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An Empirical Model to Predict Styrene Emissions from Fiber-Reinforced Plastics Fabrication Processes

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ABSTRACT

Styrene is a designated hazardous air pollutant, per the 1990 Clean Air Act Amendments. It is also a tropospheric ozone precursor. Fiber-reinforced plastics (FRP) fabrication is the primary source of anthropogenic styrene emissions in the United States. This paper describes an empirical model designed to predict styrene emission factors for selected FRP fabrication processes. The model highlights 10 relevant parameters impacting styrene emission factors for FRP processes, and helps identify future areas of FRP pollution prevention (P2) research. In most cases, the number of these parameters with greatest impact on styrene emission factors can be limited to four or five. Seven different emission studies were evaluated and used as model inputs.

INTRODUCTION

The Air Pollution Prevention and Control Division (APPCD) of the U.S. Environmental Protection Agency's (EPA) National Risk Management Research Laboratory (NRMRL) is conducting research to reduce styrene emissions from open mold processes in the fiber-reinforced plastics (FRP) manufacturing industry. Open mold spraying processes are commonly used by the FRP manufacturing industry. These processes are used to manufacture boats, bathtubs, shower stalls, truck caps, body panels for recreational vehicles and trucks, swimming pools, and so forth. When polyester resins or gel coats are applied to open molds, styrene is emitted by evaporation. Based on Toxic Release Inventory reports,[1] annual styrene emissions from U.S. FRP manufacturing industries (including boat building) are estimated to be approximately 25,000 tons (2.3×10^{11} g), with more than 50% of these emissions attributed to spraying of open molds.

IMPLICATIONS

The mathematical model described herein can be used to predict styrene emission factors for FRP manufacturing processes. The model highlights parameters affecting styrene emission factors and can, therefore, help identify future areas of FRP P2 research. The model is more accurate in predicting styrene emission factors for open mold spraying processes than the values listed in the Compilation of Air Pollution Emission Factors (1988 Revision).

Maximum Achievable Control Technology (MACT) standards for the reinforced plastics composites and boat building source categories are currently scheduled to be promulgated by November 2000. Pollution prevention (P2) techniques, such as changes in equipment and resin formulations, may be used to reduce styrene emissions from some FRP products manufactured with open mold processes. P2 opportunities for the FRP industry were investigated to assist in the standards development process, to obtain more accurate styrene emission factor estimates, and to identify the factors influencing emissions.

Currently, the most commonly used method for estimating styrene emission factors for FRP manufacturing processes is AP-42, the EPA's Office of Air Quality Planning and Standards (OAQPS) manual for estimating air emissions from manufacturing processes[2] (see Table 1a). In AP-42, emissions of styrene are presented in terms of an emission factor range for each FRP manufacturing process (gel coating, spray lay-up, hand lay-up, pultrusion, etc.). The emission factors are presented as a percentage of available monomer. If the monomer is styrene, the emission factors are in percentages of available styrene (AS).

Recent tests conducted by the EPA and others (see Table 2) indicate that styrene emission factors for FRP processes may be higher than those published in AP-42. In addition, the AP-42 emission factor ranges are not correlated with conditions known or believed to affect emissions. For example, the emission factor for spray lay-up with a styrene vapor suppressant ranges from 3 to 9% AS, but the conditions that would produce specific values within this range are not provided.

The EPA's APPCD, in cooperation with Research Triangle Institute (RTI), has developed an empirical model to provide better styrene emission factor estimates for selected open molding FRP fabricating processes. The model uses parameters that are known to affect styrene emissions. As a result, the relevance of such parameters can be understood, and future P2 research areas can be identified. This paper describes an empirical model designed to predict styrene emission factors for various FRP manufacturing processes. It also suggests future P2 research and model development.

DESCRIPTION OF MODEL

This empirical model, developed to predict emissions from open molding FRP fabrication processes, is

$$EF = EF_b \bullet (MF)_1 \bullet (MF)_2 \ldots \bullet (MF)_k \qquad (1)$$

where EF is the emission factor, as a percentage of the styrene in the gel coat or resin; EF_b is the baseline emission factor, that is, the emission factor from a process under fixed, typical operating conditions; and $(MF)_{1,2\ldots k}$ are the applicable modification factors, which are based on changes in parameters known to affect styrene emissions (gel time, styrene content, thickness, etc.).

Baseline emission factors were calculated for each process to simplify this modeling approach. The baseline emission factors were calculated under fixed, typical operating conditions. This baseline emission factor is then multiplied by a series of modification factors. If all of the conditions at a particular plant were equal to baseline conditions, each of the modification factors would be given a value of 1.0, and the predicted emission factor would equal the baseline emission factor. At present, the model assumes that the effect of each modification factor is independent from those of the others. This assumption may introduce errors, especially when conditions result in nearly all calculated modification factors being substantially above or below 1.0.

Seven emission studies were evaluated and used as model inputs (see Table 3). Most of these studies include a statistical analysis of the significance of trends being examined; readers are, therefore, encouraged obtain these documents for further information.

Baseline Values

Baseline emission factor values are shown in Table 4. Baseline values for gel coating and resin spray-up were derived from an EPA/RTI study.[3] In this study, "dry-material-off-mold" (i.e., material that misses the mold, falls on the floor, and dries there) was measured to complete the material balance. Dry-material-off-mold was found to be an important parameter in modeling styrene emission factors.

Due to the limited number of studies, an assumption was made that all types of resins (orthophthalic, dicyclopentadiene [DCPD], vinyl ester, etc.) have the same level of emissions for a given styrene content. This assumption will be discussed later in this paper.

Example Calculations

The following example, based on the gel coating thickness modification factor, illustrates how various modification factors were developed:

Table 1a. Emission factors for uncontrolled polyester resin product fabrication processes (100 × mass of VOC emitted / mass of monomer input).[a] (Table adapted from Table 4.12-2 of AP-42.[2])

Process	Resin NVS	Resin VS[b]	Emission Factor Rating[h]	Gel Coat NVS	Gel Coat VS[b]	Emission Factor Rating[h]
Hand layup	5 – 10	2 – 7	C	26 – 35	8 – 25	D
Spray layup	9 – 13	3 – 9	B	26 – 35	8 – 25	B
Continuous lamination	4 – 7	1 – 5	B	c	c	
Pultrusion[d]	4 – 7	1 – 5	D	c	c	
Filament winding[e]	5 – 10	2 – 7	D	c	c	
Marble casting	1 – 3	1 – 2	B	f	f	
Closed molding[g]	1 – 3	1 – 2	D	c	c	

[a] Ranges represent the variability of processes and sensitivity of emissions to process parameters. Single value factors should be selected with caution. NVS = nonvapor-suppressed resin. VS = vapor-suppressed resin.
[b] Factors are 30-70% of those for nonvapor-suppressed resins.
[c] Gel coat is not normally used in this process.
[d] Resin factors for the continuous lamination process are assumed to apply.
[e] Resin factors for the hand layup process are assumed to apply.
[f] Factors unavailable. However, when cast parts are subsequently sprayed with gel coat, hand and spray layup gel coat factors are assumed to apply.
[g] Resin factors for marble casting, a semiclosed process, are assumed to apply.
[h] AP-42 emission factors are assigned the following quality ratings (see AP-42 Introduction): A= excellent, D = below average, B = above average, E = poor, and C = average.

Table 1b. Typical resin styrene percentages.

Resin Application	Resin Styrene Content[a] (wt. %)
Hand layup	43
Spray layup	43
Continuous lamination	40
Filament winding	40
Marble casting	32
Closed molding	35
Gel coat	35

[a]May vary at least ±5%.

Table 2. Comparison of AP-42 resin sprayup and gel coating emission factors with recent test results.

Emission Factor Source	Gel Coat Sprayup (NVS) (%)	Ratio to AP-42 (%)	Resin Sprayup (NVS)	Ratio to AP-42 Midpoint	Resin Sprayup (VS) (%)	Ratio to AP-42 Midpoint
AP-42 Emission Factor.[2]	26 – 35	1.0	9 – 13	1.0	3 – 9	1.0
EPA/Southern Research Institute (SRI) testing at Eljer Plumbingware (now Carolina Classics), June 1993, with EPA Method 25A.[10] (Full-scale production testing.)	48	1.6	–	–	20 / 12[a]	2.7 / 2.0
EPA/Radian (RTP) testing at Venetian Marble, VA.[11] (Full-scale production testing.)	68	2.2	–	–	–	–
EPA/Radian testing at General Marble, NC.[12] (Full-scale production testing.)	97	3.2	–	–	–	–
Radian testing, gel coat spraying of side-wall panels for trailers and recreational vehicles.[13] (Full-scale production testing.)	42 / 29[b]	1.4 / 1.0	–	–	–	–
Composite Fabricators Association (CFA)/Dow Phase I testing in Freeport, TX, September-December 1995, average values for all experimental runs.[5] (Pilot-scale testing.)	51	1.7	25	2.3	–	–
EPA/RTI pollution prevention testing at Reichhold Chemicals in June 1995.[3] (Pilot-scale testing.)	63 / 54[c]	2.0 / 1.7	27 / 18[c]	2.5 / 1.6	11	1.8
Testing at Lasco Bathware in Yelm, Washington, August 1996.[14] (Full-scale production testing.)	53 / 45[d]	1.7 / 1.5	–	–	20	3.3
Testing at Lasco Bathware in Moapa, Nevada, June 1996.[15] (Full-scale production testing.)	33 / 49[d]	1.1 / 1.6	–	–	16	2.7
NMMA testing at U.S. Marine, in April 1997, average values for all boat mold runs.[8] (Full-scale testing, controlled conditions.)	51	1.7	18	1.7	–	–

Notes: "–" = process or condition not tested; NVS = non-vapor-suppressed; VS = vapor-suppressed.
[a]20% = first layup, 12% = second layup.
[b]42% = baseline gel coat, 29% = high performance gel coat with fast gel time. Robotic spray guns inside a total enclosure.
[c]Values are for normal spraying and controlled spraying, respectively.
[d]Values are for gel coat and barrier coat, respectively.

(1) Composites Fabricators Association (CFA) testing in October 1995[4] indicated an average emission factor of 56.2% AS for a gel coat thickness of 18 mils (0.018 in.), and an emission factor of 47.5% AS for a gel coat thickness of 24 mils.

(2) A gel coat thickness of 20 mils was chosen as the baseline. The choice of 20 mils is somewhat arbitrary, but it is believed to represent a typical thickness for a single application layer within the FRP industry. Using linear interpolation between the two laminate thicknesses, the emissions for a laminate thickness of 20 mils would be 53.3% AS.

(3) If the resin spray-up emission factor for 24 mils is 47.5% AS, and the emission factor for the baseline 20 mils is 53.3% AS, the modification factor for 24 mils is 47.5/53.3, or 0.891. Similarly, the modification factor for 18 mils is 56.2/53.3, or approximately 1.055.

(4) The equation for a straight line passing through modification factors of 1.055 at 18 mils and 0.891 at 24 mils is $y = 1.546 - 0.0273x$, where x = gel coat thickness in mils.

A sample calculation for emissions from gel coat spraying, with a thickness of 25 mils, and all other conditions equal to those of the gel coating baseline, is presented in Table 5. The calculated emission rate in Table 5 is 47.1% AS, which is considerably higher than the AP-42 range of 26–35% AS.

In the sample calculation in Table 5, the thickness value of 25 mils is an extrapolation beyond the maximum test condition of 24 mils. Extrapolation frequently results in a higher degree of uncertainty than interpolation, particularly if the extrapolation is considerably beyond the range of data for which the model was developed. The various ranges of data used to develop this model include (1) resin spray-up styrene content, 31.6–50.9%; (2) gel coat styrene content, 25.4–40%; (3) hand lay-up styrene content, 35–42%; (4) distance from gun to mold, 15–36 in.; (5) dry-material-off-mold, 5.68–15.70%; (6) thickness for gel coating, 18–24 mils; (7) thickness for resin spray-up, 40–80 mils; (8) thickness for hand lay-up, 41–88 mils; (9) gel time, 15–30 min; (10) application rate, 2–4 lb/min; (11) temperature 73–85 °F; and (12) velocity, 0–123 ft/min.

Modification Factors Equations

Ten parameters that influence styrene emission factors are included in the model. To quantify the impact of these

Table 3. Emission studies used as model inputs.

Model Parameter	Emission Studies Used as Input to Model						
	1	2	3	4	5	6	7
Baseline emission factors							
Resin sprayup		5-1					
Gel coat spraying		6-1					
Hand layup (with bucket/paint roller)	20-1						
Flow coating			2-1				
Pressure-fed rolling			1-1				
Modification factors							
Styrene content for sprayup	20-2[a]	24-2		26-16			
Styrene content for hand layup, pressure-fed rolling, flow coating	20-2						
Styrene content for gel coat spraying	20-2	18-2					
Distance from spray gun to mold							8-2
Dry-material-off-mold, as a percentage of total material sprayed		12-2					
Laminate/gel coat thickness	40-4	12-2					
Cup gel time	40-4						
Application rate	40-2						
Air temperature						18-2	
Air velocity (above 40 fpm)	40-2	12-2					
Air velocity (below 40 fpm)					3-3		
Styrene suppressant		11-3		10-2			

[a]20-2 indicates 20 test runs, at 2 test conditions.
Emission studies: Study 1—CFA/Dow Phase I[5]; Study 2—EPA/RTI Pollution Prevention (EPA, 1997)[3]; Study 3—CFA/Dow Phase II[4]; Study 4—EPA/RTI Filled Resin[7]; Study 5—Pultrusion Industry Council Phase II[6]; Study 6—Dow Filament Winding[9]; and Study 7—NMMA Boat Manufacturing.[8]

Table 4. Chosen baseline values and baseline conditions.

Process	Gel Coating	Resin Sprayup	Hand Layup Roller	Pressure-Fed	Flow Coater (with chop)
Baseline emission value (%AS)	54.8	18.9	12.3	12.6	11.3
Styrene content, neat (%, by weight)	38	38	38	38	38
Styrene suppressant	N/A[a]	No	No	No	No
Distance from spray gun to mold (in.)	15	15	N/A	N/A	15
Dry-material-off-mold, as a percentage of total material sprayed (%)	6	6	N/A	N/A	N/A
Thickness (0.001 in.)	20	70	70	70	70
Gel time (minutes)	15	15	15	15	15
Application rate (lb/min)	2	4	N/A	N/A	N/A
Air temperature (°F)	75	75	75	75	75
Air velocity (ft/min)	100	100	100	100	100

N/A = not applicable.
[a]Not enough data were available to develop a modification factor for this parameter. Normally, gel coats do not come with styrene suppressant, except some used for the interior of boats.

parameters, modification factor equations shown in Table 6 were developed based on various studies (see Table 3). Some of the parameters that influence styrene emission factors are discussed below.

Neat Styrene Content. Background data related to the neat styrene content modification factor for resin spray-up are shown in Figure 1. Neat refers to the styrene content (percent by weight) before filler is added. The second order modification factor quadratic equation is also shown. This type of curve is probably more accurate than a linear regression in describing emission factor behavior at low styrene contents (below 33% styrene). A linear regression fitted through the data would result in prediction of negative emission factors at very low styrene contents, which is obviously a physical impossibility. Figure 1 illustrates that styrene content is predicted to have a large effect on emission factors in resin spray-up. For example, the modification factor for a neat styrene content of 38% is 1.0, but the modification factor for a neat styrene content of 42% is 1.21; in other words, emission factors (expressed as % AS) are predicted to increase by 21% when the styrene content is raised 11%, from 38 to 42%.

Background data used to generate the styrene content modification factor equation for gel coat spraying are from a test EPA/RTI conducted in June 1995[3], and the CFA Phase I testing.[5] The resulting modification factor equation is a second order quadratic equation, $y = 0.55 + 0.011x + 0.00002x^2$. The predicted effect of styrene content on gel coat emission factors is much less than for resin spray-up emission factors.

Table 5. Example calculation (gel coat spraying).

Parameter	Value	Modification Factor Equation[a]	Modification Factor Calculated Value
Styrene content (% by weight)	38	0.553 + 0.011x + 0.00002x2	1.00
Distance from spray gun to mold (in.)	15	0.868 + 0.00088x	1.00
Dried-material-off-mold/total material sprayed (%)	6	0.862 + 0.023x	1.00
Laminate/gel coat thickness (mils; i.e., thousandths of an inch)[c]	25	IF x < 40: 1.546 - 0.0273x; IF 40 ≤ x ≥ 80: 0.492 - 0.0009x; IF x >80: 0.420	0.86
Cup gel time (min)	15	0.97 + 0.002x	1.00
Application rate (lb/min)	4	1	1.00
Air temperature (°F)	75	0.724 + 0.00368x	1.00
Air velocity (ft/min)	100	IF x < 38: 0.64 + 0.0088x; IF x ≥ 38: 0.96 + 0.000405x	1.00
Baseline value (%AS)			54.8
Overall modification factor			0.86
Calculated emissions (%AS)			47.1[b]

[a]In equations, x denotes the value for the applicable parameter.
[b]The AP-42 emission factor range for gel coating 26-35%AS.
[c]Thickness refers to the thickness for one laminating session, which might include 2-4 passes with the spray gun.

Air Velocity. The predicted effect of air velocity over the mold is depicted in Figure 2. It can be seen that air velocity over the mold has little effect on emissions for air velocities in the range of 50–200 ft/min. This result is based on the same tests[3,5] mentioned earlier.

Figure 2 shows that reductions in air velocity (for air velocities below approximately 40 ft/min) are predicted to produce reductions in emissions. For air velocities near zero (i.e., no air exchange, as could be found in an enclosed space), the predicted emission reduction is up to 36% (a modification factor of 0.64), relative to emissions at 100 ft/min. Data for air velocities below 40 ft/min are available from a test[6] conducted by the Society of the Plastics Industry/Pultrusion Industry Council (SPI/PIC) and a bench-scale test conducted by RTI that measured curing emissions from paint lids. Model predictions for air velocities below 40 ft/min are based on the average values of these two tests. Figure 2 shows that the model predictions below 40 ft/min have a great deal of uncertainty which is caused by the wide variation in results of these two tests. Further, neither of these tests represented resin spray-up or gel coating processes because spray guns were not used to apply the resin material. Therefore, it may be inappropriate to extend the results to spray-up or gel coating. However, it is reasonable to expect some reduction in emissions at very low velocities because a reduction in "refresh rate" over the part surface tends to reduce evaporation rate.

Dry-Material-Off-Mold. Operator spraying technique appears to have a significant effect on emission factors for gel coating and resin spray-up. The challenge is to develop methodologies that can help quantify and correlate

Table 6. Modification factors for styrene emission factor prediction model.

Parameter	Units for x	Modification Factor Equation for Gel Coating	Modification Factor Equation for Resin Sprayup	Modification Factor Equation for Hand Layup, Pressure-Fed Roller, Flow Coater
Neat resin styrene content	%	$0.553 + 0.011x + 0.00002x^2$	$0.003x + 0.000614x^2$	0.24 + 0.02x
Styrene suppressant	YES/NO	Not applicable	IF NO: 1.00; IF YES: 0.64 + 0.005y[a]	IF NO: 1.00; IF YES: 0.50 + 0.005y[a]
Distance from spray gun to mold	in.	0.868 + 0.0088x	0.692 + 0.0205x	1[b]
Dry-material-off-mold/total material sprayed	%	0.862 + 0.023x	$0.906 + 0.0007x + 0.0025x^2$	Not applicable
Thickness[c]	mils	IF x < 40: 1.546 - 0.0273x; IF 40 ≤ x ≤ 80: 0.492 - 0.0009x; IF x>80: 0.420	IF x < 40: 3.34 - 0.0583x; IF 40 ≤ x ≤ 200: 1.14 - 0.002x; IF x > 200: 0.740	IF x < 40: 3.34 - 0.0583x; IF 40 ≤ x ≤100: 1.63 - 0.009x; IF x >100: 0.730
Cup gel time	min	0.97 + 0.002x	0.97 + 0.002x	0.79 + 0.014x
Application rate	lb/min	1	IF x<4: 1.408 - 0.102x; IF x ≥4: 1.0	Not applicable
Air temperature	°F	0.724 + 0.00368x	0.724 + 0.00368x	0.724 + 0.00368x
Air velocity over mold	ft/min	IF x < 38: 0.64 + 0.0088x; IF x ≥ 38: 0.959 + 0.000405x	IF x < 38: 0.64 + 0.0088x; IF x ≥ 38: 0.959 + 0.000405x	IF x < 38: 0.64 + 0.0088x; IF x ≥ 38: 0.959 +0.000405x

[a]In modification factor for resin spraying with styrene suppressant, y represents amount of filler (by weight), in the resin, as applied. For example, sprayup of a styrene-suppressed resin with 50% filler (by weight, as applied) would have styrene suppressant modification factor of 0.89.
[b]Only applies to flow coater.
[c]Thickness refers to the thickness for one laminating session, which might include 2-4 passes with the spray gun.

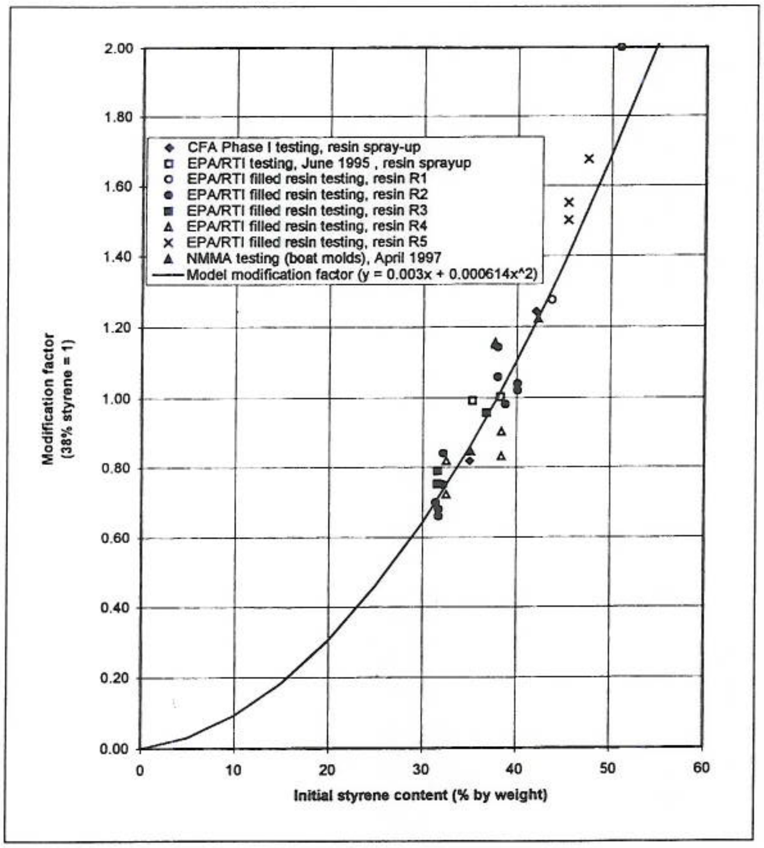

Figure 1. Modification factor for initial styrene content during resin spray-up.

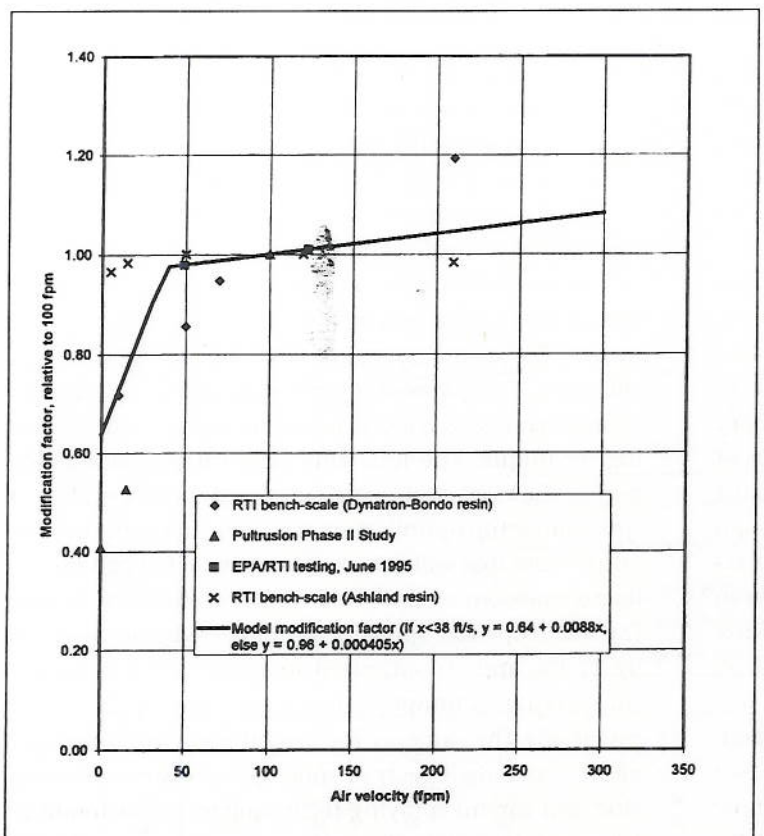

Figure 2. Background data for air velocity modification factor.

operator spraying technique with styrene emission factors. In the summer of 1995, the EPA and RTI conducted tests[3,7] that demonstrated that emission factors could be correlated with transfer efficiency, which relates to operator spraying technique. In these tests, transfer efficiency was defined as the amount of wet material on the mold immediately after spraying stopped, divided by the total amount of material sprayed. However, it would be very difficult to measure transfer efficiency, especially with large molds in a production situation, since the mold would have to be placed on a high-accuracy, high-capacity scale. During these tests, the amount of dry-material-off-mold was also measured, which relates to both transfer efficiency and operator spraying technique. The amount of dry-material-off-mold, a much easier measurement than the amount of wet-material-on-mold, also correlated with styrene emissions. The ratio of the amount of dry-material-off-mold and the amount of material sprayed was then used as a model input.

The modification factor for the dry-material-off-mold for resin spray-up was developed using data from the testing that the EPA/RTI conducted in 1995[3] for both controlled and normal spraying. During controlled spraying, the mass of dry-material-off-mold averaged 5.7% of the total material sprayed. For the normal resin spray-up, the mass of dry-material-off-mold represented 15.7% of the total material sprayed.

At present, no tests have been conducted to quantify the amount of dry-material-off-mold for large female parts such as boat hulls, although both the CFA[5] and the National Marine Manufacturers Association (NMMA)[8] measured their emissions. However, spraying large female molds can be assumed to generate significantly less dry-material-off-mold than spraying small (25 ft^2) male molds, which were used during the EPA/RTI tests.[3] The emissions of tests conducted by CFA[5] and NMMA[8] were not substantially lower than those measured during the EPA/RTI tests. Therefore, the model modification factor equation for dry-material-off-mold is a curve ($y = 0.90 + 0.0007x + 0.0025x^2$) that reaches a minimum at approximately 10% lower than the value measured during the EPA/RTI tests.[3]

The modification factor equation for the dry-material-off-mold gel coat spraying is $y = 0.862 + 0.023x$. This modification factor equation was derived from the results of the EPA/RTI test[3] using both controlled (emission factor of 54.2% AS and dry-material-off-mold of 6.4% of the total material sprayed) and normal (emission factor of

62.5%AS and dry-material-off-mold of 13.1% of the total material sprayed) gel coat spraying.

Distance from Spray Gun to Mold. Another parameter reflecting operator spraying technique that appears to have an effect on emissions is the distance from the spray gun to the mold. Figure 3 depicts available data from two sources for the distance-from-spray-gun-to-mold modification factor. One source is a study conducted by the CFA in 1996,[5] which used a variety of mold sizes and shapes. Tests were conducted using both controlled and uncontrolled spraying. During controlled spraying, the spray gun was held approximately 12 in. from the mold and maintained perpendicular to the mold surface. In uncontrolled spraying, the spray gun was held approximately 19 in. from the mold surface and allowed to have an angle of up to 45° from the mold surface. Analyzing the CFA data, based on these distances and angles, an average distance from the spray gun to the mold surface of approximately 23 in. was assumed. This assumes that approximately half of the total time was spent spraying perpendicularly from a distance of 19 in., and half of the total time was spent spraying at a 45° angle from 19 in., which produces a distance of 27 in. However, during these controlled and uncontrolled spraying comparisons, spray gun pressure was also varied, with higher pressures used during the uncontrolled testing. Therefore, the effect of distance may be compounded by comparing controlled with uncontrolled test results in this study since a new variable was introduced. Another source of data in Figure 3 is a study conducted by the CFA in February 1997.[9] In this study, a gun was held in a stationary position perpendicular to a mold at fixed distances of 12, 24, and 36 in. from the mold. The peak exhaust concentration was measured at each distance. Although peak exhaust concentrations during spraying do not necessarily correlate with spraying emissions, the data from this study are included in Figure 3 because the distance from the spray gun to the mold was carefully controlled.

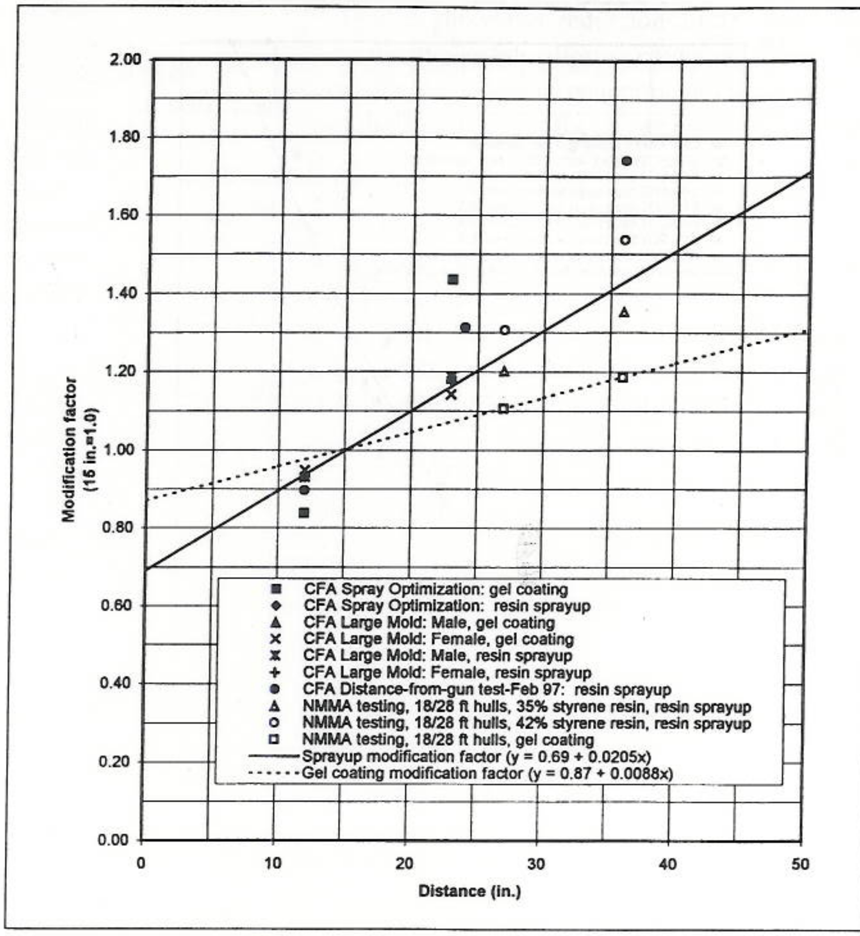

Figure 3. Modification factor for distance from spraying gun tip to mold.

A final set of data in Figure 3 is based on results of a study that the NMMA conducted of emissions from laminating 18- and 28-ft hulls. When laminating the 28-ft hull, the spray gun was, on average, farther from the mold than during spraying of the 18-ft hull. This greater distance produced higher emissions. The modification factor equations for distance-from-the-mold are based on fitting these NMMA results alone. This is due to the problems in assessing the CFA results, as described in the preceding paragraph.

Another parameter, not included in the model but shown to have an effect on styrene emissions, is the spray gun tip pressure/tip size, as demonstrated by the CFA optimization study conducted in 1996.[5] The study showed that, for any given tip size, increasing tip pressure increases emissions. This parameter was not included in the model because its effect was found to interact with operator spraying technique. The following observations were made during the CFA's resin spray-up optimization study: (1) spray gun setup optimization (i.e., spraying with the lowest pressure that will achieve an adequate fan pattern) reduced emissions by 9.1% relative to baseline conditions; (2) careful operator spraying technique reduced emissions by 21.4%; and (3) optimized spray gun setup plus careful spraying technique reduced emissions by 20.4%, or essentially the same as for careful spraying technique alone. Since the effects of spray gun pressure optimization and careful spraying technique were not found to be cumulative, the effects of spray gun pressure are not included in this model.

Thickness. It is possible to predict the general behavior of certain modification factors, based on knowledge of the physical principles that the modification factor is describing. In the case of thickness, it would be expected that the modification factor would have a steeper slope as thickness approaches zero, and a near-horizontal slope as thickness approaches infinity. The thickness modification factor equations for all processes are presented in this manner, as shown in Table 3.

MOST SIGNIFICANT PARAMETERS

In most cases, the number of parameters with greatest impact on styrene emissions can be limited to the four or five parameters with the largest impact on emission predictions. Figures 4 and 5 depict the five factors with the greatest impact for gel coating and resin spray-up, respectively, based on typical conditions found at FRP facilities. The x-axes in Figures 4 and 5 have the chosen baseline conditions in the center of the graph and approximate minimum and maximum conditions on the left- and right-hand sides of the graph, respectively. For example, the scale for velocity has a midpoint at 100 ft/min, the baseline velocity. The minimum and maximum values for velocity are 0 and 200 ft/min, respectively. A velocity of 200 ft/min represents the maximum velocity found in a spray booth.

Example Scenarios

An approach to reducing styrene emissions from gel coat spraying is to decrease the amount of overspray, material not landing on the mold (see Figure 4). The model predicts that gel coat spraying emissions, expressed as % AS, can be reduced by approximately 12% (modification factor is lowered to 0.88) if the amount of dry-material-off-mold is reduced from 6 to 1% of the total material sprayed.

Another potential way to reduce gel coating emissions is to decrease the air velocity over the mold to near zero. This produces a predicted reduction of approximately 36% (modification factor of approximately 0.64) relative to a velocity of 100 ft/min over the mold. However, such a reduction in air velocity over the mold is unlikely to be achieved in open spraying situations. Operator exposures to styrene would probably increase to unacceptably high levels. In order to produce these very low air velocities, sophisticated air handling techniques or spraying enclosures would be required.

In the case of resin sprayup, reducing the styrene content in the resin will result in emission factor reductions.

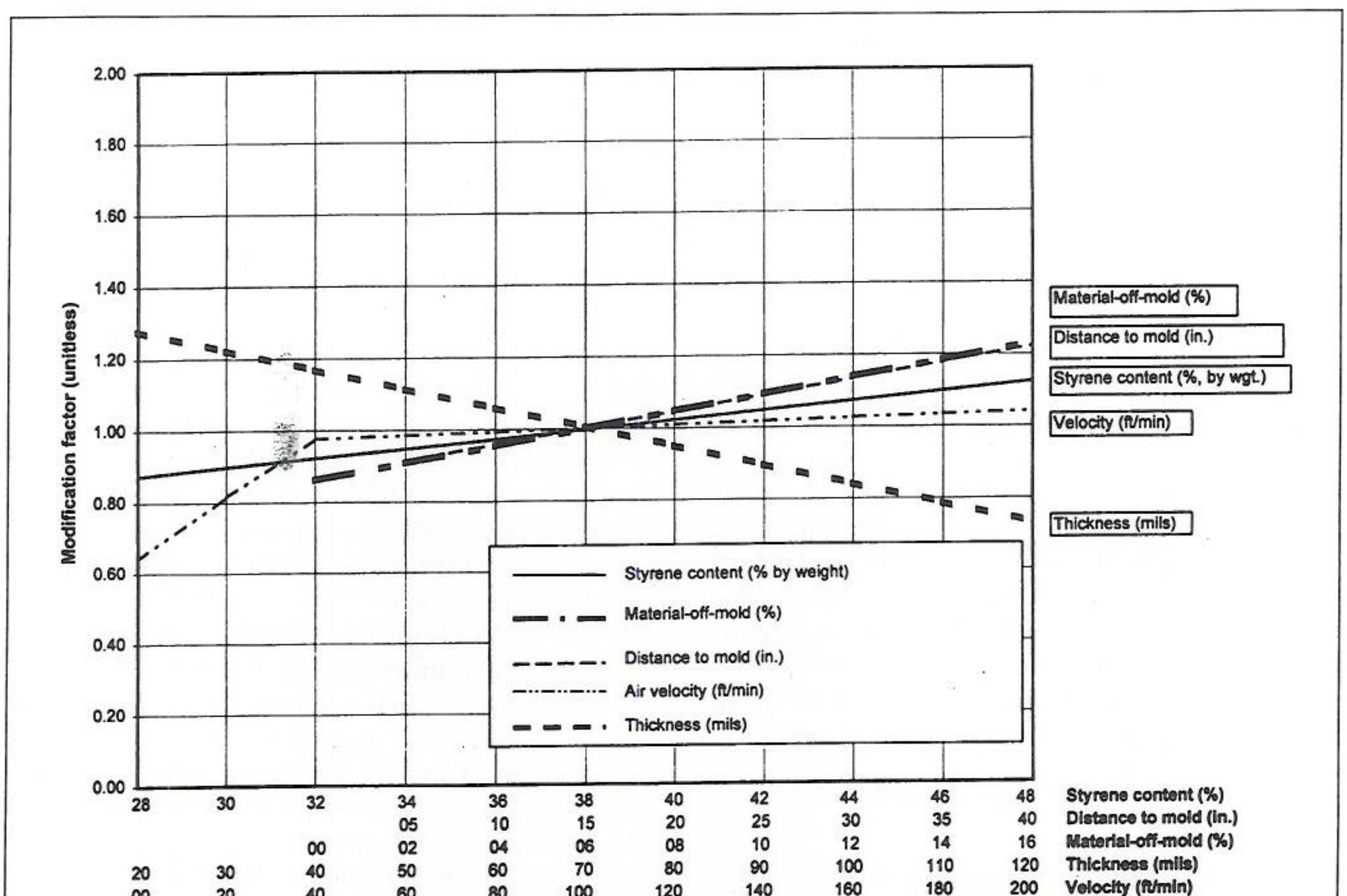

Figure 4. Important modification factors for gel coating.

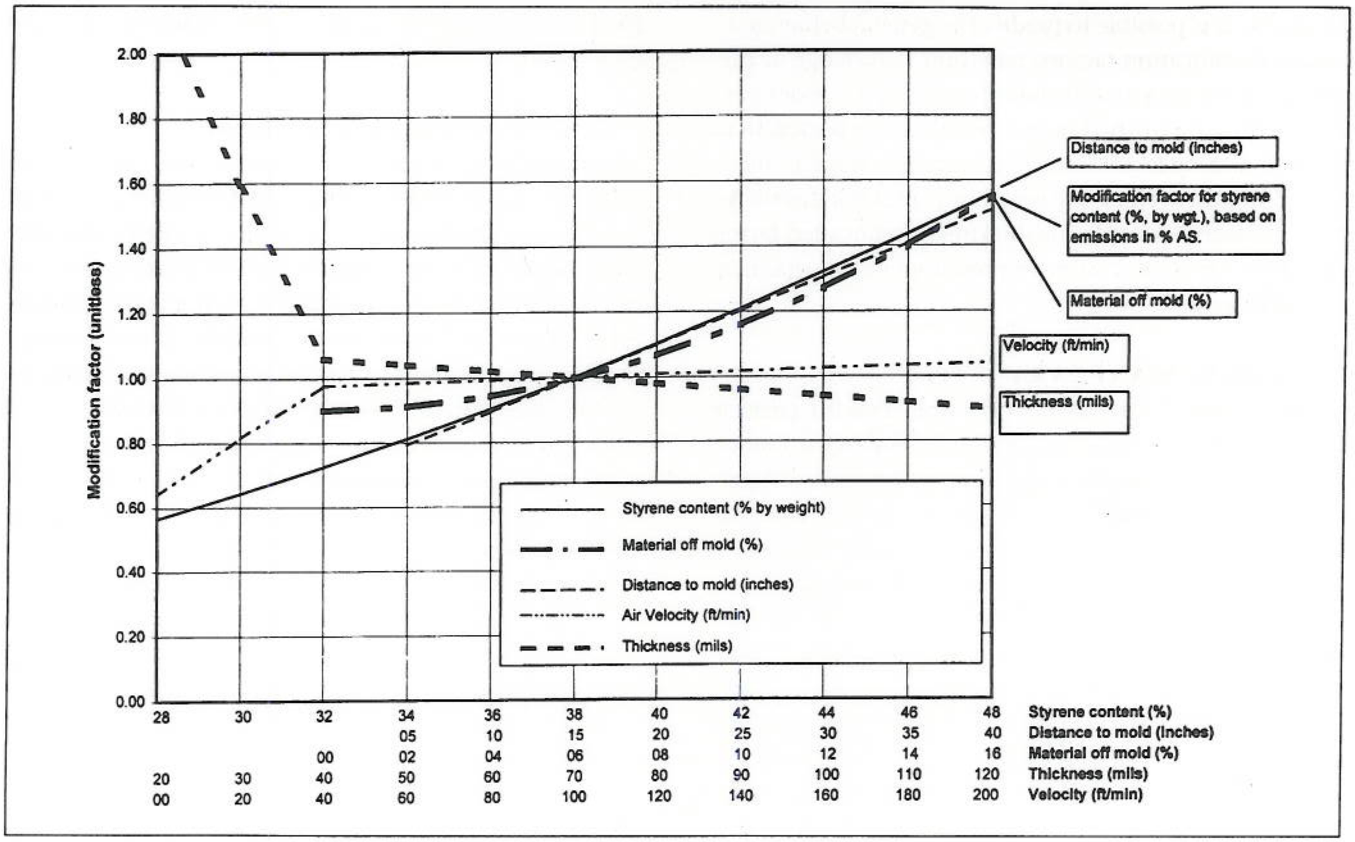

Figure 5. Important modification factors for resin sprayup.

The styrene content curve is one of the steepest curves in Figure 5. A predicted emission factor reduction of approximately 18% (modification factor of 0.82) can be achieved by reducing styrene content from 38 to 34%.

NEW EMPIRICAL MODEL VERSUS AP-42

Neither the new empirical model nor AP-42 are statistically derived models. Therefore, standard regression measures, such as R^2, do not necessarily provide good measures of model performance. However, since quantitative measures of the performance of the models are important, we have analyzed the performance of both models for selected testing results. The results of this analysis are summarized in Table 7.

Table 7 includes testing programs with the processes of gel coating, sprayup (with unfilled and filled resins), and flow coating. For each testing program, the table lists the number of test runs in the testing program, and the average test result (in %AS). Table 7 includes columns showing the calculated average bias for each model (in %AS)

$$Avg.\ Bias = \sum_{i=1}^{n} (P_i - O_i) /n \qquad (2)$$

where *Avg. Bias* is the average bias, P_i are the model predictions, O_i are the individual observations (i.e., test results), and n is the number of test runs.

Table 7 also includes columns showing the calculated mean-squared error (MSE) for each model, defined as

$$MSE = \sum_{i=1}^{n} (P_i - O_i)^2 /n \qquad (3)$$

The MSE criterion provides an overall indication of model performance, and includes both bias and imprecision components.

If the average bias listed in Table 7 is positive, it means that the average model prediction is higher than the average test result. Conversely, if the average bias is negative, the model, on average, is underpredicting the results. For example, in the CFA/Dow Phase I gel coating tests, the average value for the 20 test runs was 51.7% AS. For these test results, the new EPA model has a bias of 4.5, which means that the average EPA model prediction for these test results was 56.2% AS. The average bias of AP-42 was –21.2% AS, because the AP-42 midpoint is 30.5% AS.

Lower values for average bias and MSE indicate a more accurate model. It can be seen from Table 7 that the new model is clearly more accurate than AP-42; average bias and MSE values are generally significantly lower for the new model than for AP-42. In fact, the predictions of the new model are more accurate than AP-42 in 9 out of 11 of the situations listed in Table 7.

The two situations where the new model was less accurate occurred during EPA/RTI filled resin testing. In one

Table 7. Comparison of selected testing results with predictions of the EPA model and AP-42.

Test Program	Process/ Conditions	Number of Data Points	Average Test Value (% AS)	EPA Model		AP-42 Model (Midpoint)	
				Average Bias (% AS)	Mean Squared Error	Average Bias (% AS)	Mean Squared Error
CFA/Dow Phase I[5]	Gel coating	20	51.7	4.5	27.3	–21.2	484
NMMA Boat Manufacturing[8]	Gel coating, boat molds	6	49.6	1.9	8.5	–19.1	371
CFA/Dow Phase I[5]	Sprayup	20	24.9	1.1	9.5	–13.9	237
NMMA Boat Manufacturing[8]	Sprayup, boat molds	12	18.4	1.5	2.5	–8.1	78.2
EPA/RTI Filled Resin[7]	Sprayup, Filled Resin #1 (Ortho, VS)	5	12.0	14.5	239	–6.0	40.4
EPA/RTI Filled Resin[7]	Sprayup, Filled Resin #2 (DCPD, VS), Filled Resin #3 (DCPD,NVS), Filled Resin #4 (DCPD, VS)	22	14.4	2.1	14.0	–7.5	63.3
EPA/RTI Filled Resin[7]	Sprayup, Filled Resin #5 (DCPD, VS, BPO-catalyzed)	4	12.5	12.5	173	–6.5	42.4
CFA/Dow Phase II[4]	Sprayup, filled resin	5	19.1	–0.4	2.1	–9.1	86.2
NMMA Boat Manufacturing[8]	Flow coating	8	11.9	–3.4	18.9	–4.4	19.8
EPA/RTI Pollution Prevention (EPA, 1997)[3]	Flow coating	3	14.2	–4.3	18.9	–6.7	45.4
CFA/Dow Phase II[4]	Flow coating	2	11.5	0.0	0.00	–4.0	16.0

situation (Filled Resin #1, an orthophthalic resin with styrene suppressant), the model predictions are significantly higher than test results. This can be contrasted with the model's accurate predictions for Filled Resin #2, a DCPD resin with styrene suppressants. As a result of further testing, the model may need to be changed to address the apparent difference in emissions between the two types of resins.

It is important to realize that all of the studies referred to in Table 7 were used for at least part of the new empirical model development. It would be better if test results that are independent of either the new model or AP-42 were available. To date, tests that have well-documented process conditions and that are completely independent of the new model or AP-42 are not available.

Emission Factors as %AS

All of the data in this paper are presented as %AS, that is, units that are used in AP-42 Table 4.12-2. However, the true benefits of reducing styrene content are emphasized if emission factors are expressed as pounds of styrene emitted per pound of resin used. This fact is illustrated by comparing Figure 6 with Figure 5. The only modification factor line that has changed is the line for styrene content; this line is steeper in Figure 6.

RESEARCH FOR FURTHER MODEL DEVELOPMENT AND VALIDATION

Additional tests for resin type and operator spraying technique are recommended to further develop and validate the model. As indicated above, the EPA/RTI filled resin testing appeared to indicate that different resins with similar styrene content can produce substantially different styrene emission factors. However, an assumption used in the development of the model is that different resin types with equal styrene content have equal emission factors (all other conditions are the same). This model assumption could be checked by conducting comparison tests among different resin types. In the case of operator spraying technique, the model uses two parameters: distance from the spray gun to the mold and dry-material-off-mold (expressed as a percentage of total material sprayed). These two parameters eliminate the need for wet transfer efficiency measurements, which would be very difficult for large molds, or in production situations. Further tests are needed to refine the modification factor equations for these two parameters. It may even be worthwhile to develop and conduct a comprehensive, statistically designed test program to develop an improved model.

ACKNOWLEDGMENTS

Trade organizations, including the Composite Fabricators Association, National Marine Manufacturers Association, and the Society for the Plastics Industry/Composites Institute conducted much of the testing used to develop this model.

CONVERSION TABLE

To convert from	To	Multiply by
Inches (in.)	Meter (m)	0.025
Feet (ft)	Meter (m)	0.3048
Square feet (ft^2)	Square meter (m^2)	0.0929
Pounds (lb)	Kilogram (kg)	0.454
Fahrenheit (°F)	Celsius (°C)	(°F – 32)/1.8

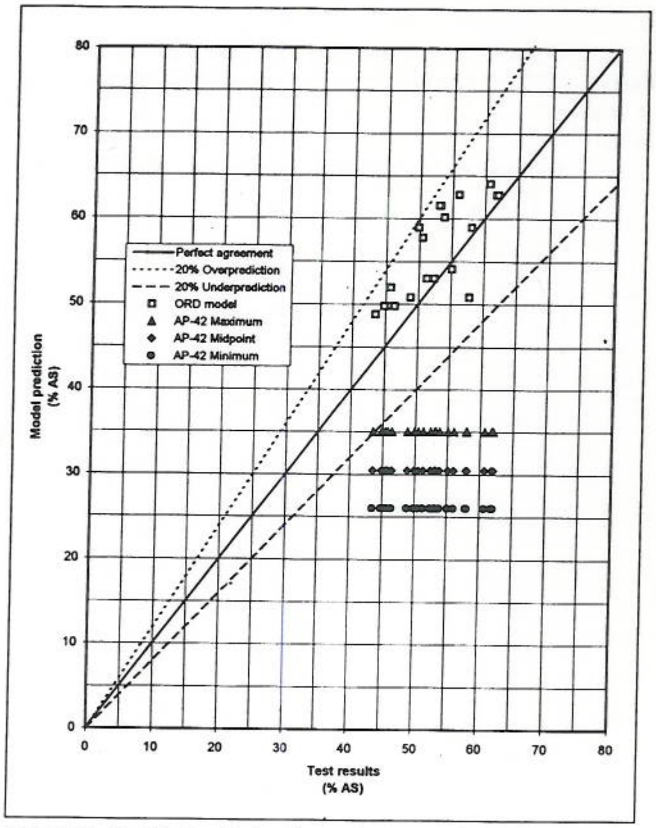

Figure 6. Modification factors for resin sprayup, for emissions as a percentage of resin used.

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