

# Experimental Test Results from an Environmental Protection Agency Test Method for Determination of Vapor Suppressant Effectiveness

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The results obtained from laboratory experiments conducted using Environmental Protection Agency (EPA) subpart WWWW of 40 Code of Federal Regulations (CFR) part 63 (1)-test method are discussed in this article. The original test method was developed to measure the effectiveness of wax suppressants used to reduce hazardous air pollutant (HAP) emissions from unsaturated polyester (UP)/vinyl ester resins. Wax additions of ~1.5% by weight to commercial UP resins suppress HAP emissions through the formation of surface barrier films. However, the tests performed in this study included the use of limestone and an adjunct, organic fiber reinforcement, rather than the wax. The addition of either commercial product to the UP formulations tested in this study was also shown to reduce HAP emissions. Suppression was a combination of absorption and an increased diffusion path barrier for the volatile organic carbon (VOC) components. Based on the limited data obtained, it was shown that the oil absorption characteristics of the two adjunct products could be used to estimate the expected level of vapor suppression for a specific resin formulation. Values reported in the literature for the oil adsorption characteristics of the adjunct limestone and the commercial biomass fiber were used in the laboratory tests. Although the oil adsorption characteristic of any ingredient added to a base resin formulation is indicative of its potential for emissions reduction, the EPA test protocol is still required to be performed for validation. Such screening tests will always be needed due to the variability associated with commercial UP resins and the evolution of customized UP/fiberglass composite formulations developed by custom molding shops.

**Keywords** adjuncts, composite formulations, hazardous air pollutant reduction, unsaturated polyester resins, vapor emissions

## 1. Introduction

Following solicited input, several commentators requested that the Environmental Protection Agency (EPA) develop a test method for the determination of the effectiveness of vapor suppressants used with unsaturated polyester (UP) resins. The commentators further suggested that the vapor suppression test method offered by the Composites Fabricators Association be used. In response, the EPA published a proposed test method as appendix A to subpart WWWW of 40 Code of Federal Regulations (CFR) part 63(1). In this document, the EPA emphasized that this method was designed to evaluate the effectiveness of wax, film-forming vapor suppressants when used in bulk UP resins. Furthermore, the EPA specified that the test results were to be used only with the proposed hazardous air pollutant (HAP) emissions factor equations.

Film-forming vapor suppressants are typically wax additives, which may be added to the UP resin by the manufacturer or the end-user. The EPA had established through its own emission studies that such wax-based additives are most effective

as vapor suppressants primarily during the curing stages for the polyester resins. For example, with open-molding processes, as much as 50% to 55% of volatile organic carbon (VOC) or HAP emissions occur while the resin and reinforcement are being applied to the mold, and before any surface films have had a chance to self-assemble. Hence, even a fully formed film barrier that is 100% effective will reduce total VOC emissions from open-mold processes by only 45% to 50%. Moreover, the effectiveness of the film-forming wax is dependent on the type of UP formulation being used. Hence, the EPA requires that each resin/wax formulation be tested individually to quantitatively determine the level of vapor suppression.

Many custom shops using UP/fiberglass (FG) spray-up operations object to the use of waxes to reduce HAP emissions. Their objections stem from the cured polymer surfaces that are generated, which are wax-rich in composition. Such surfaces are not always the final finished surface and lead to poor interfacial bonding when subsequent layered applications of the FG/UP resin are required. In such cases, the wax-rich surfaces must be sanded and washed with solvents to restore adhesion. Hence, many shops that use UP spray-up operations to manufacture, for example, tubs, pools, and spas avoid the use of wax-impregnated resins for HAP emissions reduction. Many custom spray applicators may, however, use other adjuncts in UP resin formulations that also appear to reduce vapor emissions during processing. Therefore, one goal of this study became the quantitative determination of VOC suppression achieved using adjunct additives in UP formulations.

The overall principle of the EPA test protocol is based solely on precise, gravimetric determinations for weight loss

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differences. Two UP formulations were prepared and cured; one with and one without the candidate VOC suppressant. A demonstrative reduction in the mass of VOC lost during the elapsed time from the start of UP resin spray-up until a full cure is achieved represents a measure of the effectiveness of the suppressant being tested. Because this EPA test protocol does not require the determination of the individual components contained in the volatile vapors released, the overall process is simplified. And, although some very specific procedures have been established with the test protocol, the final determination of the level of VOC suppression is determined solely by a gravimetrically determined weight loss for each specific resin system, with and without the purported vapor suppressant. The EPA then allows positive results from the tests to be used as an input to the organic HAP emissions factor equations for the estimation of emissions. Although the test protocol does not provide a total emission rate for the entire fabrication process, any positive reductions in HAP emissions established by this procedure may be used by a manufacturer to claim emissions credits.

It is important to note that many commercial UP resins are routinely combined with adjunct materials. In subpart WWWW of 40 CFR, part 63, the EPA defines fillers as:

“... inert organic or inorganic materials used to modify the resin properties, extend the volume, and to lower the cost. Fillers include, but are not limited to; mineral particulates; microspheres; or organic particulates.”

The test protocol also clearly states that:

“This test is not intended to be used to determine the vapor suppressant effectiveness of filler.”

Although limiting in scope, these EPA qualifiers suggest that “fillers” may in fact suppress VOC emissions but that their effect should not be quantified by this procedure. Because the WWWW part 63 procedure defines a protocol for a specific weight loss measurement, it would seem reasonable that it could in fact be used to measure weight loss suppression from resin systems that use adjunct fillers for whatever reason. The hypothesis that vapor suppression may occur remains the same as that for subpart WWWW of 40 CFR, part 63. Simply stated, a reproducible difference between the weight losses for any unfilled UP resin system and the same UP resin, but with an added adjunct material, represents a measure of VOC suppression by the added material. This basic gravimetric determination described by the EPA protocol formed the basic tenet on which this study is based.

### 1.1 Objectives of This Study

The work described herein is based on the published EPA protocol, appendix A to subpart WWWW of 40 CFR part 63 (Ref 1). This procedure was followed in detail. The major difference was the procedure was used to assess the effectiveness of two adjunct materials used with UP resins that were not wax additives but behaved as VOC suppressants. The primary objective, therefore, was to demonstrate that the EPA gravimetric method could also be used to quantify VOC suppression achieved by adjunct materials, including fillers, when incorporated into UP resin formulations. To be considered affirmative, the results of our tests required the same level of reproducibility and precision as that achieved by the round-robin tests using wax suppressants as reported by EPA in the

*Federal Register* (Ref 2). The tests reported in the *Federal Register* indicated that variations in the performance of a wax-based vapor suppressant could be as large as 25%. Clearly, the protocol involves measurements of small differences and variable UP resins.

A second objective related to the use of the EPA protocol for our tests was to help to identify the difficulties encountered with the published procedure. With this second goal, any positive feedback for use with future tests was possible and might be incorporated in the development of future round-robin tests directed specifically at the assessment of any filler on VOC emissions in UP spray-up operations.

## 2. Experimental Procedures

The experimental procedure used in this study followed the EPA test protocol previously referenced. Hence, the specific procedural details of the protocol will not be repeated, but a summary with comments on the different steps is given in Table 1.

### 2.1 Resins Used in the Tests

Two well-established commercial UP resins were used in our tests. The characteristics of the resins manufactured by Eastman Chemical Co. (ER) (Kingsport, TN) and Cook Composites and Polymer Co. (CR) (Kansas City, MO) are listed in Tables 2 and 3 (Ref 3), respectively.

The diversity inherent with polyester resins is evident with the two resins selected for our experiments. As indicated in Tables 2 and 3, viscosity, the amount of catalyst recommended, gel time, and peak exotherm may all vary between products, even before a molding shop has implemented its fabrication procedures and technology. Thus, the addition of limestone to the UP resin formulation represents an added heat sink, which will reduce the peak exotherm of the resin unless the amount of catalyst added is changed. Due to their good absorption characteristics, some organic fiber adjuncts are known to retard and even prevent gel formation unless adjustments are made to the amount of initiator and/or monomer available. Hence, fabricators frequently modify manufacturing procedures when adjunct materials are added to a standard UP resin. In many instances, it is changes in the amount of initiator used that typically provide the quickest success.

In this study, a proprietary formulation is used from two FG/UP composite fabricators. The investigation was limited by the two commercial catalysts used by the fabrication shops. A summary of the specific characteristics attributed to these two catalysts is represented in Table 4.

### 2.2 Description of Adjunct Materials Used

The reinforcement materials used in the study were based on formulations developed by FG/UP fabricators. The major reinforcement was standard FG strand applied using a chopper gun. Resin grade crushed limestone and a commercial, organic-based fiber, Renfil (RF) (Impact Associates, Littlefield, TX), were two additional adjuncts used in the shop recipes. The latter two materials were found to affect the UP curing process, while the FG was considered to be nonreactive with respect to polymerization chemistry but to be essential to the final physical properties of the composite. Due to the high surface area-to-volume ratio for the crushed limestone, and particularly for

**Table 1 Summary and comments of test setup for subpart WWW of 40 CFR part 63**

1. Two laboratory balances were positioned in enclosures so that air flow does not perturb the readings. Balances should be accurate to  $\pm 0.01$ .  
Comment: Because small differences are being measured in these tests, balance accuracy to  $\pm 0.001$  g is recommended.
2. The resin in the pan is brought to room temperature for testing. The test temperature must be between 70 °F (21 °C) and 80 °F (27 °C), and the test temperature cannot vary more than +2 °F (+1 °C) in measurement during the run. Temperature and weight are recorded simultaneously.  
Comment: Because most room temperature are  $\sim 77$  °F ( $\sim 25$  °C), a test range of 70 to 85 °F (24 to 30 °C) is more workable. Also, because the thermometers are to be accurate to  $\pm 2.0$  °F ( $\pm 1$  °C), a temperature rise of  $< +3$  °F (2 °C) is probably more realistic for the tests with negligible loss of accuracy.
3. An insulating spacer was placed beneath the pan to prevent the balance from becoming a heat sink.  
Comment: Cardboard should not be used, because cardboard can lose adsorbed moisture during peak exotherm and skew weight measurements being recorded with the balance. A nonabsorbent pad should be used.
4. Relative humidity levels were recorded during the experiment and should vary no more than  $\pm 15\%$  during the test runs.
5. The appropriate glass fiber mat and resin roller were made ready.  
Comment: The precise mass and weight percent of glass fiber to be used in each formulation is important because it becomes the basis by which the necessary quantities of resin, filler, and initiator specified in the formulation are calculated. Also, many FG/UP resin spray-up fabrication shops do not employ rollout.
6. All test runs were processed in a manner that produced the same gel time for the unfilled and filled resins (i.e.,  $\pm 2$  min).  
Comment: Gel time determination represents a critical and difficult specification to be reproduced in the test. It can vary greatly for different resin formulations and the type of initiator of adjunct used. The recommendations suggested in the EPA protocol should be closely adhered to during the pretest and test procedure. UP resin manufacturers also develop their own specifications for gel time, which do not meet shop specifications.
7. The EPA procedures specify periodic data recording and calculations for six replicate samples. These should be strictly adhered to during the tests.  
Comment: In baseline tests, it is recommended that recordings be made at 1-min intervals rather than at 5-min intervals, because they offer a clearer definition of the curing process. Also, there are significant differences in the bulk viscosities for unfilled resin formulations and formulations that contain adjuncts. Unfilled resins flow freely, while resins that contain adjuncts may require pour patterns and more rolling.
8. Finally, it must be remembered that differences in weight loss between tests do not convey complete information with respect to VOC suppression for commercial FG/UP spray-up operations. Reduced emissions are also possible with continued developments in airless spray guns, nozzle design, and proprietary resin/adjunct modifications.

the RF, both materials exhibit elevated oil absorption characteristics. As mentioned earlier, oil absorption behavior, which is related to physical structure, usually necessitates modifications in the manufacturing procedures. Absorption levels for the two products used in the tests are listed in Table 5.

It is hypothesized that when materials having larger oil absorption characteristics are incorporated into a UP resin, the more significant will be the reduction in VOC emissions during manufacturing processes. This is because absorbed molecules (i.e., molecular styrene, which makes up  $\sim 40\%$  by weight of the uncured UP resin) are less energetic than the same styrene molecules in the bulk solution. Therefore, absorbed molecules are much slower to transfer to the vapor phase, even following

elevated temperature excursions during polymerization. In addition, depending on the level of loading, the use of adjunct materials will create longer diffusion paths for VOC to traverse from the bulk to an exposed surface. Both mechanisms may be synergistic in the degree of VOC suppression that is ultimately achieved.

In the next section, the development of an empirical model for the polymerization process of a base UP resin is discussed. Insights from the model and measurements on the unmodified baseline resin gave rise to an equation for an expected percentage of weight loss (VOC emissions) when adjunct materials are used. A weight loss estimated in this manner was then compared with the measured weight losses determined experimentally using the EPA test protocol.

### 2.3 A Model of the Emissions Process

The curing of FG/UP composites represents a complex technology that is perhaps more art than science (Ref 6). For commercial processes, the polymerization reaction must be completed in a reasonable time and must produce a finished product. Production schedule demands and the use of relatively large masses of resin frequently combine to generate distinctive “peak exotherms” that must be dealt with during fabrication. The progressive elevation in temperatures leading up to an exotherm accelerates both the polymerization process and the mass transfer of uncured resin moieties (VOCs) to the gas phase. Frequently,  $>5\%$  of the combined mass of the UP resin and FG can be lost as volatile emissions during manufacture. Five percent does not sound like much, but stricter environmental standards necessitate the curtailment of these VOC or HAP emissions, and molding operations that successfully do so can in certain situations receive regulatory emission credits.

To better understand VOC emissions during UP polymerization, a dynamic model of the process was generated. The assumptions for the model are given in Table 6.

Details of the model described in Table 6 will not be provided in this article, but the model was used to generate data for comparison with the experimental results generated with the EPA test protocol. This comparison provided insights into the loss of VOC during the polymerization process and led to a relatively simple correlation among the final total percentage of VOC weight loss, the oil absorption characteristics of adjunct materials, and the weight fractions of styrene and adjunct that were used in the molding process. This relationship is given in Eq 1:

$$y = R_o - \sum_{i=1}^{i=n} \left[ \frac{x_i}{(V_{fs} + x_i)} \right] * A_i \quad (\text{Eq 1})$$

where  $y$  is the percentage of total weight lost,  $R_o$  is the percentage of total weight lost for the base (unfilled) resin formulation,  $x_i$  is the weight fraction of the adjunct material ( $i$ ),  $y \equiv R_o$  when  $x_i = 0$ ,  $V_{fs}$  is the weight fraction of styrene (VOC) in the formulation, and  $A_i$  is the oil absorption number of adjunct material ( $i$ ) in grams of oil per 100 g of sorbent.

## 3. Discussion of the Results

Even though a significant number of assumptions were made in the model for the polymerization of UP resins, a com-

**Table 2 Characteristics of Eastman 733-6903 UP resin batch number EN04001051**

Characteristic	Value	Range
Nonvolatile mass, %	55.1	54.0-58.0
Viscosity, Brookfield, LVT No. 3 at 60 rpm	1118.0	1100.0-1200.0
Viscosity, Brookfield, Thixotr	4.51	4.00 lower limit
90 H <sub>2</sub> O gel time, 90 F to gel	11.53	11.00-13.00
90 H <sub>2</sub> O gel time, gel to peak exotherm	13.45	20.00 upper limit
CPP catalyst and filler ratios	1% MEKP9H	...
CPP catalyst and filler ratios GT/VIS (55% VF650) at 90F	...	...
935 Barcol reading at 60 min	73.0	0.0-99.9
CPP 90 H <sub>2</sub> O peak exotherm	227	200-230

Note: Production date, March 10, 2004. rpm, revolutions per minute.

**Table 3 Characteristics of \*Cook STYPOL 040-9958 batch number 83200400139**

Test no.	Test	Value	Typical properties
F300	Nonvolatile mess, %	59	50-60
F400	Visc. Brookfield	As follows	...
F400	MDL, SPNDL, TEMP	RVT No. 2	77DF
F400	Viscosity/rpm	1840	Report CPS at 5 rpm
F400	Viscosity/rpm	676	400-800 CPS at 50 rpm
F400	Thix index	2.72	2.6-3.6
F515.2	Cup gel time, catalyst and %	DDM-9	1.25%
F515.2	Cup gel time test at 77 °F	26.2	25-35 min
F515.2	GT to peak exotherm	14.2	Minutes
F515.2	Peak exotherm	265 °F (130 °C)	...
F301	wt/gal	9.2	9.05-9.3 lb/gal (1103 kg/m <sup>3</sup> )

Note: pm, revolutions per minute.

**Table 4 Characteristics of the peroxide catalysts used based on their material safety data sheets (MSDS)**

Product name	Characteristics	Supplier
Hi-Point 90	36-40% MEK peroxide; 9.0% active oxygen	Crompton Corp.
Hi-Point PD-1	20-24% MEK peroxide; 5.4% active oxygen	Crompton Corp.

**Table 5 Linseed oil absorption for limestone and Renfil fillers**

Adjunct material	Absorption (kg of oil/kg filler)	Reference
Crushed limestone	Low structure (0.8-1.34)	4
Renfil fiber (30/50)	Very high structure (2.2-2.8)	5

parison of experimental data with the predictions of the model for reaction temperature and weight loss as a function of time provided some valuable insights into the VOC emissions produced during composite processing. Figure 1 compares the reaction temperature-time profile for both the model and the experimental data for the polymerization of ER 733-6903. Ordinate error bars of 10% were arbitrarily assigned to both data sets. When compared with the experimental data, the model gave a higher peak exotherm, 194 °C (280 °F) versus 120 °C (250 °F), respectively, and a retarded approach to the peak exotherm, 30 versus 25 min, respectively. However, the slopes of the initial and final portions of the temperature-time profiles

**Table 6 Assumptions used to generate a dynamic model for unsaturated polyester polymerization**

1. The polymerization rate is primarily a function of temperature, and the molar concentrations of both styrene monomer and the initiator.
2. Polymerization is rapid and homogeneous, and the reduced thermal conductivity of the reacting polymer mass generates a transient adiabatic temperature rise which is uniform throughout (i.e., large thermal gradients do not exist within the uniformly reacting resin mass).
3. Heat losses are by natural convection to the surroundings and from latent heat requirements for styrene being transferred from the liquid to the vapor phase.
4. Initial conditions for temperature, styrene and initiator concentrations, as well as the temperature dependencies for the reaction rate constants, vapor pressure of styrene, and latent heat of styrene are known.
5. Initial time steps of 5 min are taken to compute the mass of styrene that reacts, the 5-min adiabatic temperature rise that is produced, both heat and mass losses, and the subsequent update of properties for the new temperature prior to the next time iteration. One minute time intervals rather than 5-min intervals were used just prior to the onset of a peak isotherm.
6. Profiles of temperature and the fractional weight lost, as styrene monomer, were generated as a function of time until all the styrene had reacted and/or the incremental weight loss was negligible (<0.005%).

are similar. The similitude in these portions of the process suggests that the assumptions made in the development of the model were at least partially correct, and that perhaps tweaking of the kinetic parameters might yield a better overall correlation. Such adjustments were not made, however.

Additional insights into the mechanistic differences between the model predictions and the experimental data are

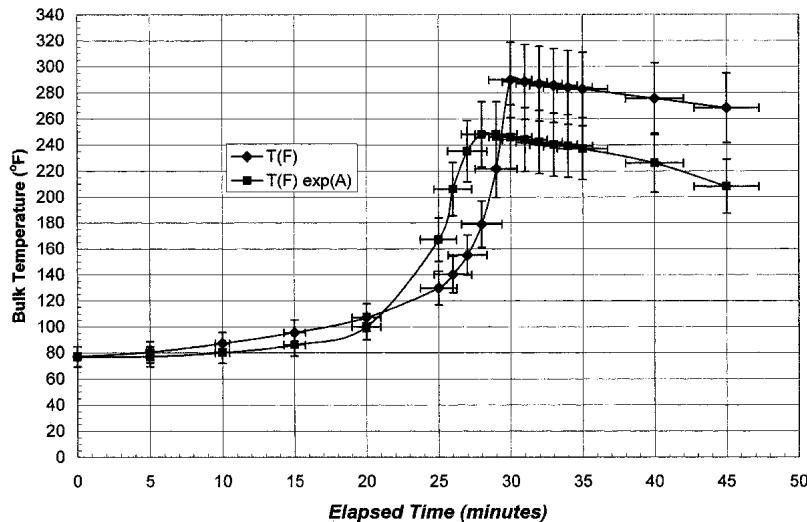


Fig. 1 Temperature profile (°F) for 100 g of ER 733-6903 and 1.5% Hi-Point 90 initiator

inferred from a second plot of fractional weight loss versus time, as shown in Fig. 2. For fractional weight loss (VOC) versus time, a greater divergence between the experimental data and the model predictions is apparent. As shown, the experimental data are represented by a slightly compound curve, which can also be adequately described as a linear relationship. The model, however, predicts an exponential rise in the fractional weight loss-time profile to a point at which all of the styrene has either polymerized or escaped as VOC. The exponential rise results from the model being based on styrene vapor loss driven by the temperature dependence of vapor pressure and is estimated using an evaporation calculator (Ref 7). This concept appears to be true during the first 5 min of UP polymerization but thereafter falters, and the divergence between the model and experimental data becomes pronounced. Based on the data, it is hypothesized that after the initial 5 min, VOC emissions are controlled by the diffusion of styrene monomer to the exposed surface of the polymerizing mass, not by the vapor pressure of liquid styrene. This occurs because the vapor pressure for the styrene is primarily a function of temperature. Diffusive mass transfer, however, is a function of both temperature and a concentration gradient. Therefore, during the first 5 min, as styrene is increasingly consumed in the bulk polymerization process, its gradient for diffusion to an exposed surface is significantly decreased. The decreased rate of diffusion is accompanied by a decrease in the rate of VOC loss. Then, as the temperature continues to rise in response to the reaction exotherm, the coefficient of diffusivity increases and the VOC loss begins to accelerate again, producing the observed compound weight loss curve. Surprisingly, this slight compound curve for the weight loss-time profile from the start to peak exotherm can be adequately approximated by a linear regression.

This observed approximate linearity for the fractional weight loss as a function of time led to the development of a VOC loss relationship given by Eq 1. This equation provides an estimate of the “final” equilibrium percentage weight loss. Hence, once the average weight loss of a base UP resin formulation ( $R_o$ ) has been established with six experiments using the EPA protocol, it is possible to estimate what the addition of a specific adjunct material will have on VOC reduction. This assumes that an oil adsorption number, and the weight fractions

of the adjunct materials and styrene monomer in the UP are known. Actual experimental data for VOC loss using the ER polyester resin with limestone and the RF fiber are depicted in Fig. 3 and 4. The use of Eq 1 to estimate the percentage of equilibrium weight loss is also illustrated in the following discussion.

For Fig. 3 the following procedure was followed:

#### For baseline:

- ER 733-6903 resin mass was ~100 g and contained 45% styrene.
- To the UP resin, ~1.5 g (1.5%) of Hi-Point 90 (MEK peroxide) were added.
- The average percent weight loss by the EPA test protocol was 3.77%.

#### UP resin formulation with 10% limestone:

- ER 733-6903 = 100 g
- 10% CaCO<sub>3</sub> = 100 \* (0.10/0.90) = ~11.11 g of CaCO<sub>3</sub>
- Hi-Point 90 peroxide = 0.015(111.11) = 1.67 g
- Styrene fraction of UP resin, and  $V_{fs} = 0.45$
- The average weight loss by the EPA test protocol was 3.28%
- The percentage of VOC loss as determined by Eq 1 was:  $y = 3.77 - \{[(0.10)/(0.45 + 0.10)]1.08\} = 3.57\%$ , or an error of ~10%

The experimental results reported as VOC loss versus time using four different limestone loadings and the previous UP resin formulation are given in Fig. 3. The theoretical predictions for percentage of VOC losses using Eq 1 for the same four UP formulations are given in Table 7 for comparison.

The preceding information suggests that the use of Eq 1 yields conservative weight loss estimates, which on average were ~10% in excess of the actual measured losses as determined by the EPA protocol. Equation 1 is conservative because it considers only the effects of absorption and neglects reductions in diffusive mass transfer caused by use of the adjunct materials. Also, the oil adsorption number used for limestone in Eq 1 is with respect to linseed oil, not styrene (Ref 8). The

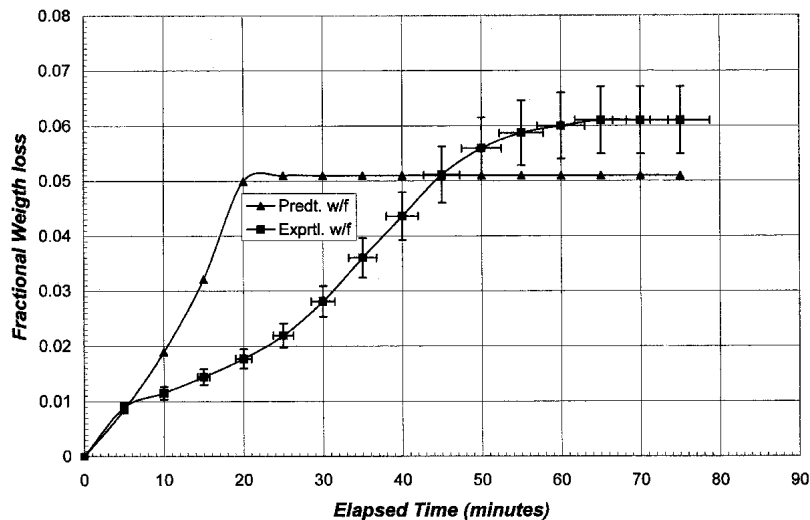


Fig. 2 Predicted and experimental fractional weight loss for ER 733-6903 and 1% Hi-Point 90 initiator

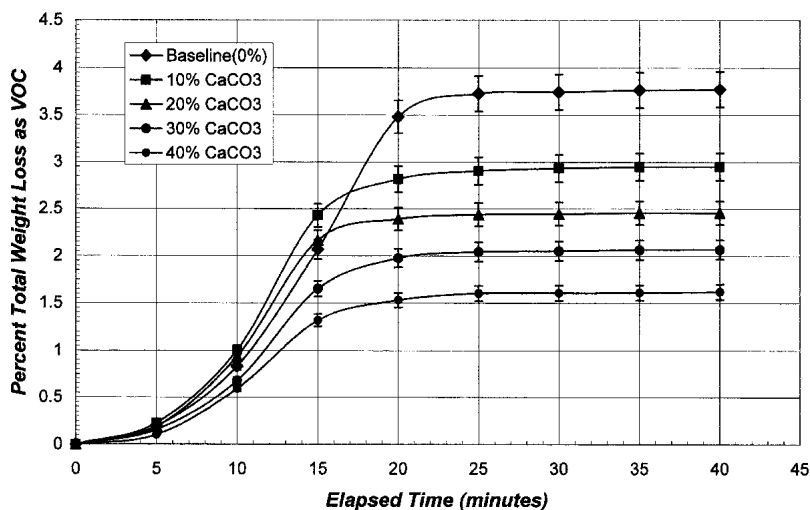


Fig. 3 Percentage of weight loss profile for ER 733-6903 with 1.5% Hi-Point 90 initiator and different limestone filler loadings, and 5% error bars

liquid styrene used in the UP resin may exhibit higher oil absorption characteristics for the crushed limestone being used in this UP formulation. Moreover, the oil absorption numbers are determined for ambient temperatures without consideration of a peak exotherm. Without knowing the diffusion effects or the specific oil absorption for styrene/limestone, Eq 1 represents only a conservative approximation for VOC losses, because it gives a higher VOC loss than does the EPA protocol.

Figure 4 depicts the experimentally determined percentage of weight loss versus time profile as determined for the same ER UP resin, but this time for a different proprietary formulation used by a molding shop. In this instance, the shop had been using FG (16% by weight) and UP-ER (50.4% by weight) together with 33.6% by weight of limestone. Desiring property improvement and cost cuts, the shop made the decision to remove a portion of the FG and replace it with the same mass of less expensive RF fiber. The addition of RF 30/50 was targeted at a loading of ~4% by weight, which lowered the FG content to 12%. The experimental data displayed in Fig. 4 suggest that the use of RF 30/50 in this manner reduced VOC emissions to an average level of only 1.25% based on the total

UP composite mass. This 1.25% VOC loss is down from the experimental average of 2.43% VOC loss without the RF 30/50. Once again, Eq 1 was used to provide a comparison with the experimental results:

$$\begin{aligned} \text{Estimated VOC loss (\%)} &= y \\ &= 2.43 - (1.07 * 0.597 + 2.5T * T0.15) \\ &= 1.42\% \end{aligned}$$

The estimated VOC loss of 1.42% is again conservative when compared with the 1.25% VOC loss measured experimentally using the EPA procedure. Therefore, the use of RF fiber in this case would have resulted in a ~50% reduction in VOC emissions, as determined by the EPA test,  $[100 * (2.43 - 1.25)/2.43]$ . This compares to an ~40% VOC reduction using Eq 1.

In a similar process for the manufacture of UP/FG tanks, a spray gun with chopped FG and CR "STYPOL" UP resin was used. The CR resin contained 41% liquid styrene, and the existing composite formulation consisted of 30% FG and 70% UP resin on a weight basis. It was proposed to modify this formulation to contain only 22.5% FG, 7.5% RF 30/50, and 70% UP

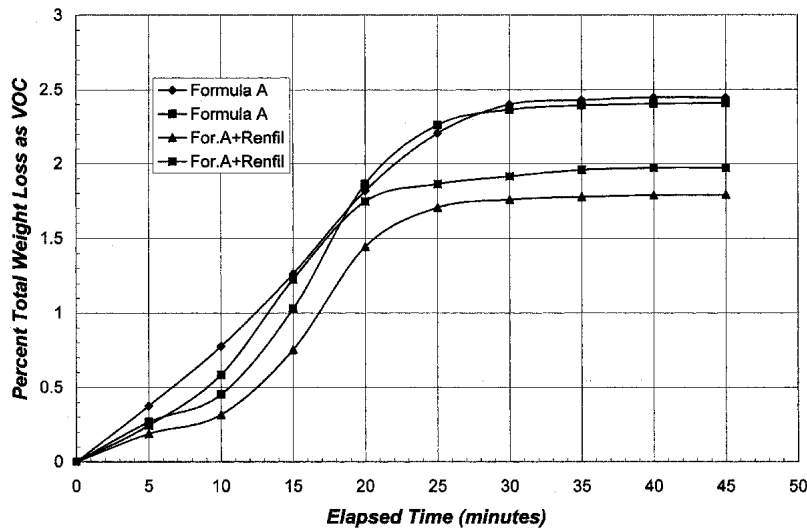


Fig. 4 Percent of weight loss as VOC during cure of proprietary formulation of the ER resin, limestone, and RF

**Table 7 Percent VOC losses predicted using Eq 1 and those determined experimentally using the Environmental Protection Agency test protocol for unsaturated polyester resin and limestone**

$x_i$	$V_{fs}$	Loss by Eq. 1, %	EPA exp., %	Error, %
0.10	0.405	3.56	3.28	8.5
0.20	0.36	3.38	3.07	10.2
0.30	0.32	3.25	2.95	10.1
0.40	0.27	3.13	2.70	15.7

Note: Conditions:  $R_o = 3.77$ , and  $A_i = 1.08$ .

resin. Using the EPA protocol, the gravimetric determination of the VOC loss for the old formulation averaged 4.37% (range 4.77-4.01%). When RF fiber was used to replace a portion of the glass fiber, the average percentage VOC loss was reduced to an average of 3.39%. The use of Eq 1 resulted in the prediction of a higher, more conservative VOC loss of 3.9%. Based on the experimental data, the use of RF fiber to replace a portion of the FG in the formulation was found to provide a ~22% reduction in VOC emissions.

## 4. Conclusions

Based on a limited number of experiments using two commercial resins, two commercial adjuncts, and commercial shop formulations, the use of the EPA test protocol published as appendix A to subpart WWWW of 40 CFR part 63 appears to be adequate for the determination of HAP emissions for UP resin composites. Comparisons of the averages for the required six experiments for the UP formulations with and without adjunct materials suggest that the use of limestone and RF fiber can be effective in the reduction of VOC (HAP) emissions. However, in some cases the improvements in average reductions are small, and data scatter challenges statistical significance. Moreover, the same commercial resins used with various shop formulations involve highly variable procedures,

which can lead to difficulties in maintaining compliance with the requirements of the EPA protocol. The authors found that even small adjustments in the amount of initiator used in a given formulation made a significant difference, but such adjustments were required if the exact procedures of the test protocol were followed.

A model developed for the UP polymerization process indicated that for many shop formulations, the VOC loss will be nearly linear with the elapsed time from initiation to peak exotherm. This suggested that the possible VOC suppression achieved with adjunct materials used in UP composites could be correlated with oil the absorption characteristics of the adjunct. An equation was developed based on this concept, which used the weight fraction of volatile styrene present in the base UP resin together with the weight fraction of adjunct material used and its oil absorption number. This equation was found to be conservative for limestone and RF fiber adjuncts, and yielded smaller estimates of reductions in VOC emissions than were measured experimentally using the EPA protocol.

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