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STYRENE EMISSIONS HOW EFFECTIVE ARE SUPPRESSED POLYESTER RESINS?

BY

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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.

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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

POLYESTER RESIN
PLASTICS PRODUCT
FABRICATION
AP-42 Section 4.12
Reference Number
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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. AropolTM 8343T-12S (Sample 2) failed when the resin and laminate were cooled to 50°F, although when repeated (Sample 3), it passed. AropolTM 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.

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

Table 1

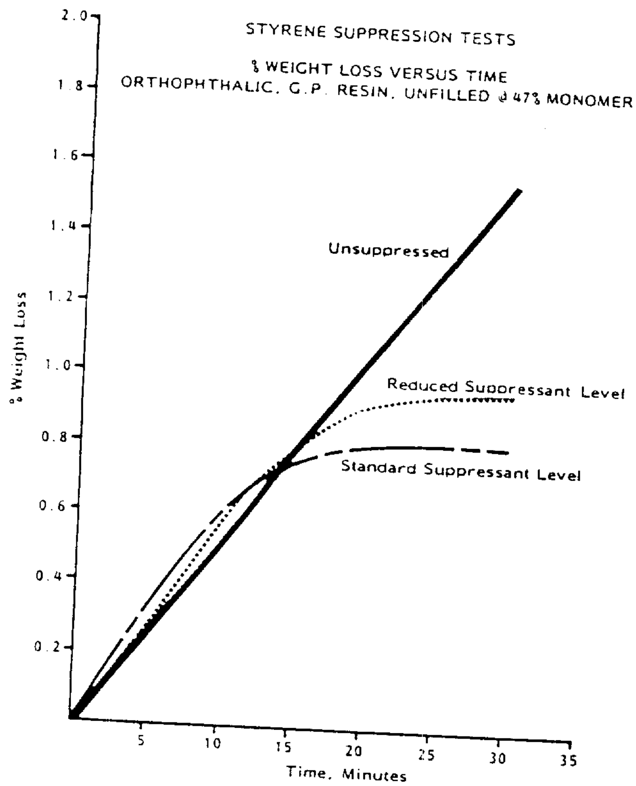


Table 2

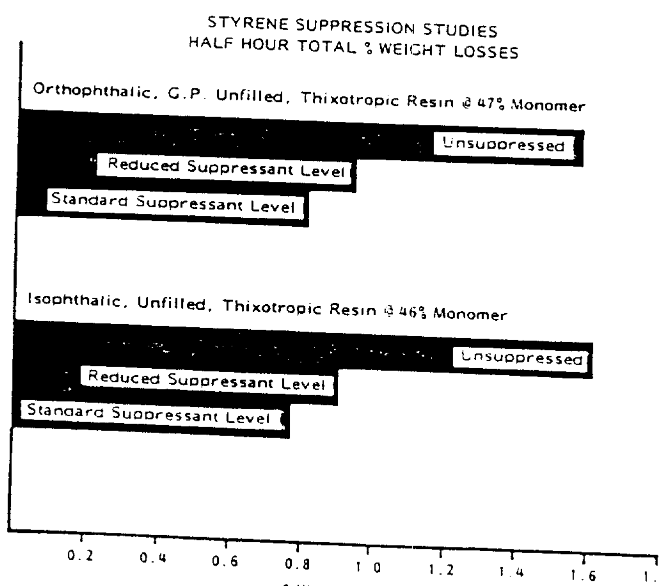


Table 3

STYRENE SUPPRESSION TESTS

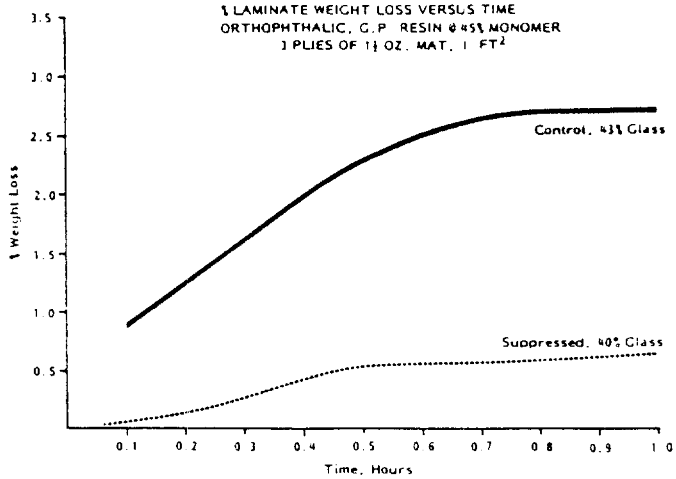


Table 4

STYRENE SUPPRESSED TESTS

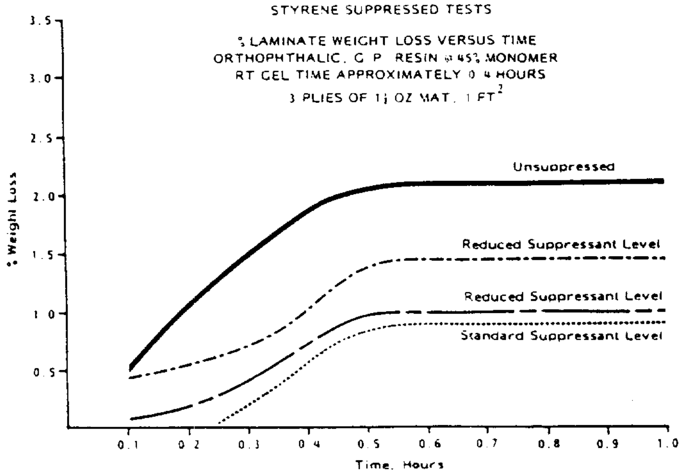


Table 5

% 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

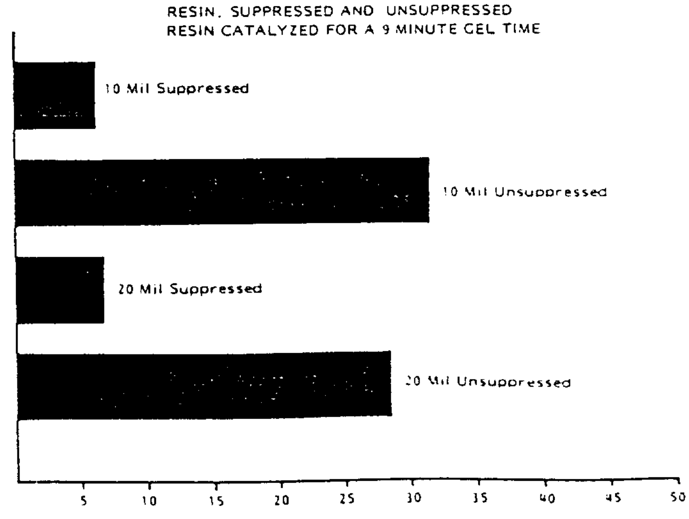


Table 8

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.

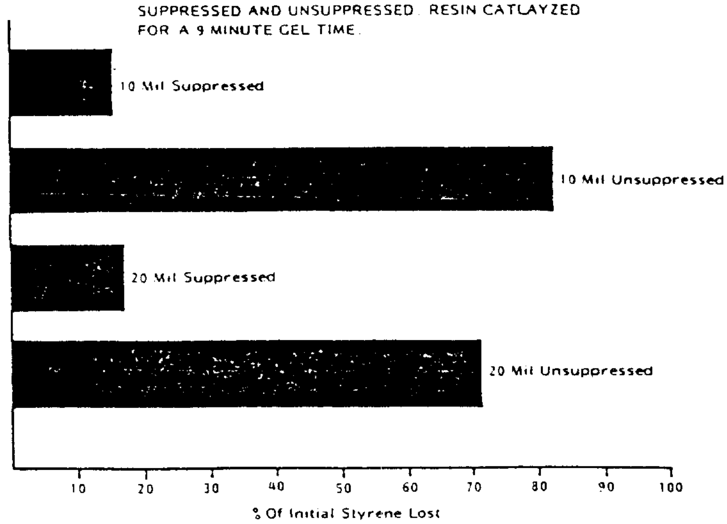


Table 9

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

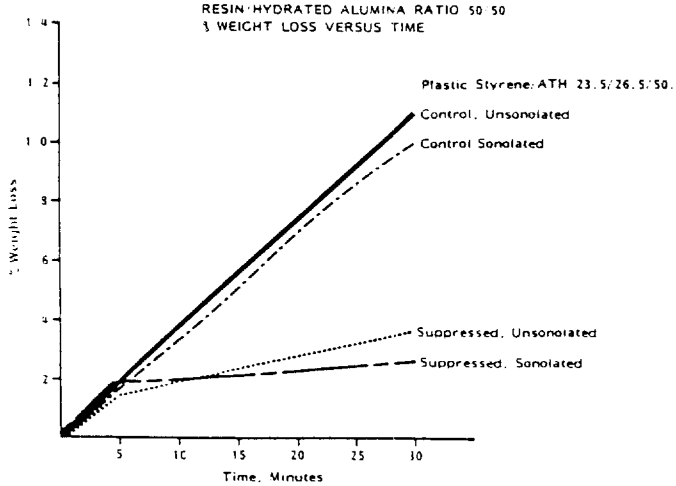


Table 10

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)

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

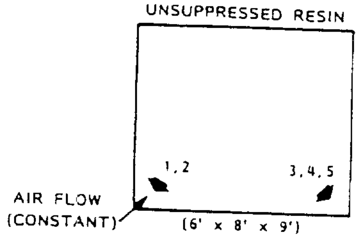
2. Suppressed Resin @ 0.38/lb = $15,200
   Styrene Loss = 500 lbs
   500 lbs of Styrene @ 0.38/lb = $190.00

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

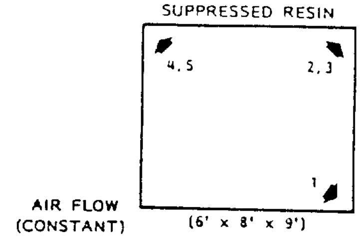


Test No.	Location And Description	Styrene Levels, ppm Drager	Styrene Levels, ppm Bendix
1.	Readings were taken when rollout was almost completed. About 1 1/2-2 ft from radius.	160	200
2.	Rollout completed. Readings taken about 1 1/2-2 ft from radius.	85	125
3.	Readings taken two minutes after radius 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

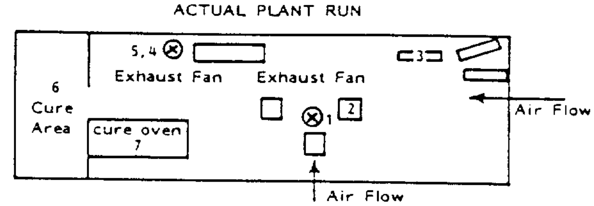
SUPPRESSED RESIN



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

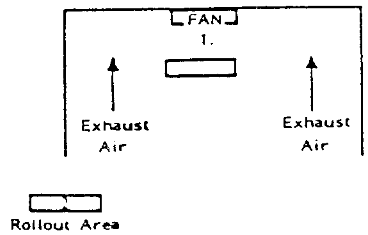
ACTUAL PLANT RUN



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

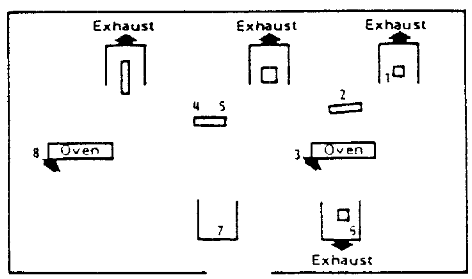
ACTUAL PLANT RUN



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

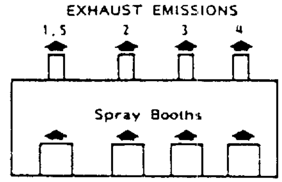


Test No.	Location And Description	Styrene Levels, PPM: Suppressed	Ashland Suppressed
1.	Inside spray booth, left side, while unit was being sprayed	300	130
2.	From top of unit-rollout completed.	100-130	160
3.	Inside oven, while units passed through	300	200
4.	Top of unit-unrolled	400	400
5.	Top of unit-rollout 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