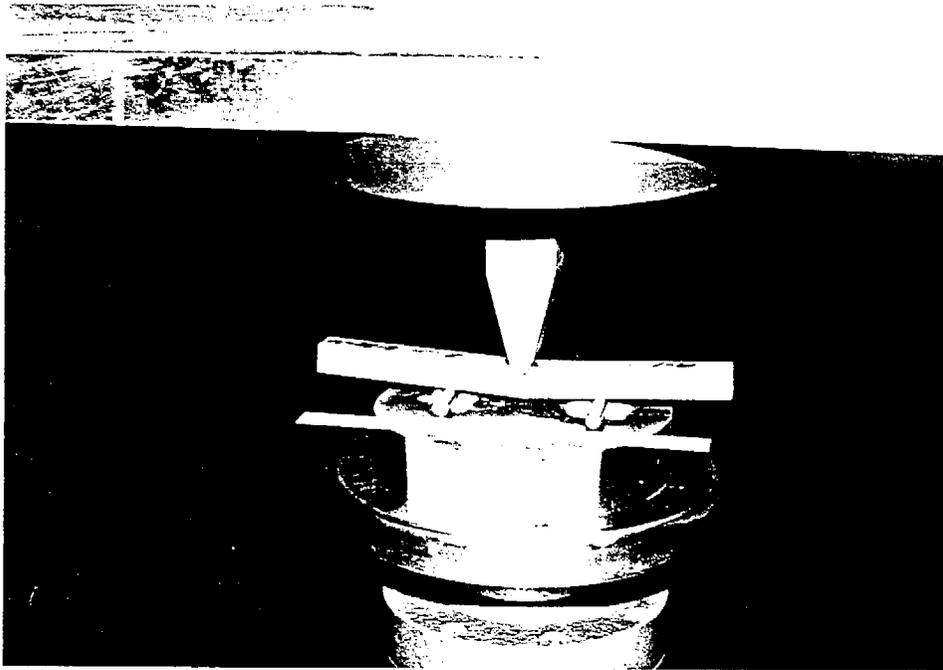


Figure 9.2-1. Standard Test Setup for Interlaminar Shear Strength Tests (Beam Has Failed in Tension).

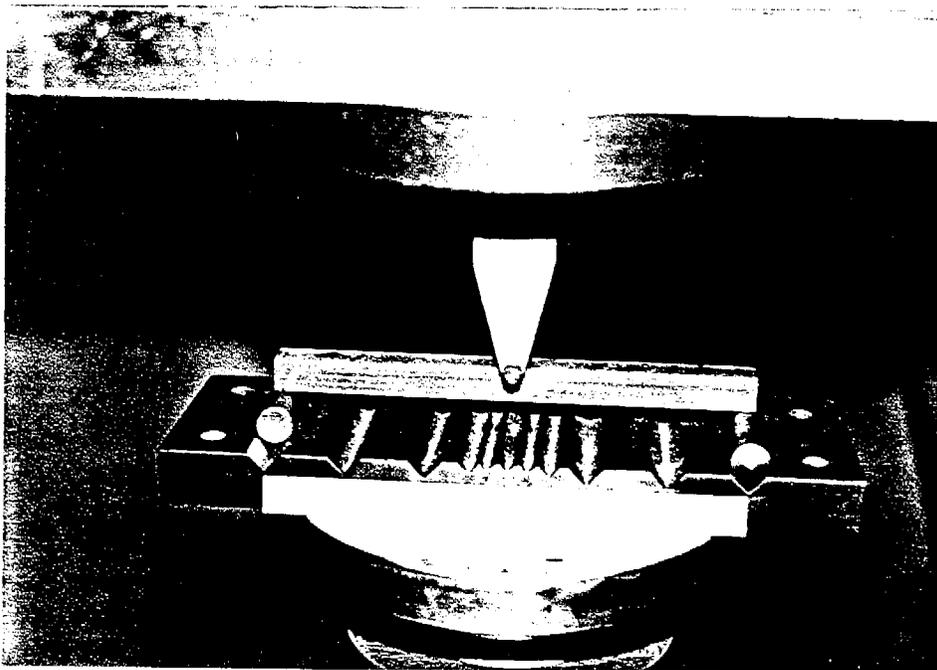


Figure 9.2-2. Standard Test Setup for Bending Tests

For a rectangular beam,

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

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

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

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

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/in²), is defined as follows:

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

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:

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

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:

<u>Laminate</u>	<u>Characteristic</u>
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	.396	.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)		Apparent Shear Stress (lb/in ²)		No. Failing in Shear
	Mean	Std.Dev	Mean	Std. Dev.	
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	L a m i n a t e			
	B	C	D	E
A	* A<B t = -3.533 d.f. = 4	A>C t = 0.0323 d.f. = 8	* A>D t = 4.058 d.f. = 7	* A<E t = -11.988 d.f. = 6
B	x	* B>C t = 2.553 d.f. = 6	* B>D t = 6.277 d.f. = 5	* B<E t = -6.645 d.f. = 4
C	x	x	* C>D t = 3.601 d.f. = 9	* C<E t = -11.200 d.f. = 8
D	x	x	x	* D<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:

<u>Laminate</u>	<u>Characteristic</u>
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, L @ 200 lbs. 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	55500	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	57400	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	71900	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	53600	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	67800	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

Bultman, H.J. 1978. "Testing," Modern plastics encyclopedia 55(10A): 378, 381-382.

CreMASchi, George, Reichhold Chemicals, Inc., Elizabeth, New Jersey. Personal communication (3 April 1981).

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

Osofsky, Irving, Science Applications, Inc., El Segundo, California. Inter-office memorandum to Michael Rogozen, SAI-464-820-048 (26 October 1981).

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

^aCount based upon upper emission estimates.

some sort of exhaust gas treatment would have to be retrofitted in existing plants, at considerable expense to the owners. 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 equipment 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 not 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.
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.

<u>Name of Firm</u>	<u>Address</u>	<u>Telephone No.</u>
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

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 CS₂ is withdrawn and transferred to a 10 ml micro-KD distillation flask column.
4. 0.5 ml of CS₂ 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 CS₂ 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 CS₂.

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 CS₂, 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.: 200⁰ 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,

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

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

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

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 METHOD¹

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.

⁶NOTE—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:

- D 618 Conditioning Plastics and Electrical Insulating Materials for Testing²
- D 2991 Recommended Practice for Testing Stress-Relaxation of Plastics²
- E 4 Load Verification of Testing Machines³
- E 18 Tests for Rockwell Hardness and Rockwell Superficial Hardness of Metallic Materials⁴

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 re-

search 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 \pm

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 ground 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/m² (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:

$$s = \sqrt{(\sum X^2 - n(\bar{X})^2)/(n - 1)}$$

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 crosshead 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

Specimen Length = L

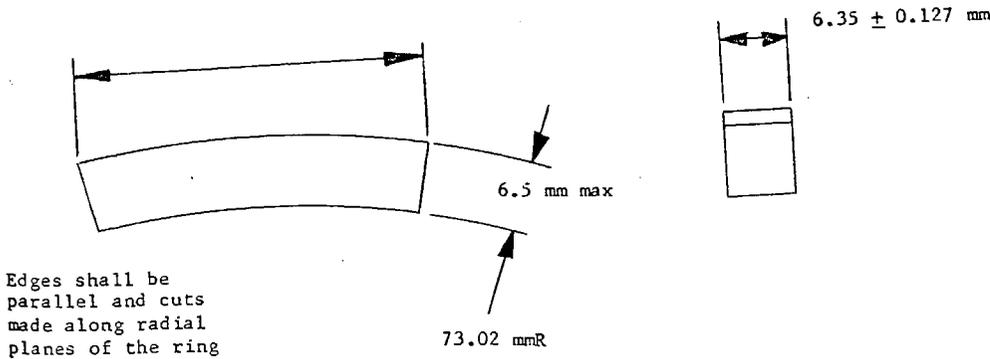


FIG. 1 Horizontal Shear Test Specimen (Ring Specimen).

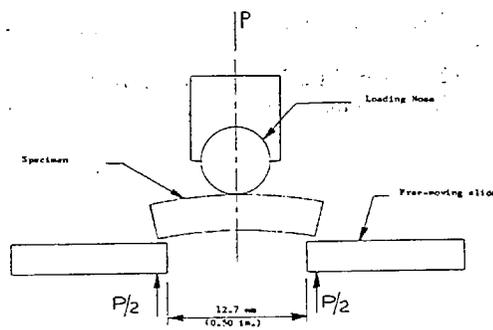


FIG. 2 Horizontal Shear Load Diagram (Ring Specimen).

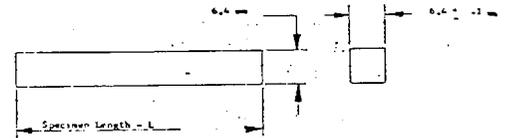


FIG. 3 Shear Test Specimen (Flat Laminate).

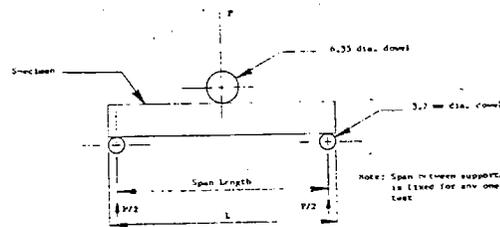


FIG. 4 Horizontal Shear Load Diagram (Flat Laminate).

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, is entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, Pa. 19103, which will schedule a further hearing regarding your comments. Failing satisfaction there, you may appeal to the ASTM Board of Directors.

Standard Method of Test for FLEXURAL PROPERTIES OF PLASTICS¹



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 materials being tested. All specification tests, however, must be run accord-

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.

ing 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.

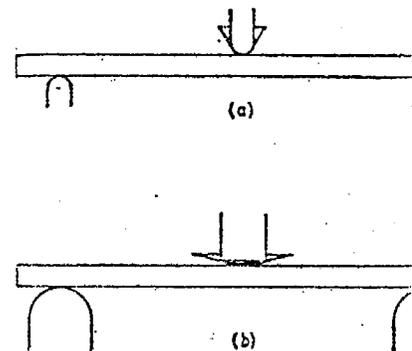
3. Significance

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

motion over the range indicated, at 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 specimen does not exceed 1 per cent of the deflection of the test specimen at test, or appropriate corrections shall be made. The load-indicating mechanism shall be essentially free from inert



(a) Minimum radius = 3.2 mm ($\frac{1}{8}$ in.)
(b) Maximum radius supports = $1\frac{1}{2}$ times specimen depth, maximum radius loading nose = 4 times specimen depth (minimum length of chord defining arc in contact with the supports = 2 times specimen depth).

FIG. 1—Allowable Range of Loading Nose Support Radii for Specimen 6.4 mm ($\frac{1}{4}$ in.)

at the crosshead rate used. The accuracy of the testing machine shall be verified in accordance with ASTM Method E 122, Verification of Testing Machines.²

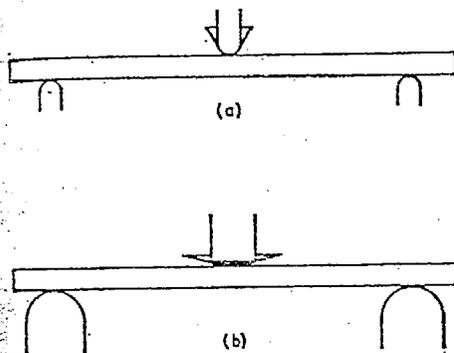
4.2 *Loading Nose and Supports*—The loading nose and supports shall have cylindrical surfaces. In order to avoid excessive indentation, or compressive failure, that is, nonrecoverable deformation or compressive failure due to stress concentration directly under the loading nose, the radius of nose and supports shall be at least 3.2 mm ($\frac{1}{8}$ in.) for specimens. For specimens 3.2 mm

² Appears in this publication.

TEST FOR FLEXURAL PROPERTIES OF PLASTICS (D 790)

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

in thickness or greater, the radius of the supports may be up to $1\frac{1}{2}$ 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).



- (a) Minimum radius = 3.2 mm ($\frac{1}{8}$ in.).
 (b) Maximum radius supports = $1\frac{1}{2}$ 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 ($\frac{1}{4}$ in.) Thick.

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

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 ($\frac{1}{8}$ in.) for all specimens. For specimens 3.2 mm ($\frac{1}{8}$ in.)

² Appears in this publication.

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 ($\frac{1}{16}$ 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 ($\frac{1}{8}$ in.) in thickness. Specimens 3.2 mm ($\frac{1}{8}$ in.) or less in thickness shall be 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 span, but in no case less than 6.4 mm ($\frac{1}{4}$ in.) on each end. Overhang shall be suffi-

TABLE 1—SUGGESTED DIMENSIONS FOR TEST SPECIMENS OF 5.3 AND 5.5 (NOTE 6).

Nominal Specimen Thickness, mm (in.)	Span-to-Depth Ratio												
	16 to 1				32 to 1				40 to 1				
	Width of Specimen, mm (in.)	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	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 (2 1/4)	30 (1 1/4)	2.0 (0.08)	90 (3 1/2)	60 (2 1/2)	4.3 (0.17)
1.6 (1/16)	25 (1)	50 (2)	25 (1)	0.8 (0.03)	80 (3)	50 (2)	2.8 (0.11)	90 (3 1/2)	60 (2 1/2)	4.3 (0.17)	120 (4 3/4)	95 (3 3/4)	6.4 (0.25)
2.4 (3/32)	25 (1)	60 (2 1/2)	40 (1 1/2)	1.0 (0.04)	100 (4)	80 (3)	4.1 (0.16)	180 (7)	130 (5)	8.4 (0.33)	240 (9 1/2)	191 (7 1/2)	12.7 (0.50)
3.2 (1/8)	25 (1)	80 (3)	50 (2)	1.3 (0.05)	130 (5)	100 (4)	5.3 (0.21)	330 (13)	250 (10)	17.0 (0.67)	480 (19)	380 (15)	25.4 (1.00)
4.8 (3/16)	13 (1/2)	100 (4)	80 (3)	2.0 (0.08)	191 (7 1/2)	150 (6)	8.1 (0.32)	640 (25)	510 (20)	34.0 (1.34)	700 (30)	510 (20)	50.8 (2.00)
6.4 (1/4)	13 (1/2)	130 (5)	100 (4)	2.8 (0.11)	250 (10)	200 (8)	10.9 (0.43)	940 (37)	700 (30)	34.0 (1.34)	1020 (40)	700 (30)	50.8 (2.00)
9.6 (3/8)	13 (1/2)	191 (7 1/2)	150 (6)	4.1 (0.16)	380 (15)	300 (12)	16.3 (0.64)	1240 (49)	1020 (40)	43.4 (1.71)			
12.7 (1/2)	13 (1/2)	250 (10)	200 (8)	5.3 (0.21)	495 (19 1/2)	410 (16)	21.6 (0.85)						
19.1 (3/4)	19 (3/4)	380 (15)	300 (12)	8.1 (0.32)	740 (29)	610 (24)	32.5 (1.28)						
25.4 (1)	25 (1)	495 (19 1/2)	410 (16)	10.9 (0.43)	990 (39)	810 (32)	43.4 (1.71)						

^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.

cient to prevent the specimen from slipping through the supports.

NOTE 2—Whenever possible, surfaces of the sheet shall be unaltered, where machine limitations possible to follow the above criteria. The unaltered sheet, both surfaces shall be to the desired dimensions and the specimens with reference to the original shall be noted. The values obtained with machined surfaces may differ from those obtained on specimens with original surfaces. Consequently, any specification properties on the thicker sheet shall be whether the original surfaces are or not.

NOTE 3—Edgewise tests are required for sheets that are so thin that satisfying these requirements cannot be achieved when depth exceeds the width, occur.

5.2.2 For Materials Less Than 1/16 in. in Thickness—Test specimens shall be 50.8 mm (2 in.) long, 12.7 mm (1/2 in.) wide, tested flatwise (1-in.) span (Notes 4 and 5).

NOTE 4—The formulas for stress in this method for calculating results when the width is small in comparison to span. Therefore, they do not apply to these dimensions.

NOTE 5—Where machine limitations exist that specimens of these dimensions measured, wider specimens or specimens of both, may be used, provided span is at least 14 to 1. All dimensions shall be reported in the report (see also Note 4).

5.3 Laminated Thermoplastic Materials and Sheet and Plate for Electrical Insulation, Carbonized Fiber and Glass-Fiber Specimens shall be tested with Table 1. For paper-based grades over 25.4 mm nominal thickness, the specimens shall be machined on both surfaces to a thickness of 25.4 mm (1 in.). For nylon- and nylon-base grades, specimens shall be 12.7 mm (1/2 in.) in nominal thickness and shall be machined on both surfaces to a thickness of 12.7 mm (1/2 in.).

5.4 Molding Materials

TABLE 1—SUGGESTED DIMENSIONS FOR TEST SPECIMENS OF 5.3 AND 5.5 (NOTE 9).

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 ^d	Length of Specimen, mm (in.)	Span, mm (in.)	Rate of Cross-head Motion (Procedure A), mm (in.)/min ^d	Length of Specimen, mm (in.)	Span, mm (in.)	Rate of Cross-head Motion (Procedure A), mm (in.)/min ^d	Length of Specimen, mm (in.)	Span, mm (in.)	Rate of Cross-head Motion (Procedure A), mm (in.)/min ^d
0.8 (1/32)	25 (1)	50 (2)	10 (3/8) ^b	0.5 (0.02)	50 (2)	25 (1)	1.3 (0.05)	60 (2 1/4)	30 (1 1/4)	2.0 (0.08)	90 (3 1/2)	60 (2 1/2)	4.3 (0.17)
1.6 (1/16)	25 (1)	50 (2)	25 (1)	0.8 (0.03)	80 (3)	50 (2)	2.8 (0.11)	120 (4 1/2)	60 (2 1/2)	6.4 (0.25)	180 (7)	95 (3 3/4)	17.0 (0.67)
2.4 (1/8)	25 (1)	60 (2 1/2)	40 (1 1/2)	1.0 (0.04)	100 (4)	80 (3)	4.1 (0.16)	150 (6)	100 (4)	12.7 (0.50)	240 (9 1/2)	130 (6)	34.0 (1.34)
3.2 (1/4)	25 (1)	80 (3)	50 (2)	1.3 (0.05)	130 (5)	100 (4)	5.3 (0.21)	200 (8)	150 (6)	17.0 (0.67)	330 (13)	191 (7 1/2)	50.8 (2.00)
4.5 (1/6)	13 (1/2)	100 (4)	80 (3)	2.0 (0.08)	191 (7 1/2)	150 (6)	8.1 (0.32)	250 (10)	200 (8)	25.4 (1.00)	480 (19)	250 (10)	67.8 (2.67)
6.4 (1/4)	13 (1/2)	130 (5)	100 (4)	2.8 (0.11)	250 (10)	200 (8)	10.9 (0.43)	300 (12)	300 (12)	34.0 (1.34)	640 (25)	380 (15)	97.8 (3.85)
9.6 (3/8)	13 (1/2)	191 (7 1/2)	150 (6)	4.1 (0.16)	350 (15)	300 (12)	16.3 (0.64)	410 (16)	410 (16)	43.4 (1.71)	940 (37)	700 (30)	114.3 (4.50)
12.7 (1/2)	13 (1/2)	250 (10)	200 (8)	5.3 (0.21)	495 (19 1/2)	410 (16)	21.0 (0.85)	710 (28)	710 (28)	25.4 (1.00)	1240 (49)	1020 (40)	158.8 (6.25)
19.1 (3/4)	19 (3/4)	380 (15)	300 (12)	8.1 (0.32)	990 (39)	810 (32)	32.5 (1.28)						
25.4 (1)	25 (1)	495 (19 1/2)	410 (16)	10.9 (0.43)			43.4 (1.71)						

^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.

cient to prevent the specimen slipping through the supports.

NOTE 2—Whenever possible, surfaces of the sheet shall be unaltered sheet, both surfaces shall be to the desired dimensions and the specimens with reference to the shall be noted. The values obtained with machined surfaces may differ from those obtained on specimens with original surfaces. Consequently, any specific properties on the thicker sheet whether the original surfaces are or not.

NOTE 3—Edgewise tests are for sheets that are so thin that satisfying these requirements cannot be when depth exceeds the width, occur.

5.2.2 For Materials Less Than 1/16 in. in Thickness—T shall be 50.8 mm (2 in.) long, 12.7 mm (1/2 in.) wide, tested flatwise with a (1-in.) span (Notes 4 and 5)

NOTE 4—The formulas for calculating the width is small in comparison with the span. Therefore, they do not apply to these dimensions.

NOTE 5—Where machine measured, wider specimens or both, may be used, provided span is at least 14 to 1. All dimensions in the report (see also Note 4).

5.3 Laminated Thermoplastic Materials and Sheet and Plate for Electrical Insulation, Carbonized Fiber and Glass Specimens shall be tested with Table 1. For paper-based grades over 25.4 mm nominal thickness, the surfaces shall be machined on both surfaces to a thickness of 25.4 mm (1 in.) and nylon-base grades, shall be machined on both surfaces to a thickness of 12.7 mm (1/2 in.)

5.4 Molding Materials

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 Pheno-*

lics, 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 or 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:

$$N = \frac{ZL^3}{6d} \dots \dots \dots (1)$$

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 curve.

8.6 Terminate the test if the maximum strain in the outer fiber has reached

0.05 mm/mm (in./in.) (Notes 7 and 8). The deflection at which this strain may be calculated by letting r = strain, mm/mm (or in./in.) as follows

$$D = \frac{rL^3}{6d} \dots \dots$$

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 strain rate provided under Procedure A may induce the specimen to yield or rupture within the required 5 per cent strain rate.

NOTE 8—Beyond 5 per cent strain rate is not applicable, and some other test methods, such as ASTM Method D 638, Test Method for Tensile Properties of Plastics,³ should be used.

9. Procedure B

9.1 Use an untested specimen for each measurement.

9.2 Testing conditions shall be the same as those described in 8.1, except that the rate of crosshead motion of the outer fiber shall be 0.1 mm/min (in./in. min.).

10. Retests

10.1 Values for properties shall not be calculated for a specimen that breaks at some obvious flaw, unless such flaws constitute a part of the material being studied. Retests shall not be made for any specimens on which a flaw has been detected. Retests shall not be calculated.

11. Properties and Calculations

11.1 *Maximum Fiber Strain*—The maximum strain in a beam of homogeneous, elastic material tested in flexure as a cantilever beam supported at two points at the midpoint, the maximum strain in the outer fiber occurs at the midpoint. The maximum stress may be calculated from

TEST FOR FLEXURAL PROPERTIES OF PLASTICS (D 790)

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:

$$D = \frac{rL^2}{6d} \dots\dots\dots(2)$$

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,* 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):

$$S = \frac{3PL}{2bd^2} \dots\dots\dots(3)$$

where:
 S = stress in the outer fiber at midspan, 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):

$$S = \frac{3PL}{2bd^2} \left[1 + 6 \left(\frac{D}{L} \right)^2 - 4 \left(\frac{d}{L} \right) \left(\frac{D}{L} \right) \right] \dots\dots\dots(3a)$$

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 638.²

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:

$$r = \frac{6Dd}{L^2} \dots \dots \dots (4)$$

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.

$$E_B = \frac{L^3m}{4bd^3} \dots \dots \dots (5)$$

where:

- E_B* = modulus of elasticity in bending, kg/cm² (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

of tests, the arithmetic mean obtained shall be calculated. Significant figures and rounding “average value” for the property in question.

11.10 *Standard Deviation*—Standard deviation (estimated) calculated as follows and reported as significant figures:

$$s = \sqrt{\frac{\sum X^2 - \frac{(\sum X)^2}{n}}{n}}$$

where:

- s* = estimated standard deviation
- X* = value of single observation
- n* = number of observations
- \bar{X} = arithmetic mean of observations.

12. Report

12.1 The report shall include the following:

12.1.1 Complete identification of material tested, including manufacturer's code number, principal dimensions, and product name.

12.1.2 Direction of cutting specimens,

maximum strain in the outer fiber, mm (or in./in.), deflection of the center of the beam, mm (or in.), and mm (or in.), and mm (or in.).

Modulus of Elasticity:
Tangent Modulus of Elasticity—The modulus of elasticity, often called "modulus of elasticity," is the slope of the straight line portion of the load-deflection curve and using

$$E_B = \frac{L^3 m}{4bd^3} \dots \dots \dots (5)$$

of elasticity in bending, (or psi), (or in.), beam tested, cm (or in.), beam tested, cm (or in.),

The tangent to the initial linear portion of the load-deflection curve, kg/cm (or lb/in.)

Modulus of Elasticity—The modulus of elasticity is the slope of the straight line portion of the stress-strain curve. It is expressed in kilograms per square centimeter (or pounds per square inch). The selected point is generally the yield point. It is determined in accordance with Eq 5 by the slope of the secant load-deflection curve.

Arithmetic 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:

$$s = \sqrt{\frac{\sum X^2 - n\bar{X}^2}{n - 1}}$$

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.