



Vapor Suppressant Effectiveness Test Protocol

Revision 3.0

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[Additional Modifications Pending]

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CFA Vapor Suppressed Resin Effectiveness Test Protocol (VSR Test)

1.0 Scope and Application

The purpose of this procedure is to determine the effectiveness of a suppressant additive with a specific resin system, by direct comparison. **The data generated by this test is used as an input value in the Unified Emissions Factor (UEF) emissions model, which then yields an emissions factor for a specific material combination of resin and suppressant additive.** The VSR test itself is not intended to quantify overall volatile emissions from a resin and is not intended to be used as a stand-alone test for emissions determination. The test is only valid when used in combination with the UEF model to generate emission factors or emission estimates.

If a resin manufacturer supplies a molder with a vapor-suppressed resin, the resin supplier will typically employ this test to provide the molder with the VSE_{resin} value as generated from this test method. This value is then used as an input number in the UEF emissions model. The value represents the effectiveness of the vapor suppressant when the resin is tested in the form supplied to the molder, and the results are considered generic. The addition of fillers or other additives by the molder may impact the effectiveness of the vapor suppressant. If the resin is processed as a filled system, in which the weight ratio of filler to resin is above 30/70, the molder and resin supplier should jointly determine the specific resin mixture to be tested. This will yield a $VSE_{filled\ system}$ value that will provide a more accurate data input into the UEF emissions model.

This test method employs a mass balance technique to establish the relative loss of the volatile component from unsaturated polyester or vinyl ester resins. The effectiveness of a specific vapor suppressant and resin mixture is determined by comparing the relative volatile weight losses from vapor-suppressed and non-suppressed resins. The volatile species are not separately analyzed.

Although the species contained in the volatile component are not important, an extended listing of potential analytes that may be contained in unsaturated polyester or vinyl ester resins is provided in Table 1.1. However, most of the resin formulations presently used by the composites industry only contain styrene monomer.

List of Volatiles		
Table 1.1		
Analyte	CAS Number	Matrices
Styrene monomer	100-42-5	Unsaturated polyester/vinyl ester resin
Vinyl toluene monomer	25013-15-4	Unsaturated polyester/vinyl ester resin
Methyl methacrylate monomer	80-62-6	Unsaturated polyester/vinyl ester resin
Alpha methyl styrene monomer	98-83-9	Unsaturated polyester/vinyl ester resin
Para methyl styrene monomer	Vinyl toluene isomer	Unsaturated polyester/vinyl ester resin
Chlorostyrene	1331-28-8	Unsaturated polyester/vinyl ester resin
Diallyl phthalate	131-17-9	Unsaturated polyester/vinyl ester resin
Other volatile monomers	Various	Unsaturated polyester/vinyl ester resin

2.0 Summary of Method

Differences in resin and suppressant chemistry often affect the performance of a vapor suppressant. The purpose of this test method is to quantify the effectiveness of a specific vapor suppressant (VS) added to a specific unsaturated polyester or vinyl ester resin. This comparative test quantifies the loss of volatiles from the laminate during the roll out and curing phases for resins formulated both with and without a suppressant additive. The quantitative results of this test are used as an input factor in the UEF emissions model, which allows the UEF to predict emissions from specific combinations of resin and suppressant. This test by itself does not measure absolute emission rates for the entire lamination process.

3.0 Definitions

3.1 Terms:

- a. **Vapor suppressant** - an additive that inhibits the evaporation of volatile components in unsaturated polyester or vinyl ester thermoset resins.
- b. **Resin-as-applied** - the specific formulation of a resin as it is applied to a mold, including fillers and other additives used to modify the neat resin.
- c. **Neat resin** - resin without fillers or other modifying additives typically added by the end user. (Excluding promoters and initiators).
- d. **Unsaturated polyester resin** - a thermoset resin commonly used in composites molding.
- e. **Unsaturated vinyl ester resin** - a thermoset resin used in composites molding for corrosion resistant and high performance applications.
- f. **Laminate** - a combination of glass fiber reinforcement and a thermoset resin.
- g. **Chopped strand mat** - glass fiber reinforcement with random fiber orientation.
- h. **Initiator** - a curing agent added to a thermoset resin.
- i. **FRP roller** - a tool used to saturate and compact a wet laminate.
- j. **Gel time** - the time from the addition of initiator in a resin to when the resin polymerizes into the gel state.
- k. **Filled resin system** - a resin, which includes the addition of inert organic or inorganic materials 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.
- l. **Highly filled resin system** - typically a resin containing >30% mineral filler by weight; or >1% lightweight microspheres by weight. The amount of filler that is added to a resin is determined by the effect on resin properties and the viscosity increase of the resin system. Highly filled resin systems are generally used in conjunction with a lower ratio of fiberglass reinforcement in the laminate. (Reference 12.2.b)

3.2 Acronyms:

- a. **VS** - vapor suppressed
- b. **NVS** - non-vapor suppressed
- c. **VSE** - vapor suppressant effectiveness
- d. **CSM** - Chopped strand mat
- e. **UEF** - Unified Emissions Factors Model

4.0 Interferences

There are no known interferences, which substantially affect the results of this test.

5.0 Safety

Standard laboratory safety procedures should be used when conducting this test. Refer to specific MSDS for material handling precautions.

6.0 Equipment and Supplies

6.1 Equipment

- a. Balance enclosure¹
- b. (2) Laboratory balances – accurate to $\pm .01$ g
- c. Stop watch or balance data recording output to datalogger
- d. Thermometer - accurate to $\pm 2.0^{\circ}$ F
- e. 14" x 14" aluminum plate, 1/16" thick
- f. 16" x 16" Mylar™ sheet, 4 mil thickness
- g. 250ml plastic tri-corner beakers
- h. Eye dropper or pipette
- i. Disposable FRP roller, 3" wide x 3/16" diameter

6.2 Supplies

- a. Chopped strand mat (1.5 oz/ft²)
- b. Initiator
- c. Resin
- d. Vapor suppressant additive

¹ Balance enclosure - The purpose of the balance enclosure is to prevent ambient airflow from affecting the laboratory balance. The enclosure may be a simple three-sided box with a top and an open face. The configuration of the enclosure is secondary to the purpose of providing a stable and steady balance reading for accurate measurements.

7.0 Reagents and Standards

This test method does not require the use of reagents or standards beyond the materials that are being tested.

8.0 Sample Collection, Preservation, and Storage

This test method involves the immediate recording data during the roll out and curing phases of the lamination process during each test run. Samples are not collected, preserved or stored.

9.0 Quality Control

Careful attention to laboratory procedure, routine equipment calibration, and replicate testing are the quality control activities for this test method. Please refer to the procedures in section

11.0. A minimum of six (6) test run pair replicates are performed for each resin and suppressant test formulation

10.0 Calibration and Standardization

The Laboratory balances are calibrated before and after each session of six test runs, using ASTM certified weights.

11.0 Test Procedure

11.1 Test Set-up

- a. The laboratory balance is placed in an enclosure to prevent fluctuations in balance readings due to air movement. Front of enclosure is left open, but positioned so that ambient airflow will not effect balance readings.
- b. The aluminum plate is covered with a plastic film. (4-mil Mylar™ film, which may be held in position with four pieces of double-sided tape on the corners of the aluminum plate).
- c. The plate and plastic film are positioned on the balance.
- d. The resin is adjusted to room temperature.
- e. Two plies of nominal 1.5 oz/ft² chopped strand mat are cut to a dimension of 12" x 12"

11.2 Resin Gel Time/Initiator Percentage

- a. Both comparison samples (i.e. without suppressant additive, and with suppressant additive) will be processed in a manner that produces the same resin gel time. All samples in a comparative test group must be processed using the same resin, initiator, initiator level, and under the same temperature and humidity conditions ($\pm 2^{\circ}\text{F}$ temperature / $\pm 5\%$ RH).
- b. Initiator level will be determined from initiator percentage specification used to measure gel time, and recorded on resin certificate of analysis²; or, if a unique gel time is required in a production laminate, initiator percentage will be determined by that specific requirement.
- c. Examples:
 - Resin "A" is determined as stated to have a 15 minute cup gel time @ 77⁰F, using 1.5% initiator. An initiator level of 1.5% would be selected for the both the non-suppressed and the suppressed test samples.
 - Based on a specific production requirement, Resin "B" is processed in a production laminate using 2.25% initiator, which produces a 20-minute gel time. An initiator level of 2.25% would be selected for both the non-suppressed and suppressed test samples.

² Resin gel time, as recorded on the resin certificate of analysis, is measured using a standard gel time procedure. This procedure typically uses a 100 gram cup sample @ 77⁰F (25⁰C), a specific type of initiator and a specified percentage of initiator.

11.3 Test Run Procedure for Non-suppressed Resin

- a. Two plies of chopped strand mat (12" x 12") are placed on the plate and the weight is measured and recorded.

- b. Required resin weight and initiator weight are calculated (refer to calculation formula in 12.2).
- c. Disposable FRP roller is placed on the edge of the plate.
- d. Balance is tared, which means balance reading is set to zero with the aluminum plate, Mylar film, glass mat, and FRP roller on the balance pan.
- e. Resin and initiator are weighed on the second balance and mixed.
- f. Resin is poured on chopped strand mat in a pre-determined pattern (see Figure 11.1).
- g. Stopwatch is started and the start time recorded.
- h. Initial weight is recorded.
- i. Plate is removed from balance.
- j. FRP roller is used to disperse resin evenly across chopped strand mat.
- k. The wet laminate is rolled to eliminate normal air voids. Rollout time should be in the range of 2-3 minutes and should be the same for all test runs.
- l. FRP roller is placed on the edge of the plate when rollout is completed.
- m. Roll-out time is recorded by stopwatch.
- n. Plate is placed back on the balance pan. The weight is recorded at the 5-minute mark.
- o. Weight is recorded every 5 minutes, until three consecutive equal weights or a weight gain is observed.

11.4 Test Run Procedures for Vapor Suppressed Resin

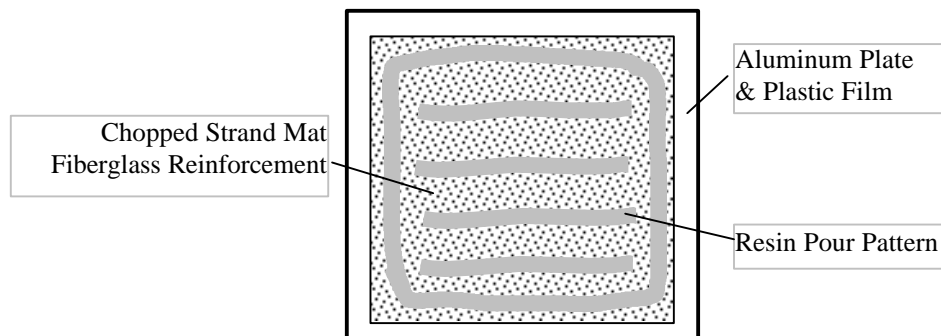
Repeat the above procedure after adding the suppressant additive to the resin as required. A consecutive non-vapor suppressed and vapor suppressed test run constitute one test pair.

11.5 Test Run Comparison Criteria

- a. The laminate roll out time must be within ± 30 seconds for each test run pair.
- b. Temperature for each pair must be maintained within $\pm 2^{\circ}\text{F}$.
- c. Resin, initiator and additives must be from the same respective batches for each test run pair.
- d. Initiator percentage must be the same for each test pair.

11.6 Resin Application Pour Pattern

a. To facilitate the distribution of resin across the chopped strand mat, and to provide consistency from test to test, a uniform pour pattern should be used. The recommended pour pattern is shown below:



12.0 Data Analysis and Calculations

12.1 Data Analysis

This test method requires only a simple mass balance calculation - no special data analysis is necessary.

12.2 Calculations

- a. Resin weight determination - Unfilled resin systems:

$$\text{CSM fiberglass weight} \times 3 = \text{Resin weight}$$

(Yields - 25:75 glass to resin ratio)

- b. Resin weight determination - Highly filled resin systems:

$$\text{CSM fiberglass weight} \times 4.55 = \text{Resin weight}$$

(Yields - 18:82 glass to resin ratio)

- c. Initiator weight determination:

$$\text{Resin weight} \times \text{Initiator \%} = \text{Initiator weight}$$

- d. Emissions loss determination (weight):

$$\text{Start weight} - \text{end weight} = \text{Emissions loss weight}$$

- e. Emissions weight loss determination (% of Resin Weight)

$$\text{Emissions loss (wt)} \div \text{Resin weight} \times 100 = \% \text{ Emissions per resin weight}$$

- f. Vapor suppressant effectiveness (VSE_i) for one test pair:

$$\frac{\text{Vapor-suppressed emissions wt. loss}}{\text{Non-Suppressed emissions wt. loss}} \times 100 = \text{VSE}_i$$

- g. Vapor suppressant effectiveness (VSE_{resin}) for resin formulation (assuming six test pairs per test session):

$$N=6$$

$$\frac{(\text{vse}_i)}{6} = \text{VSE}_{\text{resin}}$$

i

- h. Vapor suppressant resin (VSR) reduction factor for use in the Unified Emission Factor (UEF) table for application processes that use VSR:

$$(100 - \text{VSE}_{\text{resin}}) \div 100 = \text{VSR reduction factor}$$

13.0 Method Performance

13.1 Precision

The precision of this method is established by the precision of the analytical balance and the relative quantity of emissions during the test. For example, if 10% (by weight) of a 50 gram resin sample is emitted during the test, and the balance precision is 0.01 g, the precision of the emission measurement is:

$$0.01 \text{ g} \div (0.01 \times 50 \text{ g}) = 0.002 \text{ or } 0.2\%$$

13.2 Bias

The mass balance approach is generally free of any bias.

13.3 Detection Limit

The concept of detection limit is generally not applicable to the mass balance approach.

13.4 Performance Testing

Following the initial development of this test by the Composites Fabricators Association, the method has been tested by Reichhold Chemical, Inc. and BYK Chemie USA.

Reichhold reports that the method is precise and repeatable. The Reichhold performance testing included fifty test runs using ten different resin formulations. The data scatter was very slight for each formulation, as listed below:

Resin Type	(100% - VSE) Test Values		
	Test #1	Test #2	Test #3
DCPD #1	13.00%	14.74%	14.79%
DCPD #2	64.43%	66.11%	67.61%
Vinyl ester #1	70.76%	70.87%	71.03%
Vinyl ester #2	56.98%	56.94%	57.46%
Terephthalic	49.34%	49.34%	51.61%
Bisphenol Fumarate	24.59%	27.98%	-
Isophthalic #1	67.18%	58.66%	58.76%
Isophthalic #2	75.08%	75.32%	76.80%
Isophthalic #3	71.85%	71.03%	70.00%

BYK Chemie USA reports that the method is precise, easy to implement, and very repeatable.

The BYK Chemie performance testing included four test sessions (six runs per session) using two different resin formulations (suppressed and unsuppressed). The data scatter was low for each formulation, as listed below:

Resin Type	% Emission Wt. Values						Avg.
Formula #1 VS	0.86%	0.82%	1.00%	0.92%	1.06%	1.10%	0.96%
Formula #1 non- VS	3.67%	3.40%	3.36%	3.42%	3.52%	3.43%	3.46%
VSE values	23.4%	24.1%	29.7%	26.9%	30.1%	32.1%	27.7%
Formula #2 VS	1.89%	1.31%	1.86%	1.84%	2.20%	2.35%	1.91%
Formula #2 non-VS	4.26%	4.40%	4.37%	4.36%	4.62%	4.31%	4.39%
VSE values	44.3%	29.8%	42.6%	42.2%	47.6%	54.5%	43.5%

13.5 Comparison to EPA Reference Methods

This test has no corresponding EPA reference method.

14.0 Pollution Prevention

The sample size used in this test method produces a negligible emission of HAP, and has an insignificant impact upon the atmosphere.

15.0 Waste Management

The spent and waste materials generated during this test are disposed according to required facility procedures, and waste management recommendations on the corresponding material safety data sheets.

16.0 References

- *CFA Vapor Suppressant Effectiveness Test Development*, 4/3/98, correspondence with Dr. Madeleine Strum, EPA OAQPS.
- *CFA Vapor Suppressant Effectiveness Screening Tests*, 4/4/98
- *Styrene Suppressant Systems Study*, Reichhold Chemical, 11/30/98
- *Evaluation of the CFA's New Proposed Vapor Suppressant Effectiveness Test*, Technical Service Request #: ED-01-98, BYK Chemie, 6/3/98
- *Second Evaluation of the CFA's New Proposed Vapor Suppressant Effectiveness Test*, Technical Service Request #: ED-02-98, BYK Chemie, 1/26/99