Aristech Chemical Corporation
Polyester Unit
1605 Elizabeth Avenue West
Linden, NJ 07036
201/862-5600

ARISTECH

POLYESTER RESIN
PLASTICS PRODUCT
FABRICATION
AP-42 Section 4.12
Reference Number
6

September 16, 1987
JES-87-125

Mr. Arch A. McQueen
Criteria Emissions Section
Air Management Technology Branch
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dear Mr. McQueen:

We appreciate the opportunity that you have given us of reviewing the draft version of the Polyester Resin Plastics Products Fabrication supplement to AP-42.

The several suggestions that we have to offer have been included in a letter to you from R. C. Lepple which summarizes the comments of a number of members of the SPI Resin Technical Committee.

Sincerely,

Aristech Chemical Corporation

J. E. Studenberg
Manager - Research & Development
Laminating & Casting/Tech Service
Polyester Unit

jg

NOTE: See page 000019 of the So. Coast AQMD document, attached, for estimates of clean up solvents emissions.

Aristech Chemical Corporation
Polyester Unit
1605 Elizabeth Avenue West
Linden, NJ 07036
201/862-5600

ARISTECH

September 16, 1987

Mr. Arch A. MacQueen
Criteria Emissions Section
Air Management Technology Branch
Mail Drop 14
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dear Mr. MacQueen:

We appreciate the opportunity to participate in drafting the Polyester Resin Plastics Products Fabrication supplement to AP-42 and are cognizant of its importance to our industry. The Resin Management Committee of the SPI Composites Institute has solicited comments from members of their Polyester Resin Technical Committee and these comments are included herein. Companies contributing to this list of suggestions include Ashland Chemicals, Freeman Chemicals, Interplastics, Koppers Company, Norac, Owens Corning Fiberglas, Reichhold Chemicals, and Silmar, as well as Aristech.

The combined comments of these several SPI members are as follows referenced by page number:

1) 4.12-1 Change the first sentence to read: "...one fabricated from liquid polyester...".

2) 4.12-2 Line 6: Insert "cross-linked" between "and the...polyester resin" to correspond to the nomenclature on page 4.12-3. Table 4.12-1: Change "isophthalic anhydride" to "isophthalic acid", and add "neopentyl glycol" under alcohols column. Also change "Components of Polyester Resins" to "Typical Components of Resins".

3) 4.12-3 Change formula of Ethylene Glycol to "$HO-CH_2-CH_2-OH$". Also correct the formula of "unsaturated polyester" by adding the necessary hydrogen atoms to the maleic unit.

4) 4.12-4 First line: Add "within certain limits," after the semi-colon since excessive amounts of catalyst can actually inhibit the cure. Last paragraph, fifth sentence from bottom: delete "fiber/binder" and change to read "the reinforcement is in the form of either a chopped strand mat, a woven fabric or often both".

5) 4.12-5 Line 6: We suggest replacing "its use of automated equipment" with "that it uses mechanical spraying and chopping equipment for depositing the resin and glass reinforcement." Lines 8-13: we believe that this statement can apply to hand lay-up as well as spraying.

6) 4.12-8 Line 1: Replace ", or press," with ", such as compression or injection...".

7) 4.12-9 Second paragraph: Amend the last sentence as follows: "Other chemical components of the resins are emitted at trace levels, because they not only have a very low vapor pressure but also are substantially converted to polymers." Third paragraph, line 6: the statement "the resins used in filament winding often contain a higher monomer content" seems to be contradicted by the values shown in Table 4.12-3. We suggest omitting that portion of this sentence. Second line from bottom: change to read, "...hand lay-up or spray-up...".

8) 4.12-10 Second paragraph: We feel that the "0.3 to 0.6 weight percent" is much too narrow and restrictive. We would suggest a broader range of 0.05 to 2.0 percent or better yet, omit the limits by saying "...constituting up to several weight percent of the mix". Also, the next sentence seems to be restrictive by saying that the styrene losses can be reduced by 30 to 50 percent. We would suggest "...reduce VOC losses very substantially."

9) 4.10-11 Fourth line from bottom: The word "in" should be "is".

10) 4.10-12 Table 4.12-2: We received many comments about this table. A number of respondents questioned the values shown that indicate the vapor losses for spray-up are lower than those for hand lay-up. It is our experience that spray-up laminating emissions would be equivalent or even slightly higher than those found in hand lay-up. Secondly, the gel coat is usually applied the same way for both processes so we would expect that the emissions for gel coat would be essentially the same in both operations.

Enclosed you will find some supporting data from Ashland Chemicals about these processes.

Our SPI organization has taken the position that the SAI document is flawed particularly in relation to styrene emission levels. We have worked very closely with SCAQMD in Los Angeles and believe that their values are much more realistic. We suggest that you review the values in this table and possibly give more consideration to the SCAQMD Rule 1162 document.

All things considered, we feel that this is a well written document that should be helpful to the agencies using it.

ARISTECH

I am signing on behalf of the Resin Management Committee, and if you should have any further questions, please feel free to call. Thank you for permitting us this opportunity of reviewing this document.

Sincerely,

R. C. Lepple

R. C. Lepple
General Manager

RCL/dk

Enclosure

cc: J. R. Brown - Koppers
G. Carey - Alpha
J. Dockum - PPG
R. D'Roma - Interplastics
J. Gathor - Reichhold
T. King - Ashland
J. Lawrence - Cargill
C. McClaskey - Norac
R. Poet - Silmar
C. Ross - Freeman
J. Jenks - OCF
C. Randazzo - SPI w/att.

MEMORANDUM

September 9, 1987

TO: JT King

FROM: CD Dudgeon

SUBJECT: SPI Request for Comments, AP-42
<u>Compilation of Air Pollutant Emission Factors</u>

We have reviewed EPA's draft version of Polyester Resin Plastic Products Fabrication, which will be published in late 1987 as part of the Supplement to AP-42, <u>Compilation of Air Pollutant Emission Factors</u>. The critical part of this supplement is the assignment of emission factors for polyester resin fabrication processes. These factors would be used to calculate the total emissions (kg/day) for any polyester resin based on the emission factor and the actual volatile monomer content. These emission factors were given in Table 4.12-2 (attached).

The values assigned for non vapor suppressed resin and gel coat are the same values assigned as a result of Rogozen's SAI study (Reference 1 for Section 4.12).

I would summarize our experience vs. the SAI report as follows

Emission Factors

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

1. Hand lay up does not result in more emissions than spray lay up. This was shown to be a more accurate range in our testing (paper presented at the 34th Annual SPI Conference, 1979).

2. SAI number for continuous lamination based on a styrene/MMA blend. For most applications 2-6 would be more typical.

3. Pultrusion is a semi closed molding operation and emissions are lower than 6-13%.

4. Losses in filament winding are similar to hand lay up.

5. Gel coat emissions for hand lay up should be the same as for spray lay up. Emissions of 26-35% seem reasonable.

Table 4.12-2 also assigns values for vapor suppressed resins and gel coats. It appears that these numbers are based on the assumption that suppression can reduce emission 50 to 70%. Based on laboratory data this could be a logical conclusion.

Chuck

CDD/dkh

Draft Table 4.12-2
as sent to reviewers

TABLE 4 12-2 UNCONTROLLED EMISSION FACTORS FOR POLYESTER RESIN PRODUCT FABRICATION PROCESSES[a]
(100 x mass of VOC emitted/mass of monomer input)

Process	Resin		Emission Factor Rating	Gel Coat		Emission Factor Rating
	NVS	VS[b]		NVS	VS[b]	
Hand layup	16 - 35	8 - 25	C	47	24 - 33	C
Spray layup	9 - 13	5 - 9	B	26 - 35	13 - 25	B
Continuous lamination	6 - 13	3 - 9	B	c	c	c
Pultrusion[d]	6 - 13	3 - 9	D	c	c	c
Filament winding[d]	6 - 13	3 - 9	D	c	c	c
Marble casting	1 - 3	1 - 3	B	e	e	e
Closed molding[f]	1 - 3	1 - 3	D	c	c	c

[a] Reference 1. Ranges represent the variability of the processes and the sensitivity of emissions to process parameters. Single value factors should be selected with caution. NVS = nonvapor-suppressed resin. VS = vapor-suppressed resin.

[b] Factors for vapor-suppressed resins are 50 to 70 percent of those for nonvapor-suppressed resins.

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

[d] Since no specific emission test data for this process were available, factors for the similar continuous lamination process are assumed to apply.

[e] Factors unavailable. However, when cast marble parts are subsequently sprayed with gel coat, the gel coat factors for spray layup are assumed to apply.

[f] Since no specific emission test data for closed molding processes were available, factors for marble casting (a semiclosed process) are assumed to apply.

References for Section 4.12

1. M. B. Rogozen, Control Techniques for Organic Gas Emissions from Fiberglass Impregnation and Fabrication Processes, Science Applications, Inc., Los Angeles, CA, For California Air Resources Board, Sacramento, CA, ARB/R-82/165 (NTIS PB82-251109), June 1982.

2. Modern Plastics Encyclopedia, 1986-1987, 63 (10A), October 1986.

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

34th Annual Technical Conference, 1979
Reinforced Plastics/Composites Institute
The Society of the Plastics Industry, Inc.

STYRENE EMISSIONS HOW EFFECTIVE ARE SUPPRESSED POLYESTER RESINS?

BY

MICHAEL J. DUFFY*

ABSTRACT

Contact molding remains the most widely used application technique for unsaturated polyester resins. In view of adaptability of this process for the production of large plastic components, its continuing existence is of paramount importance to our industry.

The necessity of an open mold, coupled with the high ratio of surface area to mass, results in an unavoidable release of styrene monomer to the atmosphere. Proper use of exhaust fans can remove styrene vapors from the plant atmosphere and may keep employee exposure within acceptable limits. Although employee health and safety is of primary concern, the release of styrene monmer into the atmosphere must also be considered in view of EPA controls. By suppressing the release of styrene from the laminate, employee exposure is reduced, and the emission of styrene to the atmosphere is minimized. In addition, the retained styrene becomes part of the finished laminate, resulting in a cost savings.

Ashland Chemical Company has evaluated several alternatives which reduce styrene emissions after application and during cure. A family of suppressed resins which provide reduced styrene emissions and improved wetting and rolling properties during production have been introduced commercially. Laboratory data illustrating reduced styrene emissions/sq.ft. of laminate have been reproduced in actual plant production. Readings were obtained with both a Bendix Styrene Detector and a Drager Styrene Detector. On successive days readings were recorded first with the standard production resin and the next day substituting the suppressed resin. Every effort was made to duplicate all conditions including time of sampling, ventilation, and location of sampling. All readings were taken during normal produciton.

Experiments conducted under controlled conditions indicate that after application and cure, about 1900 lbs. of styrene would be lost when using a 40,000 lb. tankwagon. The use of a suppressed product reduced this loss by about 74% or 1400 lbs. Overall internal and external plant working condition are therefore improved, resin usage is extended and the customer experiences a reduced resin cost.

INTRODUCTION

The industrial need for polyester resins with reduced styrene emission levels prompted Ashland to evaluate realistic alternatives—including low volatility monomers, resin transfer and styrenated resins having suppressed emissions—before going into the field and before supplying these resins to manufacturers. This research included:

1. Evaluating percent weight loss and actual monomer loss from unfilled, glass reinforced and filled polyesters.
2. Developing test procedures for determining these losses.
3. Developing test methods to evaluate the effect of a suppressant on interlaminar adhesion.
4. The effect of suppressant cost and reduced monomer loss on economics.

Once these four requirements were satisfied, we presented our line of suppressed resins to the end-users. Evaluations were arranged to be made on two consecutive days. A Bendix and/or Drager dectector was used to monitor styrene levels for an unsuppressed (control) vs. suppressed resin or—as in one instance—suppressed vs. suppressed. Readings were made not only in the plant but, when possible, outside and directly from exhaust stacks.

LABORATORY EXPERIMENTATION

Percent weight loss data have been compiled for various resins under conditions which are usually encountered in the field. The preliminary testing was performed on unfilled, catalyzed resin weighed into a gallon can lid on a top-loading balance accurate to 0.01 grams. Readings were made every 5 minutes over a 30 minute period. This is Ashland's standard test procedure for evaluating monomer suppressants in unfilled polyesters. Styrene loss for unsuppressed resins (as indicated in Table 1), is linear over the 30 minute period. Suppressed resins can reduce this loss as much as 50% depending on the type of resin and level of suppressant lused (Tables 1 and 2). The degree to which data can be reproduced by this method is fairly consistent as the graphs in Table 2 demonstrate.

Monomer losses from glass reinforced laminates were measured from one ft.^{2}, 3 ply laminates. This was done specifically to enable the manufacturer to actually relate these values to the overall square footage of the unit being produced. In this part of the evaluation, a standard spray-up resin with a cup gel of 20 minutes was catalyzed and applied to the glass mat. The highest percent weight losses occur up to and just shortly beyond the gel time (Tables 3 and 4). The use of a suppressant can reduce the weight loss by about at least 57% and possibly up to 80%. Table 5 demonstrates the percent of the initial styrene which is lost.

The value of using a suppressant in orthophthalic, general purpose resins such as those used by the marine industry, can also be demonstrated in other resisn. Significantly decreased weight losses were also demonstrated in an isophthalic, filament winding resin when we tested suppressed and unsuppressed 10 and 20 mil films of this polyester. Tables 6, 7 and 8 dramatically illustrate just how well the suppressant worked in this area. After 24 hours, there was about a 76-81% reduction in styrene monomer loss.

Next we proceeded to evaluate those resins which have been designed to accommodate high levels of aluminum trihydrate, namely, those presently being used by the tub/shower stall industry. Here we observed not only the effects of the suppresant itself, but also how well it worked in relation to thixotropy, or the lack thereof. Although there is not enough information, it does appear that a suppressed, non-thixotropic one (Table 9). Styrene losses may be reduced by about 70% when a suppressed resin is used. In addition, the suppressant acts as a wetting agent, providing faster glass wet-out and necessitating less rollout.

INTERLAMINAR ADHESION STUDIES

Before presenting suppressed resins to the contact molding industries, it was necessary to evaluate what effects, if any, the use of a suppressant would have on interlaminar adhesion. Initally, lap shear tests were run on laminates. The first laminate, consisting of 3 plies of 1-1/2 oz. mat, was laid up. In two runs—one and three hours later—a second 3 ply laminate was applied on the first. Overlap was about one inch. As seen in table 10, this was done with three different resins, each being suppressed and unsuppressed. For the most part, lap shears were not significantly different, with credible percent differences ranging between 5.5 to 11.9

Further testing was performed to simulate a filament winding process. Laminates were made with 15 plies of 24 oz. woven roving. Each consecutive ply was rotated 90 degrees from the previous one. Fifteen additional plies were applied 24 hours later, the overlap being

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*Ashland Chemical Company
5200 Blazer Parkway
Dublin, Ohio 43017

again about one inch. Lap shears between suppressed and unsuppressed differed only by 6.6% (Table 11).

FURTHER ADHESIONS STUDIES: 24 HOUR PEEL TESTS

In a further attempt to test for interlaminar adhesion, we conducted a 24 hour laminate peel test. Concurrently, we began evaluating for secondary bonding failure at lowered ambient temperatures; at higher than normal suppressant levels; and at longer intervals between bonding.

The peel test normally consists of laying up a 3 ply, 5 × 10 inch, 1-1/2 oz. mat laminate which is allowed to cure for a pre-determined period of time. A small sectin of cellophane is placed at one end of this laminate and the second 3 ply laminate is applied. Twenty-four hours later, an attempt is made to peel the two laminates apart, working from the unbonded plies separated by the cellophane. Referring to Table 12, note that we did record some secondary bond failures. Aropol™ 8343T-12S (Sample 2) failed when the resin and laminate were cooled to 50°F, although when repeated (Sample 3), it passed. Aropol™ 8343T-12S with double the suppressant and at 50°F, also failed (Sample 5). We observed no failure in Sample 9 which consisted of two, 6 ply laminates. There was a 96 hour interval between the first and second laminates, both of which were constructed and cured at room temperature.

Based on such data, it shoud be pointed out that secondary bonding problems may occur when the resin, glass or molds are at low temperatures (below 65°F) or when the initial laminate has been allowed to cure 16 hours or more before secondary lamination is attempted. We have not been able to duplicate the time lapse problem in the laboratory. High concentrations of suppressant will cause poor bonding. Some suppressant separation can occur at low temperatures. Separated material must be redispersed prior to use by warming to about 70°F and by using mild agitation.

COST SAVINGS

The use of a suppressed resin, although in itself more expensive, can result in a savings to the manufacturer (Table 13). Based on a reduction in percent loss of initial styrene and bearing in mind that the customer has actually paid the price of the resin for the lost styrene, manufacturers can expect, under optimum conditions, a savings, of at least $100.00/40,000 lbs. of suppressed resin. According to the data accrued, about 1400 fewer lbs. of styrene are lost from the 40,000 lbs. This enables the manufacturer to produce more parts from each load of resin.

PLANT PRODUCTION TRIALS

The next step beyond laboratory experimentation was to introduce the suppressed resins to the FRP industry. Since their introduction, we have successfully evaluated these resins at a number of manufacturers. The evaluation procedure is to run, on successive days, first the standard production resin and, secondly, the suppressed resin. (Styrene levels are determined using a Bendix/Gastec and/or Drager Gas Detector.) Locations of sampling are indentical on the two days and time is as close as possible so that monomer levels and ventilation patterns are reasonably duplicated. When possible, exhaust stack readings are also made.

Laboratory studies indicated that a suppressant can greatly reduce the amount of monomer lost from a resin whether unfilled or filled with fiberglass or aluminum trihydrate. Plant trials that were conducted reaffirm this statement. After application and rolling of a suppressed resin, the styrene emission levels are significantly reduced, as demonstrated in the following sample evaluations.

Tables 14 and 15 illustrate testing done on the inside of a mold 9 feet deep. There was a constant air flow over the top of the mold, but not into it. The resin used in this evaluatin contained 50% hydrated alumina. A significant reduction in styrene levels was demonstrated.

The plant depicted in Table 16, has a highly efficient ventilation system; consequently, most of the readings taken were relatively low. Those of significance were tests numbers 2 and 3, taken directly from two units using the Bendix Detector. The readings were 950 ppm and 450 ppm for the control resin, and 200 ppm and 50-60 ppm for the suppressed resin.

Table 17, a schematic of a single spray booth within any given plant, reinforces the almost immediate effect of the suppressant and again, demonstrates the dramatic monomer level reduction. There was a 38-40% drop inside the booth and a 65-80% reduction after rollout was completed.

As depicted in Tables 18 and 19, we also evaluated our suppressed resin at a plant that was already using a suppressed resin. Readings were taken both inside and outside the plant (Tables 18 and 19). Not shown in this table are a number of operating fans and the additional operating hoods. Again, the two resins were monitored on consecutive days at about the same time of day. The results are included here to demonstrate the value of using the proper type and level of suppressant for reduction of styrene emissions not only within plant but also beyond normal plant environs.

Most units require 2-3 sprayings before completion. Tests number 4 and 5 are high because in this operation, only one spraying is required to make the unit and so the FRP back-up is thicker than normal. This thickness appears to inhibit the effectiveness of the suppressant. Rolling reduces this inhibition as the overall laminate thickness is greatly reduced.

Exhaust stack monomer readings were taken from directly inside the stacks on the top of the building while the exhaust fans were running. Results vary from stack to stack, depending on the part of the laminating process which was performed in a given spray booth. The first four readings (Table 19) were taken while units were being sprayed. The fifth reading was determined when all spraying in the plant had been stopped. The readings in Table 19 indicate that, even in a highly ventilated operation, the levels of styrene emissions can be greatly reduced when using a suppressed resin, particularly when using the proper type and level of suppressant.

CONCLUSIONS

Laboratory studies and actual plant evaluations prove that the right styrene suppressant reduces monomer loss not only to the internal plant atmospher, but also to the surrounding environment. This will improve plant working conditions as well as the health, safety and attitude of plant employees. At the proper level of suppressant and the appropriate operating conditions, excellent interlaminar adhesion is obtained. The proper level of suppressant is determined by examining the particular manufacturing operation, the type of resin used, and the final product. Although suppressed resins are somewhat more expensive, there is a definite cost savings when they are used.

MICHAEL J. DUFFY

Michael J. duffy is a Polyester Chemist in Technical Service with Ashland Chemical Company, where he is responsible for marble and contact molding resins. He has been in the plastics industry since 1969, previously as a Product Development Chemist with Koppers Company, Inc.

Mr. Duffy holds a Bachelor of Science degree in Biochemistry from Duquesne University, Pittsburgh.

Table 1

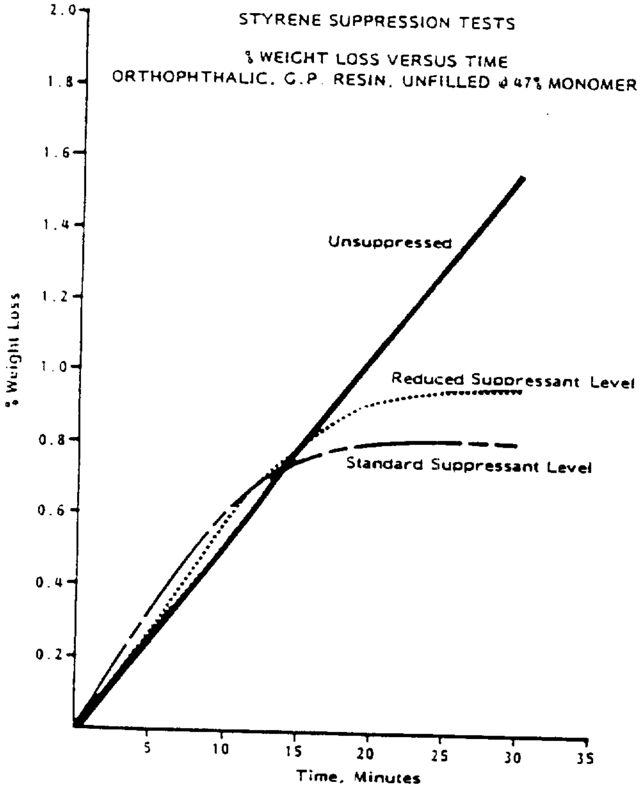


Table 2

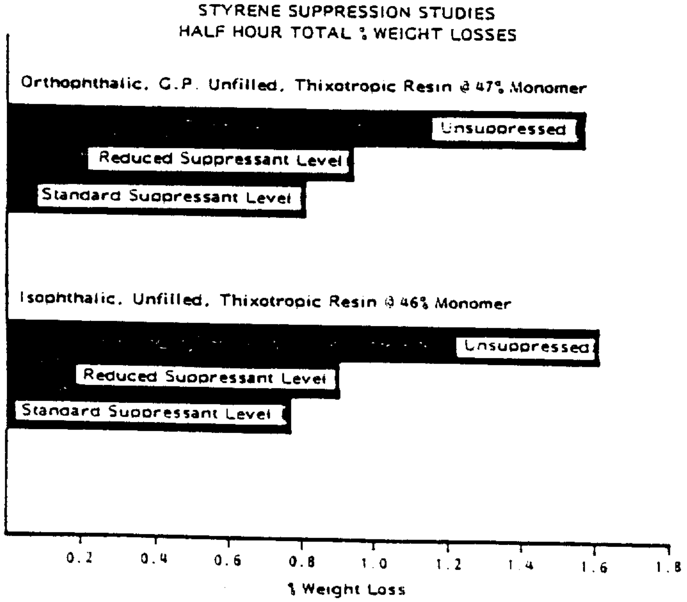


Table 3

STYRENE SUPPRESSION TESTS

% LAMINATE WEIGHT LOSS VERSUS TIME
ORTHOPHTHALIC. G.P. RESIN @ 45% MONOMER
3 PLIES OF 1½ OZ. MAT. 1 FT²

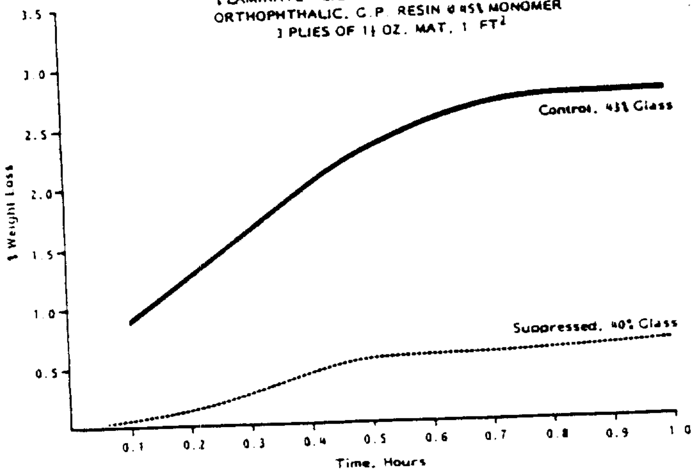


Table 4

STYRENE SUPPRESSED TESTS

% LAMINATE WEIGHT LOSS VERSUS TIME
ORTHOPHTHALIC. G.P. RESIN @ 45% MONOMER
RT GEL TIME APPROXIMATELY 0.4 HOURS
3 PLIES OF 1½ OZ MAT. 1 FT²

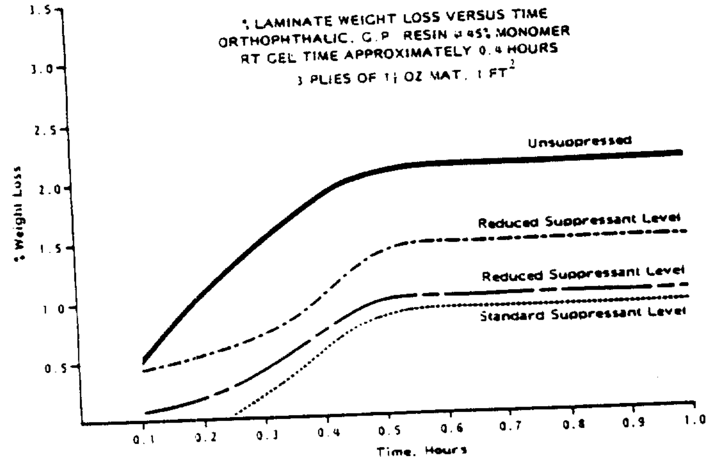


Table 5

% OF INITIAL STYRENE LOSS VERSUS TIME

3 Plies. 1 1/2 oz mat. 1 ft² Laminate
Orthophthalic. G.P. Resins @ 45% Monomer

Time. Hours	Suppressed	Unsuppressed
0.2	0.4	5.0
0.4	0.6	7.8
0.6	1.0	9.8
0.8	1.7	10.5
1.0	1.9	10.5
1.2	2.1	10.5
1.4	2.25	10.5
1.6	2.3	10.5
1.8	2.35	10.5
2.0	2.35	10.5
24.0	2.35	10.5

% Reduction In Monomer Loss ~78

Table 6

THIN FILM SUPPRESSION STUDY

24 Hour % Weight Loss From 10 and 20 Mil
Films Of An Isophthalic. Filament Winding Resin. @ 40% Styrene
Suppressed And Unsuppressed
Resin Catalyzed For A 9 Minute Gel Time

	Unsuppressed		Suppressed	
	10 mil	20 mil	10 mil	20 mil
Wt of Glass Plate. gms	586.8	577.9	613.7	595.5
Wt of Glass Plate - Catalyzed Resin. gms	592.9	588.5	623.3	613.6
Wt of Catalyzed Resin. gms	6.1	10.6	9.6	18.1
24 Hour Wt of Glass Plate - Cured Resin. gms	590.9	585.5	622.7	612.4
24 Hour Wt of Cured Resin. gms	4.1	7.6	9.0	16.9
Wt of Styrene Lost. gms	2.0	3.0	0.6	1.2
% Weight Lost	32.7	28.3	6.3	6.7
% of Initial Styrene Lost (Resin @ 40% Monomer)	82.0	70.8	15.6	16.6

Table 7

THIN FILM SUPPRESSION STUDY

24 HOUR % WEIGHT LOSS FROM 10 AND 20 MIL
FILMS OF AN ISOPHTHALIC. FILAMENT WINDING
RESIN. SUPPRESSED AND UNSUPPRESSED
RESIN CATALYZED FOR A 9 MINUTE GEL TIME

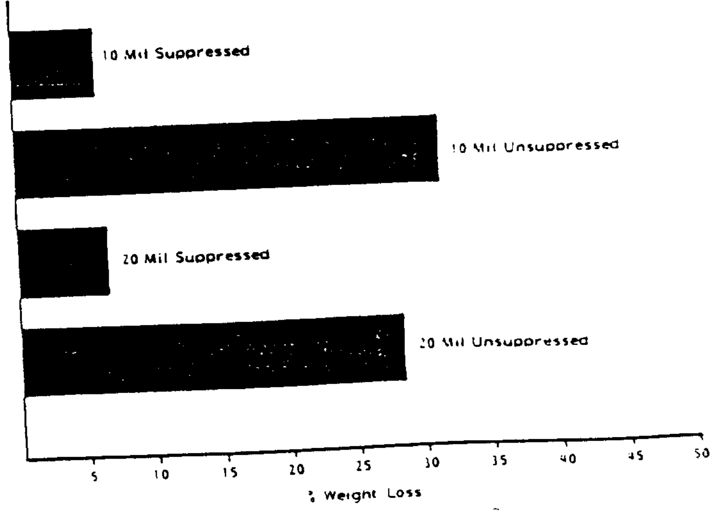


Table 8

24 HOUR THIN FILM SUPPRESSION STUDY

% OF INITIAL STYRENE LOST FROM 10 AND 20 MIL FILMS OF AN ISOPHTHALIC, FILAMENT WINDING RESIN, SUPPRESSED AND UNSUPPRESSED. RESIN CATLAYZED FOR A 9 MINUTE GEL TIME.

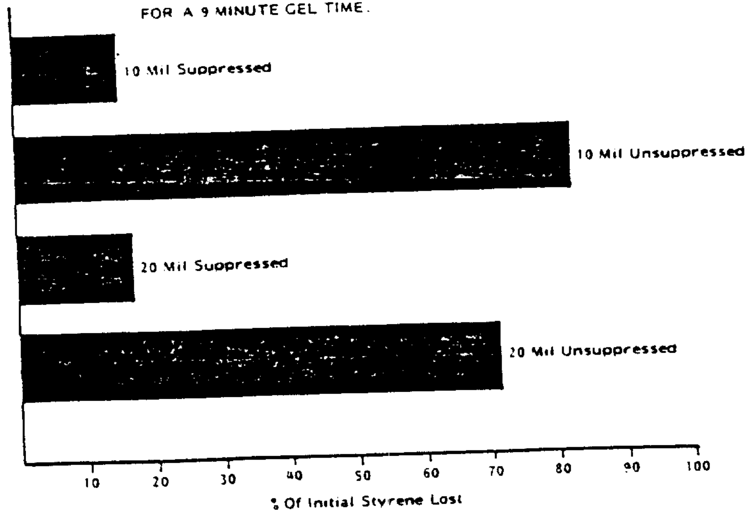


Table 9

FILLED RESIN SUPPRESSION STUDY
RESIN/HYDRATED ALUMINA RATIO 50/50
% WEIGHT LOSS VERSUS TIME

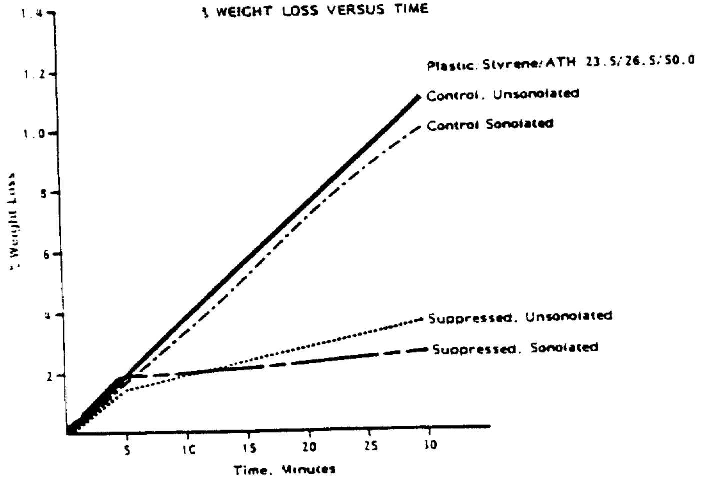


Table 10

INTERLAMINAR ADHESION STUDIES

Lap Shear Tensile Strengths, psi
Second Laminate (3 plies, 1 1/2 oz mat) Overlap Layed Up
1 Hour After First Laminate (3 plies, 1 1/2 oz mat)

	Unsuppressed	Suppressed	% Difference
Resin A @ 29% Monomer	12,290	13,180	+ 7.2
Resin B @ 47% Monomer (Filled w/50% ATH)	8,220	7,420	- 9.7
Resin C @ 44% Monomer	8,270	13,570	+ 64.1

Second Laminate (3 plies, 1 1/2 oz mat) Overlap Layed Up 3 Hours After First Laminate (3 plies, 1 1/2 oz mat)

	Unsuppressed	Suppressed	% Difference
Resin A	7,860	10,510	+ 33.7
Resin B	6,740	6,370	- 5.5
Resin C	13,220	11,650	- 11.9

Table 11

INTERLAMINAR ADHESION STUDY

Lap Shear Tensile Strength (psi)

The first laminate consisted of 15 plies of 24 oz woven roving. After 24 hours, the second laminate of like thickness was applied. An isophthalic, filament winding resin @ 40% monomer was used.

	PSI
Unsuppressed Resin	2,870
Suppressed Resin	2,680
% Difference	- 6.6

Table 12

INTERLAMINAR ADHESION STUDIES

Total laminate consists of two 3-ply 1 1/2 oz mat laminates bonded together. Sample #9 consists of two 6-ply laminates.

	Sample Description	Temp Of Resin & Laminate, °F	Time Between 1st & 2nd Laminate, Hrs	Delamination
1.	8343T-12S	77	1	No
2.	8343T-12S	50	1	Yes
3.	8343T-12S (Repeat)	50	1	No
4.	8343T-12S (One Half Normal Suppressant Level)	50	1	No
5.	8343T-12S (Double Normal Suppressant Level)	50	1	Yes
6.	8343T-12S	1st Laminate At 50 2nd Laminate At 77	24	No
7.	8343T-12S (Double Normal suppressant Level, Styrene Wipe)	77	1	No
8.	8343T-12S (Double Normal Suppressant Level, Acetone Wipe)	77	1	No
9.	8343T-12S (12 Ply 2-6 Ply Laminates)	77	96	No

Table 13

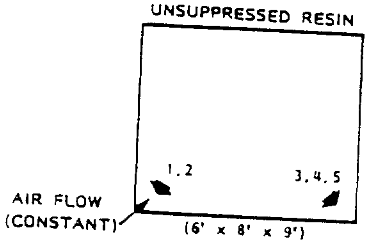
RELATIVE COST SAVINGS/40,000 LBS OF RESIN

1. Unsuppressed Resin @ 0.37/lb = $14,800
   Styrene Loss = 1900 lbs
   1900 lbs of Styrene @ 0.37/lb = $703.00
2. Suppressed Resin @ 0.38/lb = $15,200
   Styrene Loss = 500 lbs
   500 lbs of Styrene @ 0.38/lb = $190.00

Initial price difference between the two resins = $400.00
Additional cost for the unsuppressed resin due to monomer loss = $703.00
Additional cost for the suppressed resin due to monomer loss = $190.00
Additional cost of unsuppresssd less the total additional cost of the suppressed: $703.00 - ($400.00 + $190.00) = $113.00
Cost Savings = $113.00/40,000 lbs of suppressed resin.

Table 14

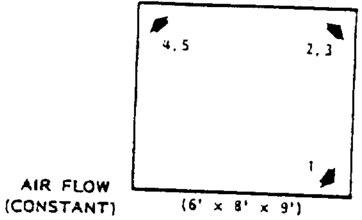
ACTUAL PLANT RUN
UNSUPPRESSED RESIN



Test No.	Location And Description	Styrene Levels, ppm Drager	 Bendix
1.	Readings were taken when rollout was almost completed. About 1 1/2-2 ft from radius.	160	200
2.	Rollout completed. Readings taken about 1 1/2-2 ft from radius.	85	125
3.	Readings taken two minutes after radius was sprayed. 1 1/2-2 ft from radius.	400	500
4.	Ten minutes after spraying. Rollout completed. About 1 1/2-2 ft from radius.	200	400
5.	Readings taken 14 minutes after spraying. Rollout completed. About 1 1/2-2 ft away.	145	100

Table 15

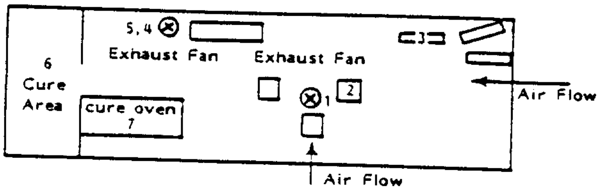
ACTUAL PLANT RUN
SUPPRESSED RESIN



Test No.	Location And Description	Styrene Levels, PPM Bendix
1.	Reading taken when rollout was completed, about 1 ft from radius	20
2.	Reading taken 2 minutes after spraying	60
3.	Reading taken 10 minutes after spraying, 6 inches from radius	20
4.	Reading taken 15-20 seconds after spraying, 2-3 inches from radius	75
5.	Reading taken 6 minutes after spraying. Rollout completed	30

Table 16

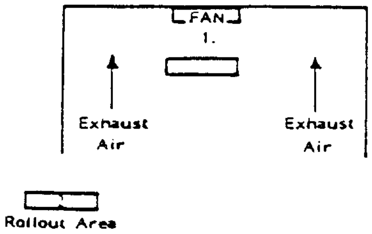
ACTUAL PLANT RUN



Test No.	Location And Description	Control	Suppressed
1.	Spray Station I, under exhaust fan, while units being sprayed	125	200
2.	From back of unit, immediately after rollout	>500	>500
	From back of unit, immediately after first reading	950	200
3.	From top of unit - rollout completed	450	50-60
4.	Behind unit while spraying	100	175
5.	Behind unit during rollout	175	100
6.	Cure area	100	65-70
7.	55°C Cure oven	50	30

Table 17

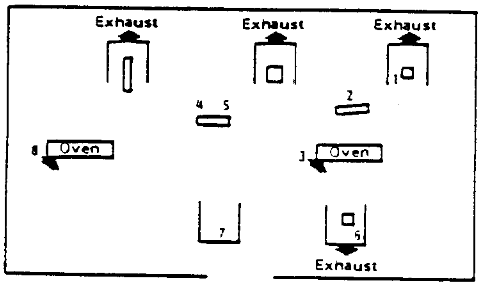
ACTUAL PLANT RUN



Test No.	Location And Description	Styrene Levels, PPM Control Drager	Control Bendix	Suppressed Drager	Suppressed Bendix
1.	Tests run 30-45 seconds after spraying	300	260	180	160
2.	Tests run after rollout was completed. Detector tubes 2-3 inches above unit.	200	250	70	50

Table 18

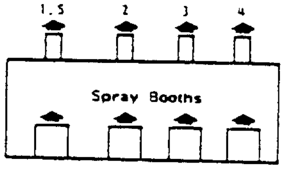
ACTUAL PLANT RUN



Test No.	Location And Description	Styrene Levels, PPM Suppressed	Ashland Suppressed
1.	Inside spray booth, left side, while unit was being sprayed	300	130
2.	From top of unit-rollout completed.	100-130	160
3.	Inside oven, while units passed through	300	200
4.	Top of unit-unrolled	400	400
5.	Top of unit-rollout completed	400	300
6.	Behind unit-sprayed but not rolled	400	200
7.	Back of booth, not running-considered a dead spot	85	60
8.	Inside oven, while units passed through	300	50

Table 19

ACTUAL PLANT RUN
EXHAUST EMISSIONS



Test No.	Location And Description	Styrene Exhaust Emission, PPM Suppressed	Ashland Suppressed
1.	Inside exhaust stack while spraying is going on	100	45
2.	Inside exhaust stack while spraying is going on	250	150
3.	Inside exhaust stack while spraying is going on	300	190
4.	Inside exhaust stack while spraying is going on	225	200
5.	Inside exhaust stack-no spraying is going on	50	10

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

RULE DEVELOPMENT DIVISION

STAFF REPORT

PROPOSED RULE 1162 - POLYESTER RESIN OPERATIONS

January 23, 1987

Prepared by: Moustafa Elsherif
Senior A.Q. Engineer

Reviewed by: David E. Schwien
A.Q. Engineering Manager

Approved by: Larry M. Bowen
Director of Rule Development

I. EXECUTIVE SUMMARY

Proposed Rule 1162 - Polyester Resin Operations (PRO) is designed to reduce Volatile Organic Compound (VOC) emissions from production or rework facilities that use polyester resin.

Polyester resin is a material uniquely capable of meeting a wide variety of specific process and end-product requirements. Products made from this material include boat or yacht hulls, storage tanks, automobile front ends, fishing rods, pools, spas, chairs, shower and tub enclosures, and panels.

For years, the District has looked at the emissions from PRO as a nuisance, primarily because one of the reactants is styrene, a malodorous chemical with a very low odor threshold (0.1 ppm).

Neither the EPA's Control Technique Guidelines (CTG) nor the State Implementation Plan (SIP) addresses the control of VOC emissions from PRO.

Although emissions and reductions of emissions from PRO are not included in the Air Quality Management Plan (AQMP), staff has determined that the total estimated VOC emissions from PRO is 22 tons/day. There are two main sources of VOC emissions: the first is the production process in which a VOC-type monomer, such as styrene (14 tons/day), is used; and the second is the cleaning process in which acetone (8 tons/day) is primarily used as a cleaning solvent.

Staff has determined that this Rule will achieve a total VOC emission reduction of up to 12.6 tons/day (5.6 tons/day from the production process and 7 tons/day from the cleaning process).

Staff has confirmed that compliance with this Rule may be achieved by either modification of the chemical reactants or by the addition of film-forming additives (vapor-suppressed resins). Add-on control equipment such as incinerators, carbon adsorbers, or condensers are technically feasible but are not expected to be economically viable for the majority of polyester resin fabricators. According to the staff's cost analysis, the cost-effectiveness for these three control equipment techniques will vary from $19,000 to $48,000 per ton of VOC emission reduction. The cost of compliance through process changes or additive technology is expected to be minimal if material savings is considered.

The proposed Rule includes exemptions for gel coat use and for use of corrosion-resistant materials (until July 1, 1990), due to the unavailability of low-emission technology. In addition, daily recordkeeping will more than likely be required for all facilities.

II. BACKGROUND

Currently, VOC emissions from PRO are not regulated by the District. Rule 442, which applies in general to the control of VOC emissions from solvents used in production processes, does not apply to PRO. The primary reason for this is the monomer (primarily styrene) used in these processes is considered a raw material and not a solvent. It is polymerized to become a part of the final cured product.

In 1982, a report was published by the Air Resources Board (ARB) based on a study done by Science Application, Inc (SAI). The report discusses California VOC emissions from PRO and various types of control technology. The report recommended that the information obtained through their survey should be incorporated into local emission inventories since no comprehensive detailed inventory of polyester resin operations existed. Also recommended was the use of vapor-suppressant additives and other material changes to control emissions. However, the report failed to address emissions from the use of cleaning materials.

Currently, the Bay Area AQMD, the Shasta County APCD, and the Ventura County APCD have rules for PRO. None of these rules were appropriate for the many diverse PROs in the District. In order to develop a rule suitable for this area, staff held several internal workshops, two public workshops, many individual and group conferences, and made several field observations to evaluate and discuss the current technologies in the polyester resin industry.

III. POLYESTER RESIN OPERATIONS

This section briefly describes the chemistry of polyester resin, the industry structure, the manufacturing process, and the cleanup operation.

A. Chemistry of Polyester Resin

Polyester resin products offer a combination of properties such as: high strength and dimensional stability with low weight; corrosion resistance; excellent dielectric properties; opportunities for parts consolidation and design flexibility; low finish cost; and moderate tooling cost.

The fabrication of polyester resin products requires a complex chemical reaction. A simple introduction will help explain the terms and the processes (please see Appendix A).

There are two types of resins. The first type is general-purpose resins. An example is orthophthalic resins, which are used by the majority of the polyester resin fabricators. These orthophthalic resins are lower-cost resins and they satisfy most of the product specification requirements. The second type is corrosion-resistant resins such as halogenated, bisphenol-A, furan, vinyl ester, and isophthalic. These resins are relatively costly and their unique molecular structures allow them to resist acids, alkalies and solvents.

B. Industry Structure

It is estimated that there are approximately 1000 firms, each with less than 30 employees, conducting polyester resin operations in the District. Most of these companies fabricate their products by spray-up, hand lay-up, and contact-molding types of processes. Approximately 50 firms, with over 30 employees each, are involved in automated processes such as paneling, pultrusion, or filament-winding. In addition to the fabricators, there are estimated to be about 700 rework and repair shops for automobiles, boats and other products.

The total amount of polyester resin materials used throughout the District is approximately 128 million lbs/years (mostly orthophthalic). This includes 7 million lbs/year for corrosion-resistant applications. The amount of acetone used is about 600,000 gals/year. Figure 1 shows the distribution by product and Table 1 shows the amount of polyester resin usage distributed by process.

For spray-up, hand lay-up and contact molding processes, gel coat is the first material to be applied to the mold and becomes the ultimate finish for the product. This gel coat must form a strong chemical bond to the fiberglass laminate. Vapor suppressant additives for the gel coat will make that bonding impossible. Also, sprayable viscosities cannot be achieved at monomer levels less than 35 percent. For these reasons, some provisions of this Rule will not apply to gel coat application.

Fabricators that make corrosion-resistant products are concerned about long-term liabilities associated with their products and must meet rigid performance standards. Currently, the amount of corrosion-resistant materials used in the District is only 7 million pounds per year. Staff believes that 3-5 years are needed to develop modifications of materials to meet the general requirements of the Rule. For these reasons, some provisions of this Rule will not apply to corrosion-resistant applications until 1990.

FIGURE 1

Estimated Resin Used
Distribution by Product

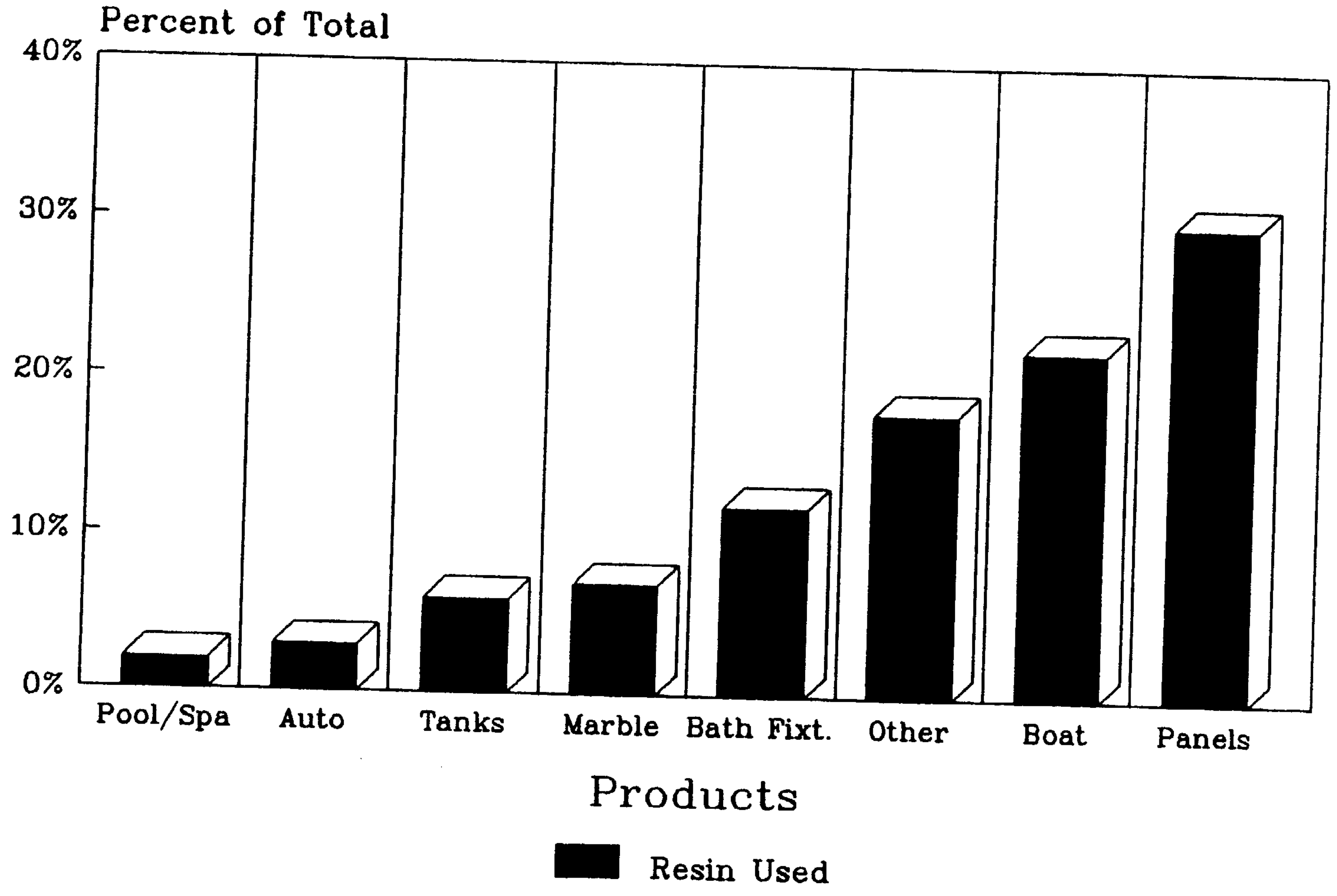


TABLE 1

ESTIMATED SCAQMD POLYESTER RESIN USAGE
(LBS PER YEAR)

CLOSED MOLDING	
BMC, SMC, RESIN APPLIED AT PRESS, INJECTION	3,500,000
OPEN MOLDING	
SPRAY-UP	50,000,000
CONTINUOUS LAMINATION	24,000,000
CASTING	22,500,000
HAND LAY-UP	15,300,000
FILAMENT WINDING	3,400,000
PULTRUSION	1,300,000
OTHER	8,000,000
TOTAL	128,000,000

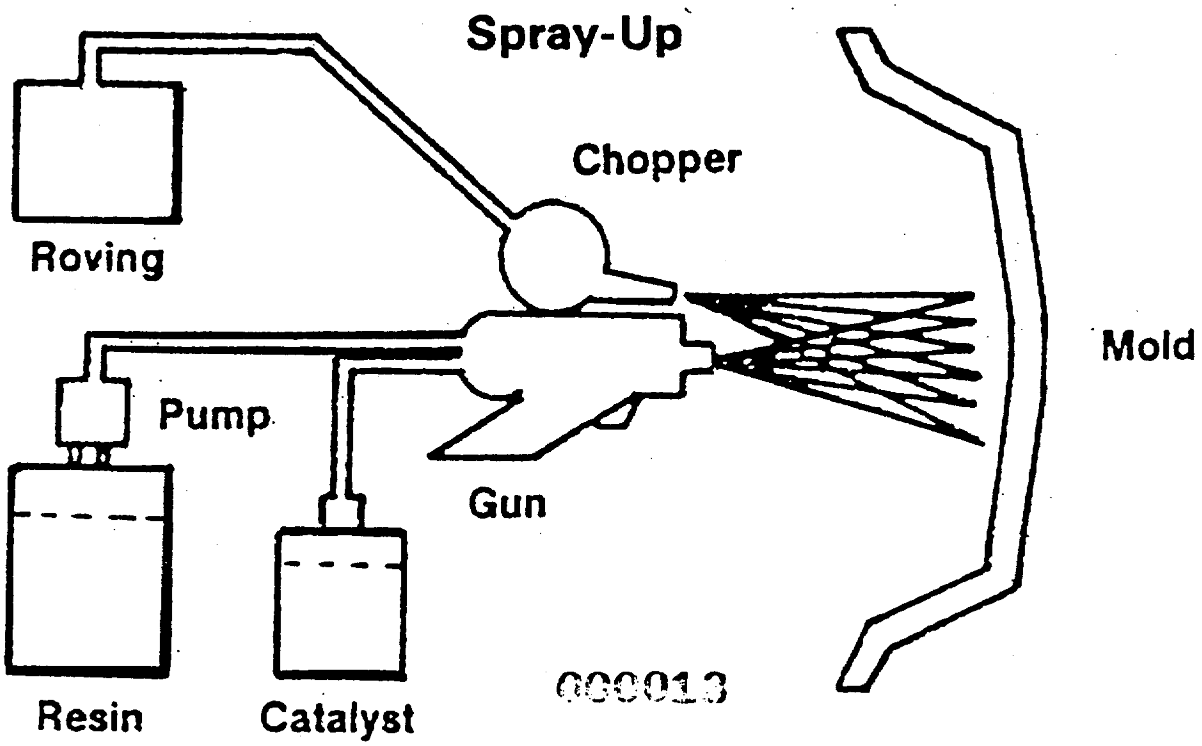
C. Manufacturing Process

In general, there are several production methods used in this industry. A survey of the PRO in the District shows that the simultaneous use of more than one method accounts for the vast majority of resin use. The following are the most common production methods:

1. Spray-up

More than half of the industry uses some form of spray application of resin onto a mold (see Figure 2). Fiberglass roving is fed into a specially designed "chopper gun" which chops the roving into approximately one-inch lengths; the gun simultaneously sprays a predetermined amount of resin and catalyst into the open mold; and the two chemical ingredients are mixed outside the gun as they exit (outside mix) or inside the gun (internal mix). Of all the production methods, the spray-up process has the highest potential for VOC emissions. Atomization of resin creates an enormous surface area of exposed resin, thus enhancing VOC loss through evaporation.

FIGURE 2



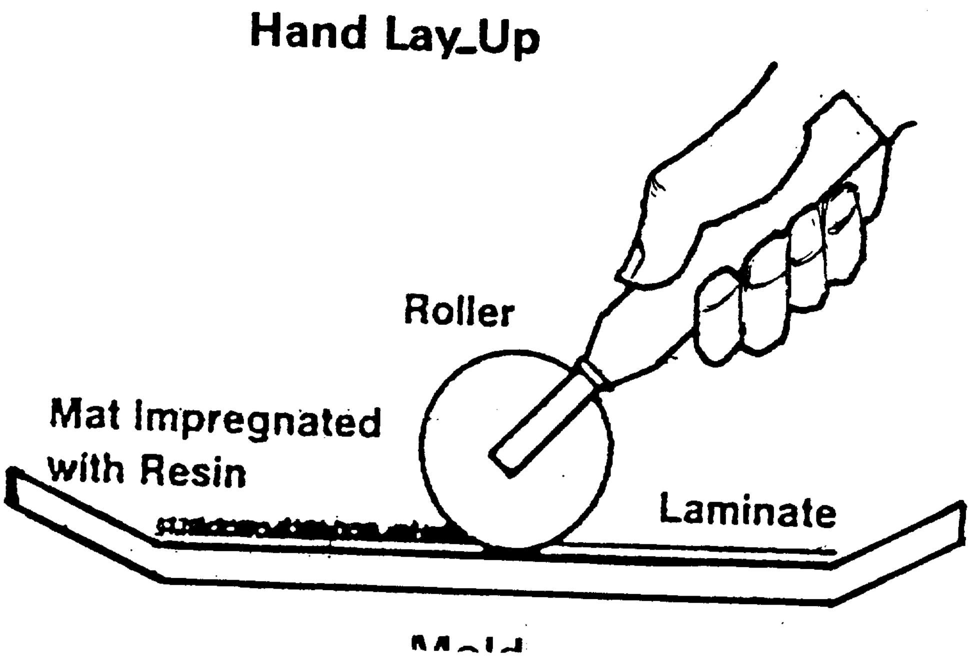
2. Hand Lay-up

This method begins with fitting chopped strands of fiberglass or woven fiberglass roving into an open mold, by hand. Catalyzed resin is then added and "wetted-out" in the fiberglass strands by use of rollers, brushes, or squeegees (see Figure 3). This method produces a higher strength-to-weight ratio product compared to products made with spray-up methods.

A relatively large surface of resin is exposed to the atmosphere for most of the production cycle and helps create a rather high VOC emissions.

A common practice in the industry is to combine spray-up and hand lay-up methods.

FIGURE 3



3. Continuous Lamination

Continuous strand fiberglass rovings are chopped and evenly distributed onto a continuously-moving sheet of cellophane or other type of non-adhering plastic sheeting (see Figure 4). The chopped glass layer is then saturated with pre-catalyzed resin and covered with a second sheet of cellophane. The glass/resin composite sandwiched between the cellophane sheeting is then pulled through a forming die and passed through a curing oven. The emerging cured panel is then stripped of its cellophane covering, trimmed along the edges, and cut to the desired length. The VOC emission per unit weight of product is not high because most of the process that has a potential to emit VOC is contained within the top and bottom cellophane sheets.

FIGURE 4

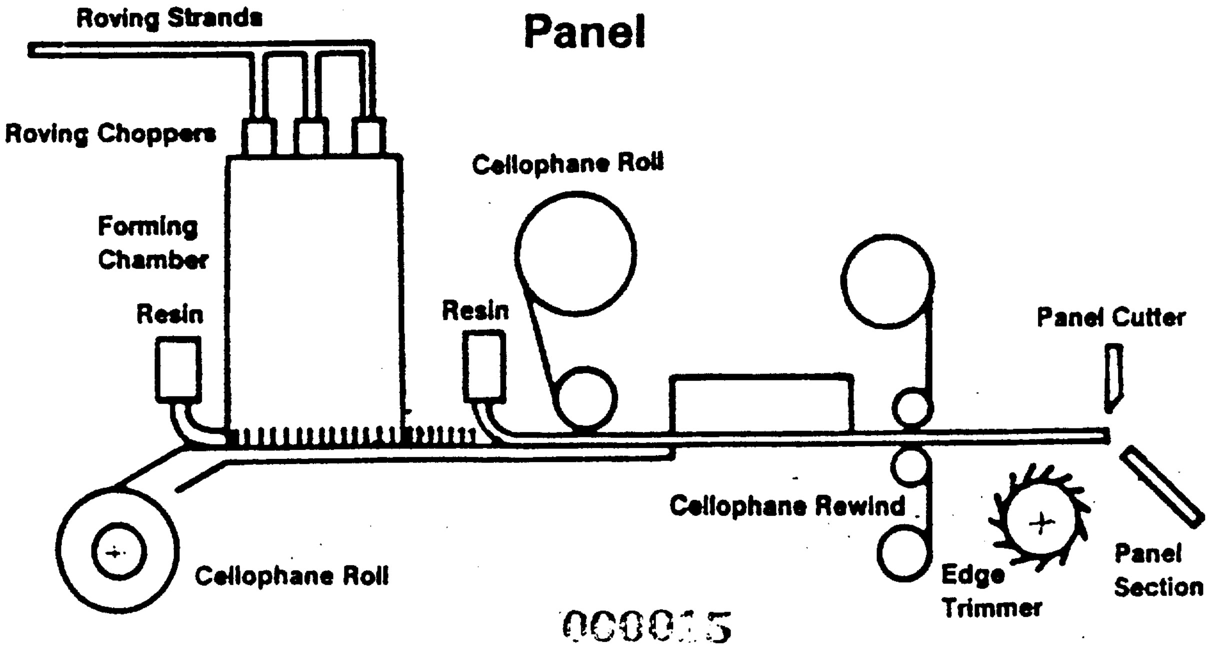
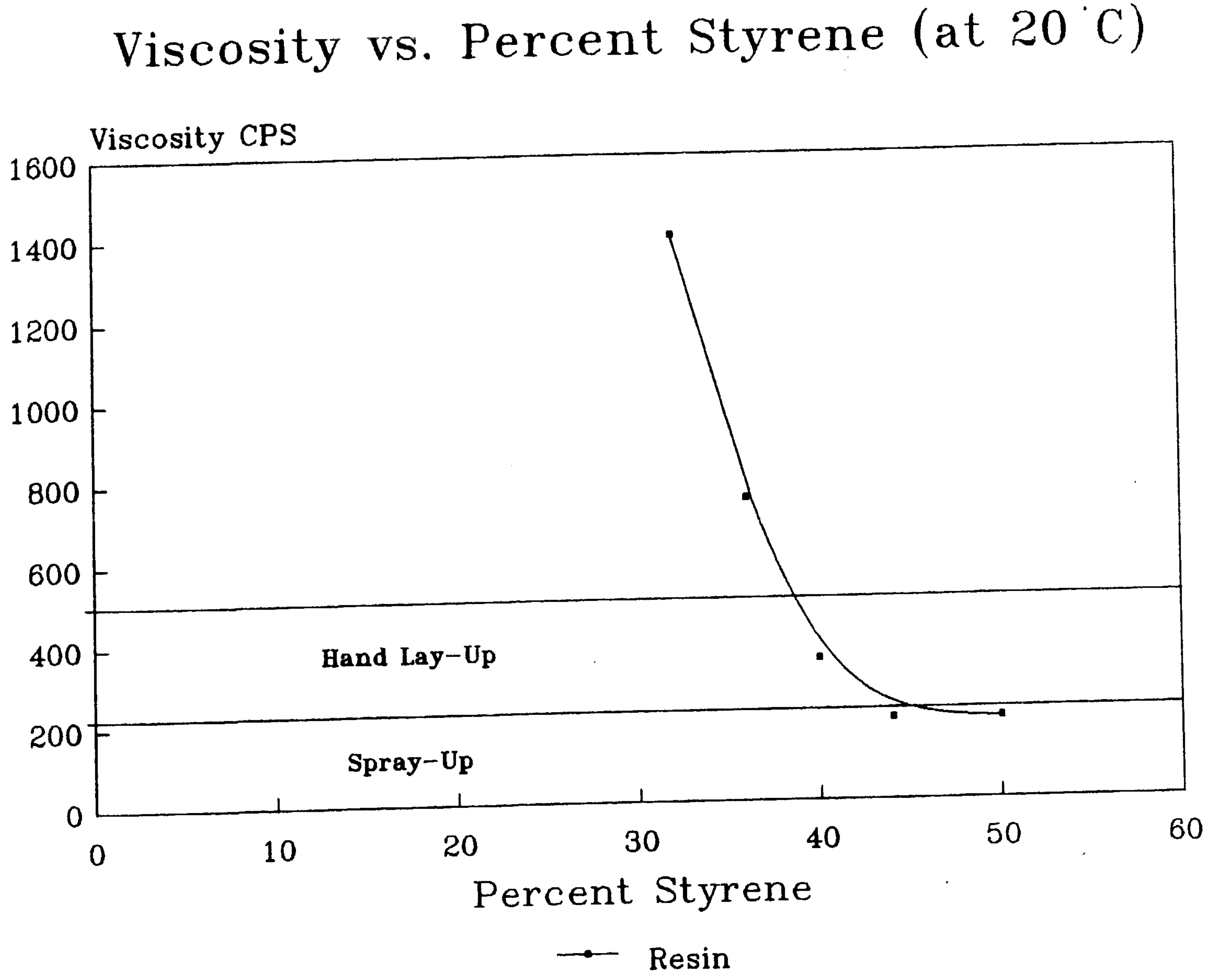


FIGURE 12

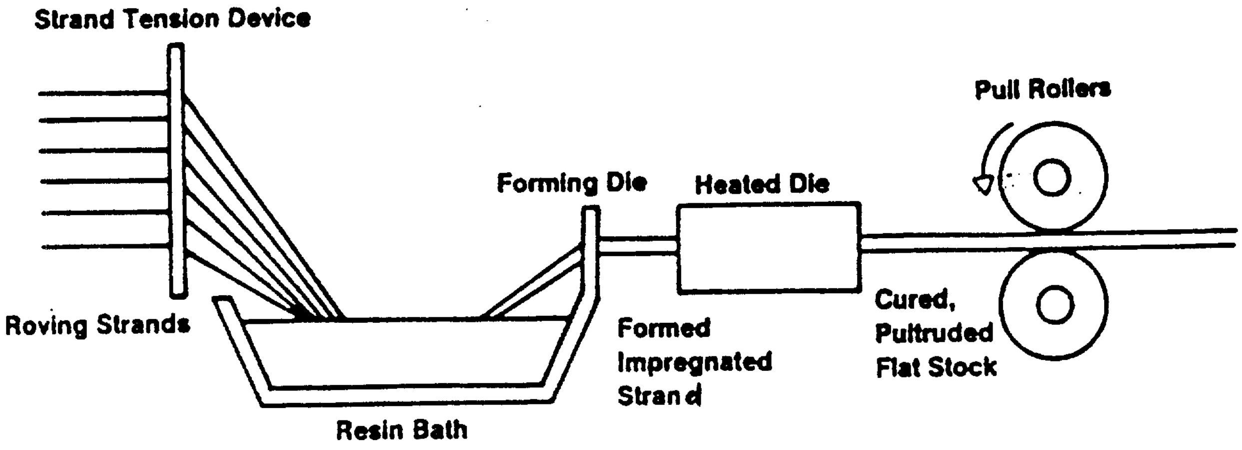

Viscosity vs. Percent Styrene (at 20°C)
Viscosity CPS
1600
1400
1200
1000
800
600
400
200
0
Hand Lay-Up
Spray-Up
0
10
20
30
40
50
60
Percent Styrene
Resin

5. Pultrusion

Continuous roving strands are pulled from a creel through a strand-tensioning device into a resin bath (see Figure 6). When thoroughly impregnated, the formed resin/glass composite is then passed through a heated die. The finished cured resin/glass stock is then cut to the desired length and packaged. The main VOC emission source is the open resin bath, since curing (also a source of VOC emissions) takes place in the enclosed die.

FIGURE 6

Pultrusion

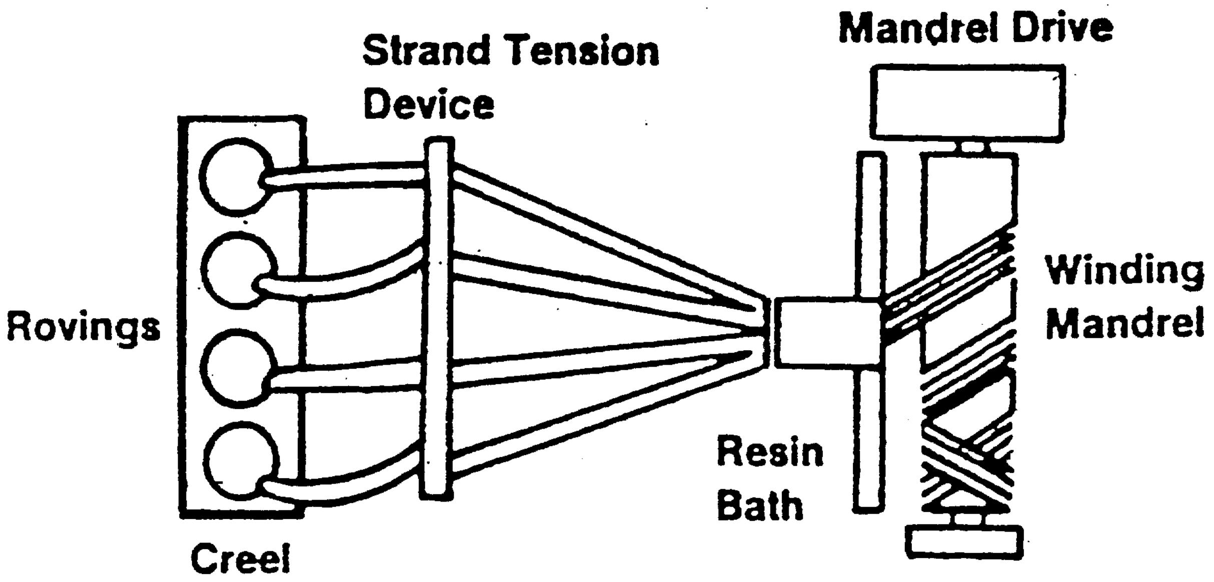


6. Filament Winding

This method is becoming increasingly popular for the manufacture of large pipes, storage tanks, and other hollow vessels which may be subject to great internal pressure (see Figure 7). Continuous strand rovings are pulled by a rotating mandrel through a strand tensioning device into a resin bath. Emerging from the resin bath, the strands, each uniformly coated, are wound onto a mandrel to the shape and pattern required for the finished product. The unit is then cured in an oven or at room temperature. The requirement for low-resin viscosity often implies the use of higher monomer concentration, causing a moderate VOC emission.

FIGURE 7

Filament Winding



D. Cleanup Operation

Cleanup of hands, tools, and spray guns is a very important part of the production cycle. Hands, brushes, rollers, and squeegees must be cleaned with a solvent (usually acetone) after applying each batch of resin. Also, spray guns must be flushed with solvent after each use and throughly cleaned daily. This cleaning prevents resin from curing on the tools and in the guns, thus rendering them unusable.

Cleaning solvent is usually available in 2-gallon containers for hand cleaning, 5-gallon containers for tool cleaning and 3- to 5-gallon containers for spray gun cleaning. Also, most resin guns have a clean solvent-supply line connected directly to the gun to flush the internal parts after each use.

IV. EMISSIONS

There are generally two major sources of VOC emissions from PRO: the resin used in the manufacturing processes and the solvent from the cleanup operations during and after the manufacturing processes.

A. Emissions From the Manufacturing Process

VOC emissions will depend on the amount of materials used, the type of products made, manufacturing methods, and business activity. The most common monomer used is styrene. Evaporation of styrene from gel coat or resin during the raw material-application process and during the curing period is the main source of VOC emissions. It is estimated that up to 10 percent of the resin is lost as overspray or by evaporation during the raw material application process. In addition, up to 8 percent of the styrene monomer in the applied resin or gel coat evaporates before polymerization is complete. There are many other factors that impact the styrene evaporation, such as gel time, temperature, and air flow. Figures 8, 9, and 10 show the amount of VOC emissions with each factor.

Staff has determined that the static laboratory test methods for measuring VOC emissions from the polyester resin materials are the best and most consistent methods available.

B. Emissions From the Cleaning Process

Cleaning solvent emissions typically account for more than 36 percent of the total plant VOC emissions. These emissions are due to the evaporation of solvent from the parts being cleaned, from atomization of solvent, from agitation of the solvent during the cleanup process, from storage of solvent in open containers, and from improper disposal of waste materials.

The number of employees applying the resin directly affects total solvent emissions because each employee must clean his hands, tools, and spray gun.

FIGURE 8

Influence of Gel Time on Styrene Emissions

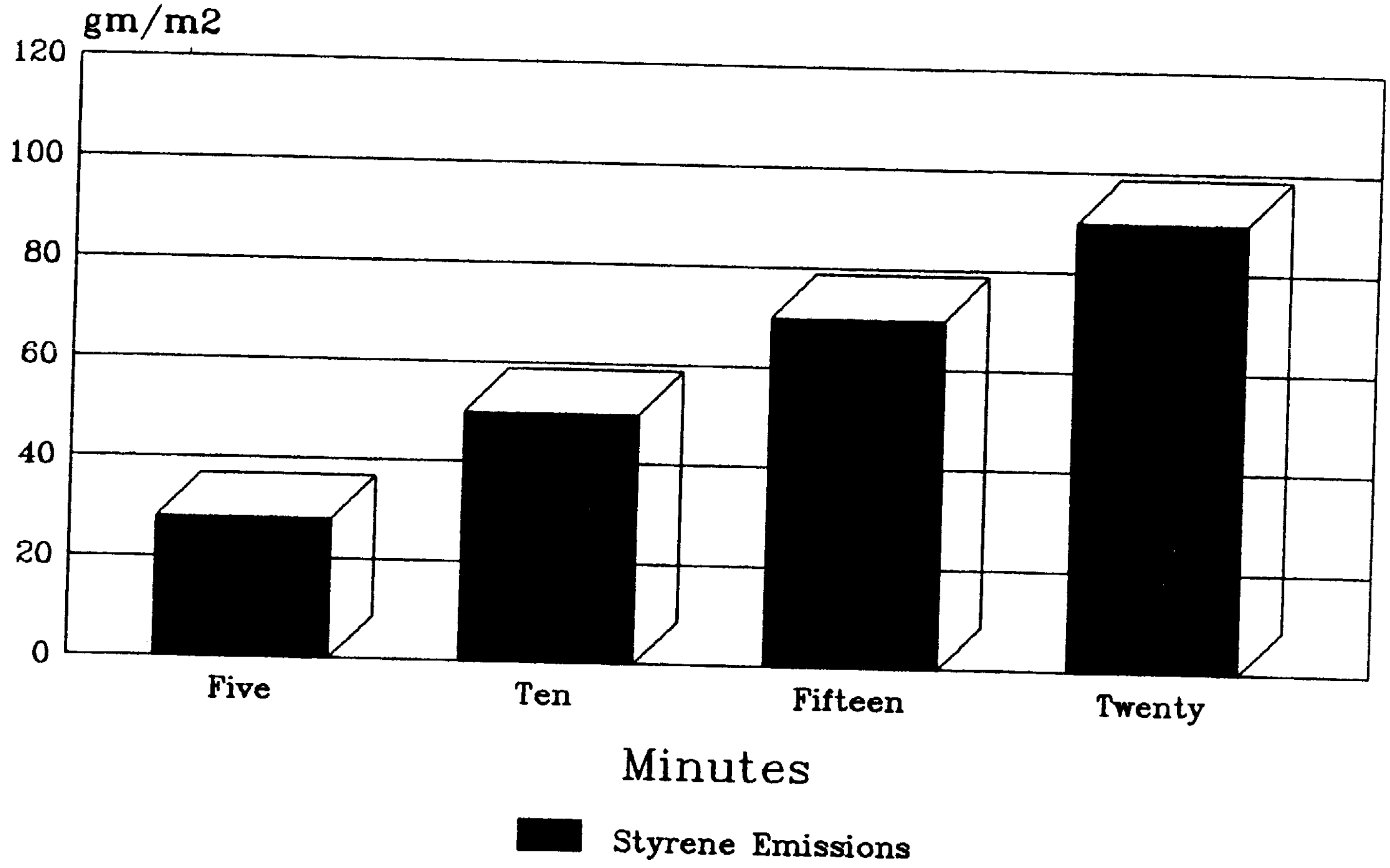


FIGURE 9

Influence of Temperature on Styrene Emissions

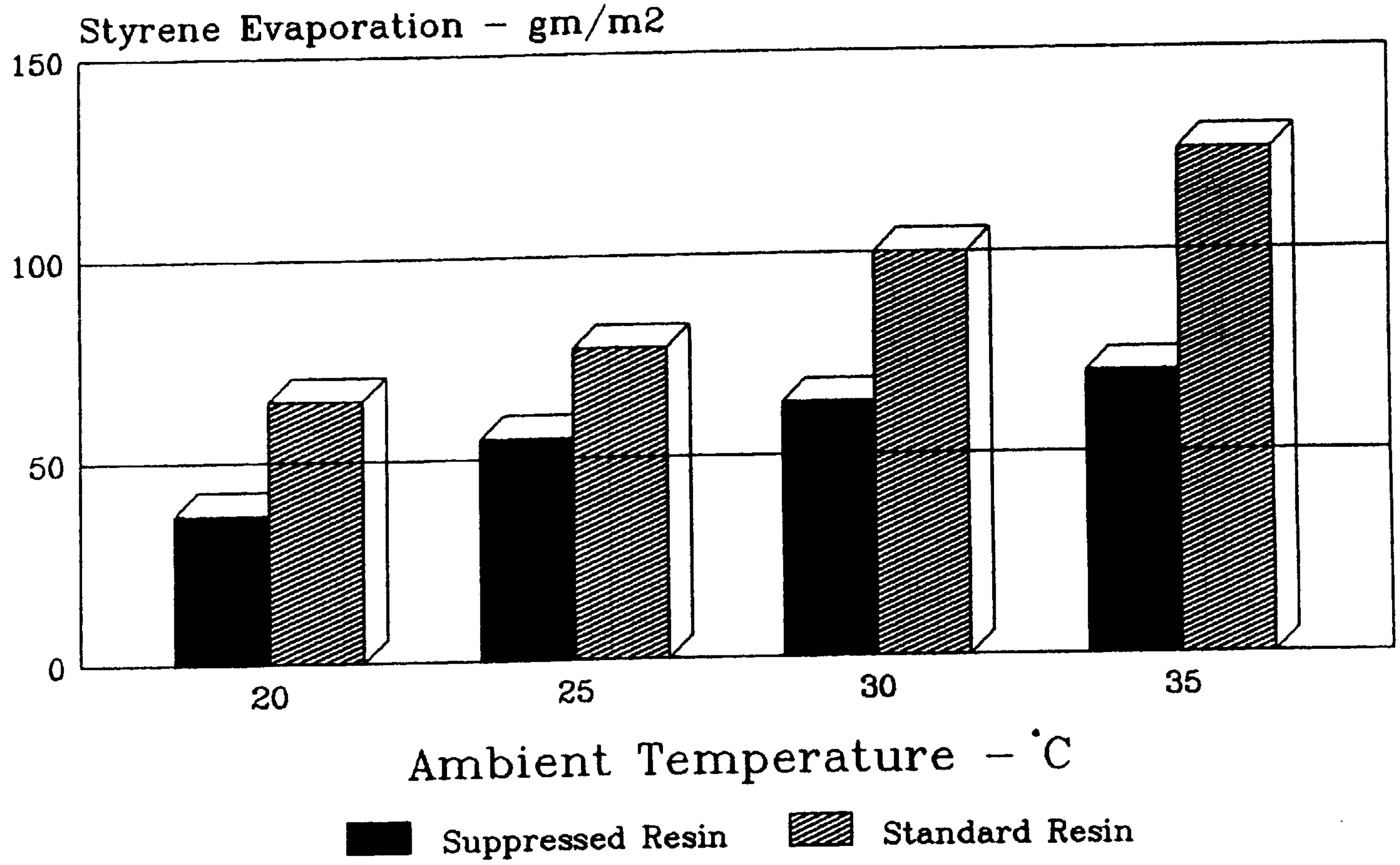
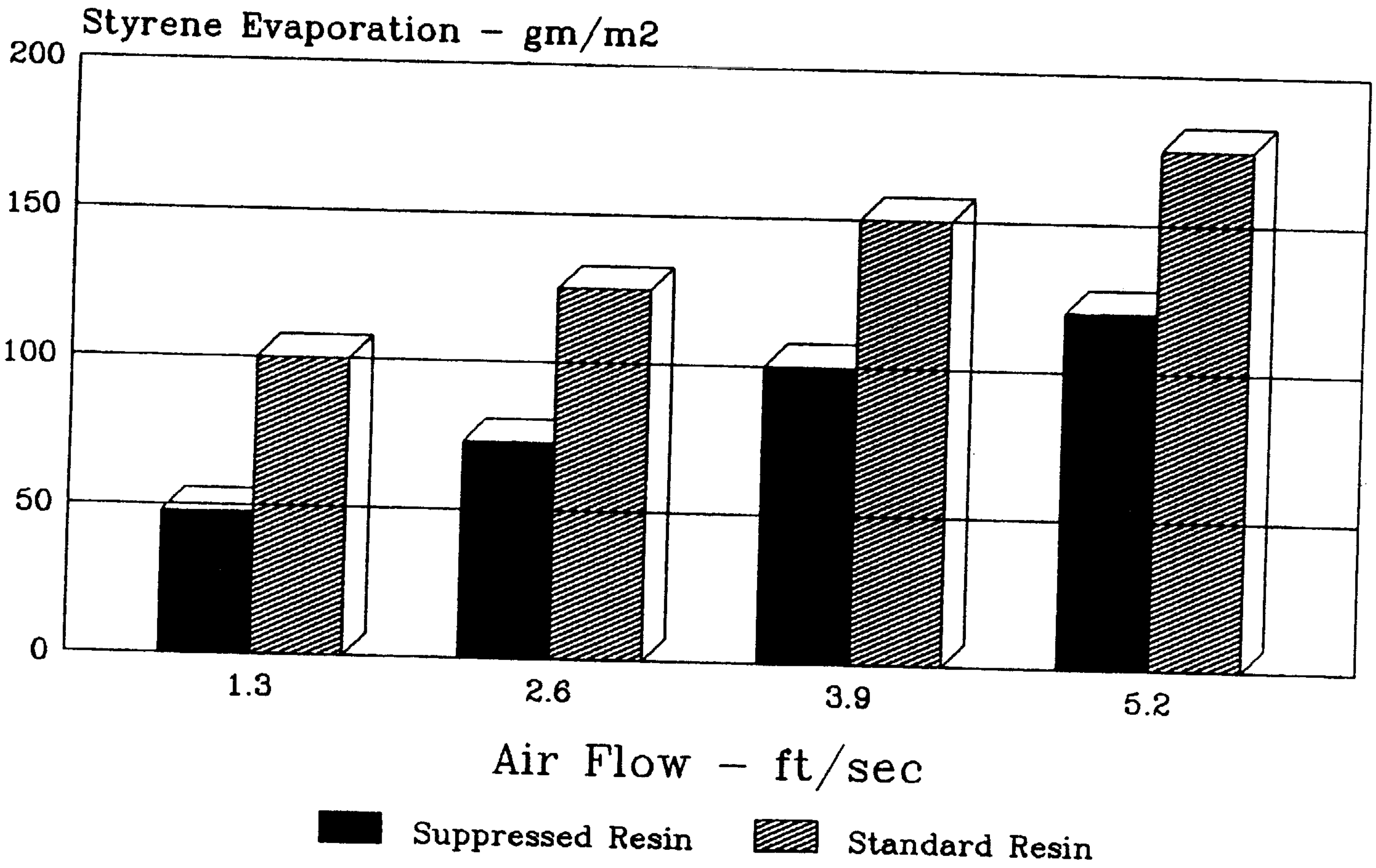


FIGURE 10

Influence of Air Flow Rate
on
Styrene Emissions



V. EMISSION CONTROL TECHNIQUES

The three control techniques are: process changes to control monomer emissions, material changes for control of acetone emissions, and add-on control equipment.

A. Process Changes

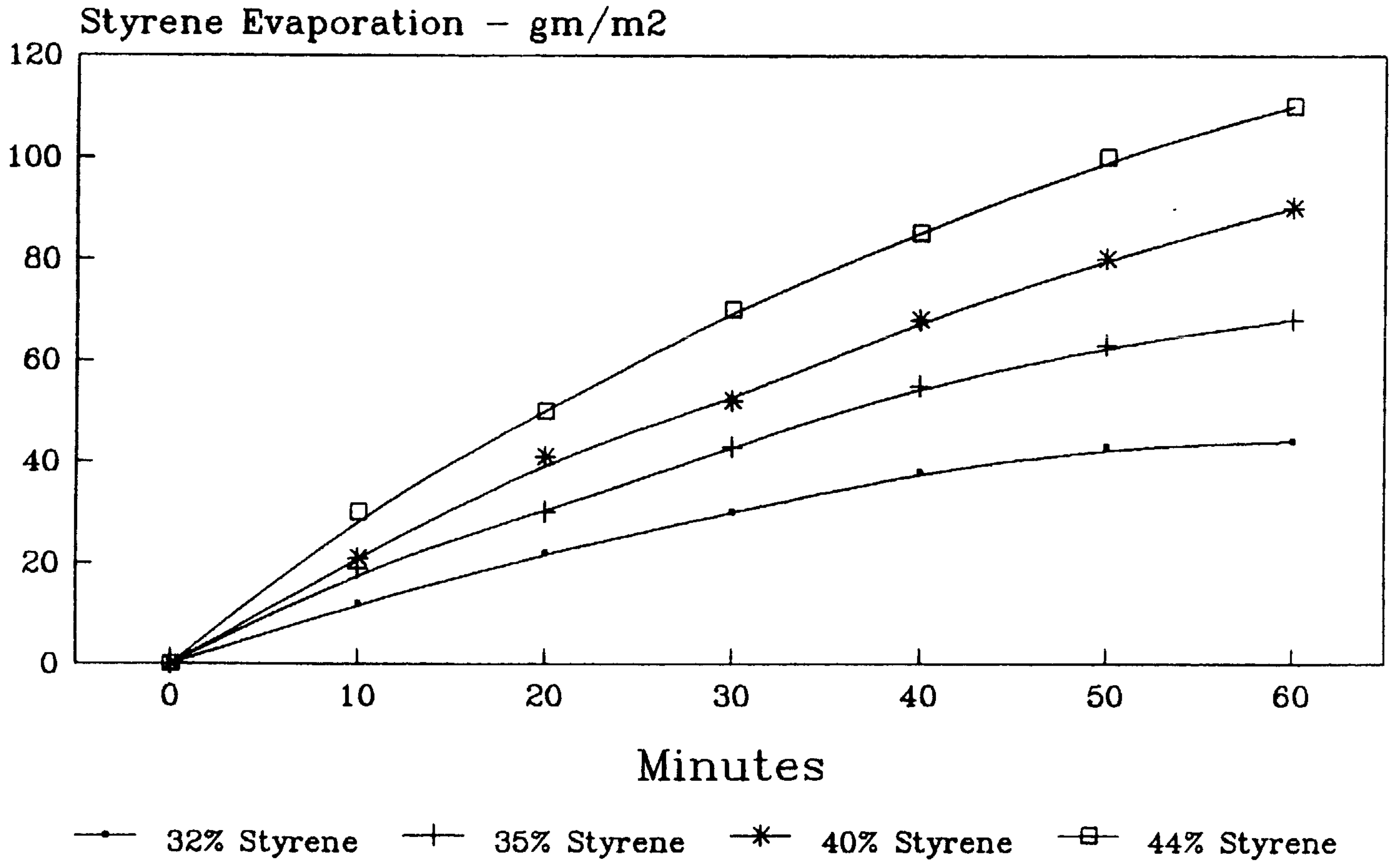
1. Modifications to Material

Reducing the resin content can reduce the emissions. This can be accomplished by either redesigning the products to require less resin or using more fillers and colorants. Most of the time, however, it is difficult to achieve the desired product properties by reducing the resin content.

The conversion to low-monomer-type resins (35-weight percent) compared to the conventional resins (40- to 50-weight percent) is a viable method for the control of some of the emission problems previously described (see Figure 11). Several companies have been marketing such resins for several years. The cost of low-monomer resins is slightly higher than the cost of conventional resins. The reduction in total styrene emissions can reach 40 percent, by weight, when a conventional resin is replaced by a low-styrene resin.

FIGURE 11

Influence of Styrene Content
on
Styrene Emissions



Another emission reduction option is to reduce the resin molecular weight to the point where resin, at only 35 percent styrene, would exhibit a low enough viscosity to readily wet the reinforcement materials. Unfortunately, resin with low monomer content might be unacceptable for the manufacture of some products because the resin would be more viscous and difficult to spray, mold, or inject (see Figure 12). Also, reduction in molecular weight usually is accomplished by a corresponding loss of desired properties (mechanical or physical) which also could severely limit the acceptability of some products.

Recently, a modified photoinitiator polyester resin was developed, but it is still under analysis. The new photoinitiator resin is a one-component resin which cures without additives when exposed to long-wave ultraviolet light. The most significant advantage of this system is the rapid curing (less gel time). In addition, the cure develops from the outside, which greatly limits styrene evaporation. Additional advantages are:

- a rapid and controlled rate of cure.
- no mixing and metering of raw materials is required.
- there is minimal waste from unused resin.
- less cleaning is needed between resin applications.

The initial testing of this modified resin shows a 40 percent reduction in emissions compared to the emissions from the conventional resins. This photoinitiator additive could be used to produce most of the polyester resin products that are up to one-inch thick.

A final option is the replacement of part or all of the styrene with another monomer. The search for such a monomer has been the subject of research by many companies for some time. The ideal material, of course, is a monomer with all of the desirable qualities of styrene (good thinning capacity, good mechanical properties, and ease of polymerzation); and one which is a low-VOC emitter, and is cost-effective as a styrene substitute.

2. Suppressed Resins

The most promising technology today for reducing VOC emissions is the use of suppressed resins. These resins decrease VOC emissions by entrapping some of the monomer that would otherwise vaporize during the exothermic curing of the resin (see Figure 13). The suppressing agent consists of paraffin or wax-like materials that are added to the polyester resin. The paraffin builds a film on the surface of the laminate which physically blocks the polymer surface from oxygen in the air and at the same time reduces styrene evaporation.

FIGURE 12

Viscosity vs. Percent Styrene (at 20 °C)

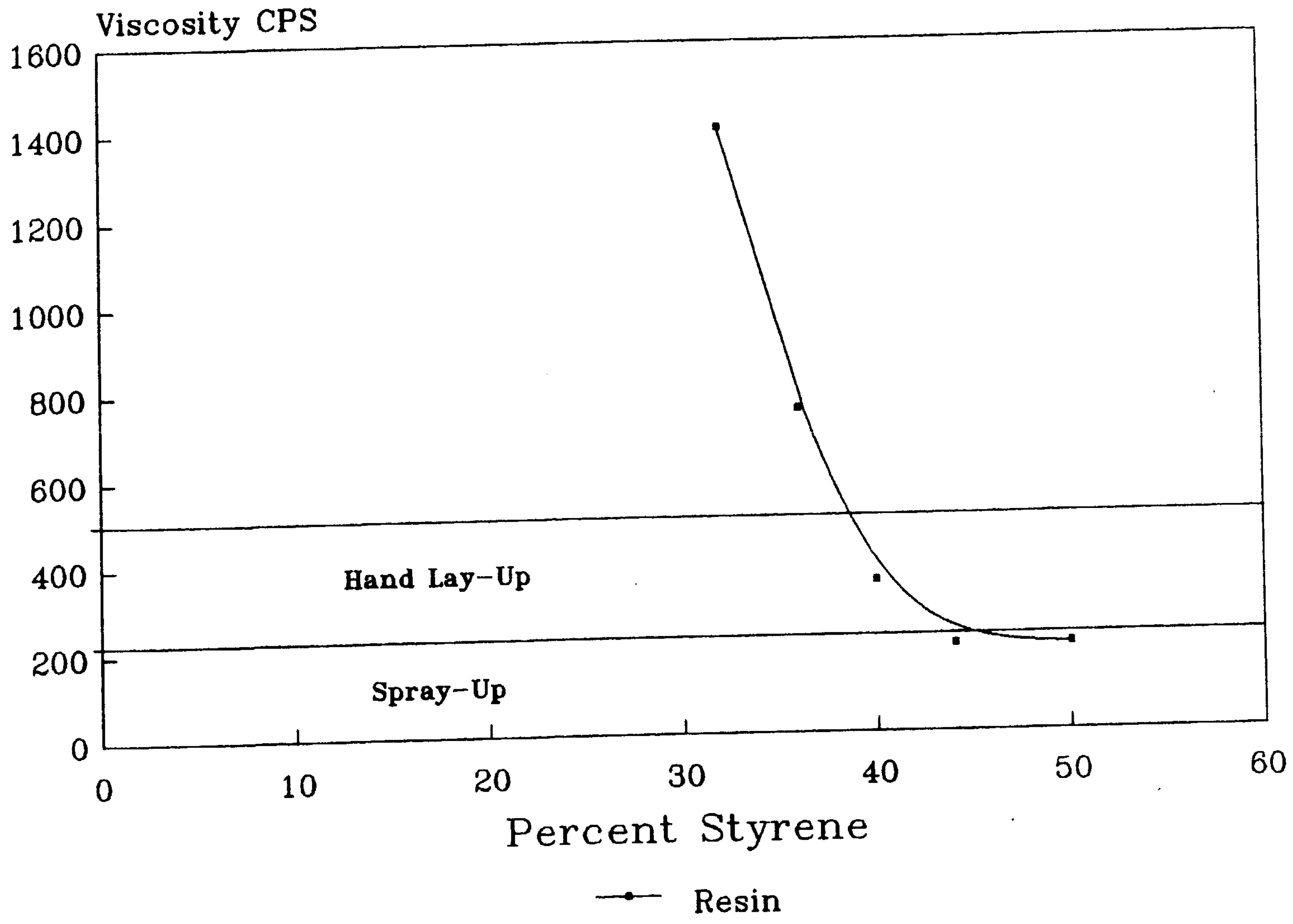
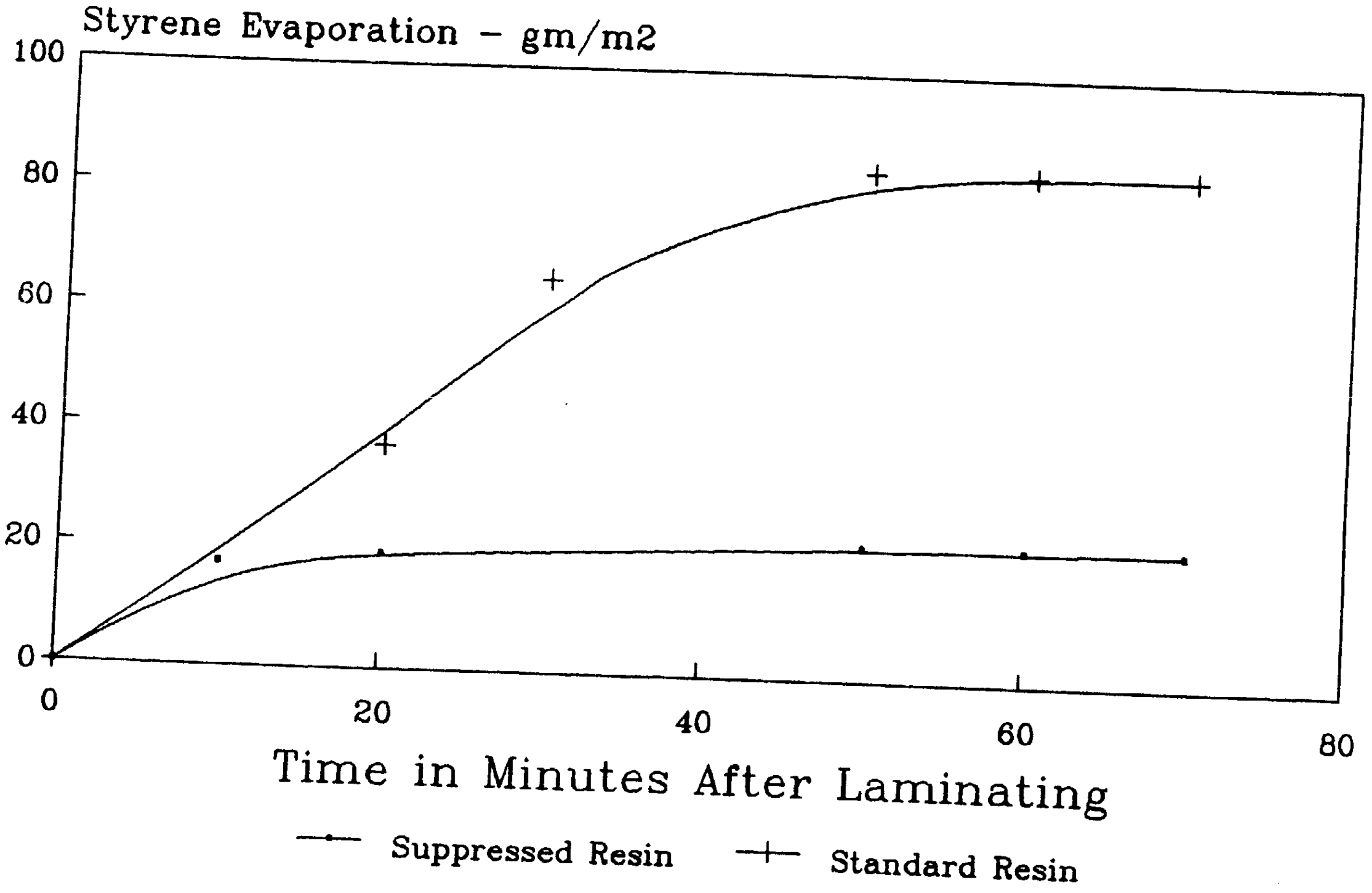


FIGURE 13

Comparison of Suppressed Resin
and
Standard Resin



Suppressed resins will reduce VOC emissions by about 40 percent, by weight. These resins are priced slightly higher than the conventional resins. However, suppressed resins will achieve material savings which should offset the difference in price. Different brands of suppressed resins vary in performance and method of suppression. (More specific information is unavailable due to claims of confidentiality.) Presently, a few manufacturers have experienced difficulty with delamination, a separation between layers of applied resin. This happens because the suppressed resin leaves a thin film of wax on the surface which can be detrimental to the adhesion of a subsequent lamination.

3. Closed-Mold Process

Use of a closed-mold process is an excellent way to reduce styrene emissions. Some of these processes are the Resin-Transfer Molding (RTM) process, the Sheet-Molding Compound (SMC) process, and the Bulk-Molding Compound (BMC) process. These processes are used only for small-size products.

B. Clean-up Solvent (Acetone) Emission Reductions

Three methods to reduce acetone emissions are: correction of employee work habits, reclamation of spent acetone, and use of solvent substitutes.

1. Correction of Employee Work Habits.

Acetone is usually available for each employee in a 2-gallon container for hand cleaning, a 5-gallon container for tool cleaning, and a 5-gallon container for spray-gun cleaning. Also, most spray guns have a clean-acetone feed line to flush the internal parts after each use.

Unfortunately, many fabricators' practices and work habits when handling and using acetone are less than ideal. Limiting the issuance of acetone to the employee, and proper training and diligent supervision with regard to the proper use and handling of acetone, will reduce solvent emissions.

2. Reclamation of Spent Acetone

There are two options for the control of spent-acetone emissions: on-site recovery or off-site recovery at a commercial solvent reclaiming facility; both offer economic and environmental benefits.

Some manufacturers simply dispose of spent acetone by allowing it to sit in open containers and evaporate. On-site acetone reclamation through the use of a distillation unit can reduce this loss. These units are available in different sizes in order to be compatible with the needs of various PRO. These units come completely assembled and can recover 90 to 97 percent of the solvent that otherwise is lost. This approach should help reduce the problems associated with the storage of dirty solvents.

Some polyester resin manufacturers dispose of spent acetone at an off-site dump. This will contribute to VOC emissions at the dump site. Spent acetone can be sent to commercial facilities that specialize in reclaiming acetone as well as other solvents. An additional benefit of this method is that the polyester resin fabricator can also have the off-site reclamation facility dispose of solid waste included in the spent acetone.

3. Use of Solvent Substitutes

Polyester resin material manufacturers have recently developed low-VOC, water-based materials to replace acetone for cleaning hands, tools, and spray equipment. These types of materials are now successfully used by most of the fabricators. However, acetone is usually used in small quantities to dip tools and spray equipment for a final cleaning in order to remove the water from the item being cleaned.

Work is ongoing to improve the new solvent substitute products and to eliminate the final use of acetone.

C. Add-on Controls

Four types of add-on control equipment were investigated: incineration, absorption, adsorption, and condensation.

1. Incineration

Thermal or catalytic incinerators are available to control emissions from spray booths, ovens and room exhausts.

In a thermal incinerator the solvent-laden air is exposed to a temperature of 1000° to 1500°F and direct flame contact for a period of 0.3 to 0.6 seconds. In the catalytic incinerator the operating temperatures are 600° to 750°F lower. In either case, the important incineration design factors are: waste gas stream flow rate, residence time, temperature, and waste gas heat content. Both incinerators can be designed to achieve 90 to 99 percent removal efficiency. However, within the District, incinerators have not, in general, been used as emission-control devices in the PRO. (One fabricator uses incineration only when the VOC emissions exceed a certain limit so it can comply with Regulation XIII, New Source Review.) Incineration is most effective when the pollutant to be controlled is at a high concentration and has a high heating value. Typically, polyester resin operations have flows. These conditions result in low heat content exhaust streams, thus leading to high supplemental fuel requirements and increasing operating costs. Therefore, incineration is not usually economically feasible for most PRO.

2. Absorption

Through the use of absorption, acetone and styrene emissions are removed from the exhausting contaminated air stream by direct contact with a liquid. The absorption takes place by a chemical reaction with one or more components, sodium hydroxide or a mixture of sodium hydroxide and sodium hypochlorite, in the water-based liquid. The estimated control efficiency is at least 70 percent.

Absorption has not been used to control styrene and acetone emissions in the District. Further investigation and testing would have to be done to determine its applicability for the PRO; as a part of this, the impact of the resulting liquid and solid waste disposal would have to be determined.

3. Adsorption

Carbon adsorption is a common control technique for removing VOC emissions from an air stream. When the carbon reaches the saturation point, hot air or steam is used to regenerate the adsorbent carbon. However, 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. Also, the presence of acetone emissions in the air stream could reduce the adsorption efficiency, since acetone has a relatively high heat of adsorption, thereby, system effectiveness is reduced when the temperature rises. In addition, particulate matter generated in the process can clog the adsorbent, thereby reducing its effectiveness and increasing the pressure drop through the system.

4. Condensation

There are two types of condensers. The first type is a surface condenser where exhaust air stream is cooled with a fluid, but does not come into direct contact with the air. The second type is a contact condenser where the exhaust air stream is sprayed with a chilled liquid. Both types are generally not practical because most PRO exhausts have VOC concentrations below 1000 ppm, and condensers work effectively with higher-VOC streams.

V. COST ANALYSIS

While all the emission control techniques described in this report are, in principle, applicable to most of the polyester resin fabricators, their implementation costs vary considerably.

The total capital costs listed below were based on vendor prices of the basic equipment and accessories. Unit electricity and natural gas cost were obtained from Southern California Edison Company and Southern California Gas Company, respectively.

A typical polyester resin fabricator was selected for this cost analysis study. Three control-equipment scenarios were evaluated.

A. Materials Used

Polyester Resin	900 Lb/Day
Gel Coat	100 Lb/Day
Monomer Percent (Styrene)	45%
Acetone	10 Gal/Day
Spent Acetone	4 Gal/Day
Manufacturing Process	Combination of Spray-Up and Hand Lay-Up.
Operating Time	8 Hr/Day, 5 Days/Wk, 52 Wks/Yr.
Emission Factor	Use 0.10 pound of VOC lost per pound of resin used.

B. Control Equipment

Incineration	90% Efficiency
Adsorption	70% Efficiency
Absorption	70% Efficiency
Interest Rate	10%
Equipment Life	15 Years

C. Operating Cost

Labor	$10.00 Hr
Electricity	$ 0.08 Kwh
Gas	$ 6.47 MM Btu
Maintenance, Tax & Ins.	11% of Installation Capital
Styrene	$ 0.85 Lb
Acetone	$1.25 Lb

Based on the above assumptions, the cost-effectiveness is as follows:

A. Control Equipment

1. Incineration Cost

The estimated annual operating cost is:

Capital Cost	$195,000
Labor	3,000
Gas	700,000
Electricity	12,000
50% Heat Recovery Credit	-350,000
Net	$560,000

With a reduction of approximately 11.7 tons per year, the cost-effectiveness would be about $48,000 per/ton.

2. Carbon Adsorption Cost

The estimated annualized cost is:

Capital Cost	$190,000
Carbon	14,000
Labor	2,000
Steam	1,000
Electricity	25,000
Total	$232,000

With reduction of approximately 9.0 tons per year, the cost-effectiveness would be about $26,000 per/ton.

3. Absorption Cost

The estimated annual operating cost is:

Capital Cost	$150,000
Labor	16,000
Electricity	9,000
	$175,000

With reduction of approximately 9.0 tons per year, the cost-effectiveness would be about $19,000 per/ton.

4. Spent Acetone Reclamation Cost

Spent Acetone Generated	8300 Gal/Year
Cost Credit for Recycling	$0.40 per gallon of acetone recycled
Annual Savings	$3,300
Acetone Recovered	(90% Recovery)

Recycling yields a cost savings of about $134/Tons. In other words, it will pay for itself in less than one year.

B. Good Housekeeping

Good housekeeping and employee training are good low-price-control techniques for reducing VOC emissions from PRO. Staff found, during several field inspections, that most fabricators' practices and work habits are less than ideal. Most of the problems are in the area of resin spraying and materials handling and are readily correctable with proper employee training and diligent supervision.

The use of closed containers for storing fresh and spent cleaning materials and waste polyester-resin materials reduces evaporation losses and also reduces odor problems.

Improved housekeeping practices will result in a cost saving to the fabricators by the elimination of unnecessary evaporation loss.

C. Materials Modification Costs

The most promising materials modification methods for reducing VOC emissions from the polyester resin operations are:

1. Use of low monomer polyester resin materials.

2. Use of vapor suppressant.
3. Use of resins with a lower molecular weight.
4. Use of photoinitiator polyester resins.
5. Replacement of styrene with other low-VOC materials.

All of the above approaches are cost-effective; however, to be sure that the use of such materials in some products is not accompanied by a corresponding loss of desired properties, additional research and development is required.

VI. SIGNIFICANT IMPACTS

A. Energy Impact

The energy impact will be minimal. The majority of the fabricators will comply by reformulating materials and will not consume additional amounts of energy or generate additional wastes.

B. Economic Impact

Small fabricators will be able to use the suppressed resin or low-monomer resin. Both are available and cost-effective. The cost impact will be minimal.

C. Environmental Impact

These proposed control measures will not result in any water pollution or in any increase in solid waste disposal. The reduction in emissions of reactive organics should reduce ozone formation in the District as well as reduce the potential for odor nuisance.

D. District Impacts

1. Enforcement

The major impact to the Enforcement Division stems from two Rule requirements: clean-up and recordkeeping. The Enforcement Division estimates 4.5 additional inspectors will be needed to implement the Rule after one year. The need will be reduced to 2 inspectors to maintain adequate enforcement thereafter.

2. Source Testing

Staff expects that approximately 20 hours per year will be needed for testing any new add-on control equipment.

3. Laboratory

Additional laboratory samples will be required in order to determine compliance with the reformulation requirements. An estimated 200-300 hours per year will be needed to analyze these samples.

4. Engineering

Engineering Division estimates that 2.5 engineer years will be required to process the new applications that will result from the adoption of this Rule.

VII. COMMENTS

A. EPA

No comments were received from the EPA.

B. ARB

The ARB finds Rule 1162 acceptable and has no suggestions for revision.

C. PUBLIC

All of the public comments were channeled through the Society of the Plastics Industry, Inc. (SPI).

Comment: Recommend that "Polyester Resin Operations" be changed to "Polyester Resin Molding Operations" to prevent confusion with Polyester Resin Producing Operations.

Reply: Proposed Rule 1162 defines PRO as the fabrication or rework of products made from polyester resin materials. The proposed Rule, therefore, does not apply to the production of polyester resin materials.

Comment: Change the definition of "Approved Composite System" since the industry refers to both resin material and reinforcements. In addition, change "additives" to "formula" in the same definition.

Reply: The proposed Rule was changed to "Approved Low-VOC Emissions Resin System." The definition applies to additives technology. Compliance by changes in formulation is the option described by subparagraph (b)(1)(A)(iv).

Comment: Include definitions for gel coats and monomers.

Reply: The proposed Rule includes both definitions.

Comment: References to "closed-mold" should be changed to "molding." There are pultrusion processes which may not fit the definition of "closed-mold" but, because of low-VOC emission, lose less than 4 percent weight.

Reply: Pultrusion process with less the 4 percent weight loss will be in compliance with the "other process requirement" option of subparagraph (b)(1)(A)(iv).

Comment: Touch-up or repair should be exempt from the subparagraph (b)(i)(B) spraying requirements because airless equipment is neither practical nor available.

Reply: If touch-up or repair of a small area is required, small amounts of materials may be applied with a conventional air-atomized spray gun. The proposed Rule will exempt touch-up or repair from the subparagraph (b)(1)(B) requirements. In our judgment, requiring that this operation be done with a spray gun that has a small resin container attached directly to the gun--as opposed to a hose connection to a large resin tank--will ensure that only a minimum amount of resin will be sprayed.

Comment: Increase the small-user exemption from 50 pounds per day to 250 pounds per day.

Reply: Neither industry nor the District has data to support an exemption limit. District staff believes that materials modification techniques are available to everyone, and use of this material should have only a minimal impact on small users. Low-VOC resin formulations will cost almost the same as the conventional polyester-resin materials. Therefore, the proposed exemption for small users was removed.

Comment: Method of analysis should be included in the Rule.

Reply: The proposed Rule references the District's "Laboratory Methods of Analysis for Enforcement Samples" manual which contains the static volatile emission test previously recommended by SPI.

Comment: Solid waste such as trim should not be required to be in a closed container.

Reply: Staff believes that solid waste is a source of odor and should be stored in a closed container.

Comment: Corrosion-resistant materials should be permanently exempted from the provisions of subparagraph (b)(1)(A) since they constitute a small portion of the total used in the District.

<u>Reply:</u> Staff believes that exemption of corrosion-resistant materials until March 1, 1990 should give the resin manufacturers time to transfer most of the existing conventional resin technology to the corrosion-resistant materials. Also, staff believes that since the need of corrosion-resistant materials is increasing, the amount of emissions will increase in the near future.

VIII. CONCLUSIONS AND RECOMMENDATIONS

Based on the information described above, staff concludes the following:

A. Neither the District nor the SPI has detailed information on the total number of polyester resin fabricators. Staff estimates there are approximately 1,050 fabricators and 700 repair shops in the District. These fabricators and repair shops use 128 million pounds of polyester resin materials and 600,000 gallons of acetone per year.

B. The estimated total VOC emissions from polyester resin operations are 22 tons/day; from the production processes, 14 tons/day; and from cleaning processes, 8 tons/day. The total VOC emission reduction is expected to be 12.6 tons/day.

C. There have been no emission control regulations for this industry because the development of technology was either incomplete or did not exist. Technology has improved during the last 12 months and is continuing to develop at a rapid pace.

D. For the majority of this industry, the add-on control techniques are not technically or economically feasible. Materials modification or reformulation, and additives technology, are the most promising methods for complying with this proposed Rule.

Staff, therefore, recommends approval of Proposed Rule 1162 for the control of VOC emissions from Polyester Resin Operations.

Appendix A

CHEMISTRY OF POLYESTER RESIN

Polyester resin materials have been classified as plastics. Plastics are various synthetic materials chemically created from organic (carbon-based) substances.

There are two basic types of thermoplastics and thermosetting plastics. Thermoplastics are those which can be formed or shaped by heat; this can be done a number of times (physical change). Thermosetting plastics are those which, when formed or reacted, require or give off heat and cannot be reformed (chemical change).

A slightly better classification than plastics is polymers. Polyesters are polymers chained together in a particular order called ester linkages (two carbon and two oxygen atoms).

Polyesters can be broken down into unsaturated and saturated. The term unsaturated refers to a chemical state in which a compound has chemically unsatisfied reactive groups readily available for attachment to other groups. In proposed Rule 1162 we deal only with unsaturated polyesters. The saturated polyesters are represented by alkyds (oil-based paints) and polyester fibers (cloth, rayon, nylon).

There are six types of thermosetting polymer resins: isophthalic, orthophthalic, halogenated, bisphenol-A, furan, and vinyl ester. The majority of the fabricators use orthophthalic for most of their products. The other resins, called corrosive-resistant resins, which are used in applications that have acid, alkali and solvent-resistant requirements, usually cost more than the general-purpose resin and require the Underwriter Laboratories' approval.

1. Orthophthalic Resins

   Orthophthalic resins are often called general-purpose polyester resins. The difference between orthophthalic and isophthalic resins is in the position of the two COOH (carboxyl) groups in the phthalic acid molecule. They are on adjacent carbons (e.g., in the ortho-position) in orthophthalic acid, and are separated by one carbon (e.g., in the meta-position) in isophthalic acid. This resin provides little corrosion resistance.

2. Isophthalic Resins

   Isophthalic resins are either rigid or flexible unsaturated polyester resins and are based on isophthalic acid and glycols of various types. These resins are non-fire-retardant and are used for moderate corrosion-resistance applications up to 180°F. They generally exhibit excellent resistance to water, weak acids, and alkalies; and good resistance to solvents and petroleum products such as gasoline and oil. The flexible isophthalics exhibit a lesser degree of chemical resistance than the rigid isophthalics of higher molecular weight.

3. Chlorendic Resins

Chlorendic resins are unsaturated halogenated polyester resins based on HET (hexachlorocyclopentadiene) acid or chloredic anhydride reacted with a stable glycol.

This resin is suitable for use at elevated temperatures, up to 350°F and is able to handle aggressive, highly oxidizing environments, concentrated acids and some solvents very well, but is poor in alkaline service. It can be formulated to achieve a Class I fire rating.

4. Bisphenol-A

This is an unsaturated, rigid polyester made by reacting biphenol-A with propylene oxide to form a glycol, then reacting the glycol with fumaric acid to produce the resin.

This resin exhibits excellent corrosion resistance to both acid and alkali up to 250°F. This is not suitable for strong oxidizing conditions.

5. Vinyl Ester

Vinyl ester resins are methacrylated epoxies that are very similar to polyester. They offer excellent physical strength and, in general, much better impact strength than rigid polyester resins. These resins exhibit excellent resistance to acids, alkalies, hypochlorites and many solvents. They are preferred for filament winding, especially for machine-made piping. Laminates are good up to 250°F.

6. Furan Resins

Furan resins are based on a furan polymer derivative of furfuryl alcohol. They exhibit excellent resistance to strong alkalies and acids containing chlorinated organics, and are superior in solvent resistance. However, the furan materials are not suitable for oxidizing chemicals and should not be used for chromic or nitric acids, peroxides, or hypochlorites. Laminates are good up to 250°F.

As shown in Table A, polymer resins do not resist all environments, nor do they respond equally to specific applications.

TABLE A

COMPARISON OF PROPERTIES OF VARIOUS TYPES OF RESINS

	Iso-phthalic	Ortho-phthalic	Halo-genated	Bisphe-nol-A	Furan	Vinyl Ester	Carbon Steel	Stainless Steel
Resistance to Acids	B	C	A	A	A	B	B	B
Resistance to Alkalies	B	C	C	A	A	A	B	B
Resistance to Peroxides	C	C	A	B	C	B	C	C
Resistance to Hypo-chlorites	C	C	A	B	C	B	C	C
Resistance to Solvents	B	C	B	B	A	B	A	A
Flame Retardance	C	C	A	C	B	C	A	A
Thermal Insulation Ability	A	A	A	A	A	A	C	C

NOTE: A = High, B = Moderate, C = Low

GLOSSARY

Definitions

These are additional definitions for technical terms used by this industry.

1. Catalyst is a substance added to the resin to make it cure more rapidly.

2. Cross-linking is a process of joining two or more polymer chains which converts a thermoplastic to a thermosetting plastic.

3. Cure is the polymerization or the transformation from the liquid to the solid state of the resin to achieve the desired physical properties, including hardness.

4. Fiberglass is a fiber similar to wool or cotton, but made from glass.

5. Gel Coat is a surface coat, either colored or clear, which provides a cosmetic enhancement and exposure protection.

6. Inhibitor is a substance designed to retard or prevent a chemical reaction.

7. Polymer is a large chemical chain composed of identical cross-linked groups, such as polystyrene.

8. Resin is any of a class of organic polymers of natural or synthetic origin used in reinforced products to surround and hold fibers, and is solid or semi-solid in the cured state.

9. Thermoplastic Materials are those materials that repeatedly soften when heated and harden when cooled.

10. Thermoset Materials are those materials that undergo an irreversible chemical-curing reaction by the action of heat or catalyst.

11. Vapor Suppressant is a substance added to the resin to minimize the outward diffusion of monomer vapor into the atmosphere.