Guidelines for Calculating Emissions from Polyester Resin Operations

(December 2016)

The purpose of this document is to provide operators with guidelines in estimating volatile organic compound (VOC) emissions from the use of materials in polyester resin operations subject to District Rule 1162. The methodologies used in this document are consistent with 40 CFR Part 63, subpart WWWW.

Starting with Fiscal Year 1999-2000, operators of polyester resin operations that are subject to Rule 1162 must use the methodologies in this guideline for calculating and reporting VOC emissions in the District Annual Emissions Reporting (AER) Program. In addition to the definition of terms in Rule 1162, the first section of this document describes the types of polyester resin operations that may be encountered. The next two sections discuss the air emissions associated with polyester resin operations and the use of emission factors and equations. The last section provides instructions and examples of how VOC emissions are calculated and reported in the AER.

DESCRIPTION OF OPERATIONS

Atomized Mechanical Application means application of resin or gel coat with spray equipment that separates the liquid into a fine mist. This fine mist may be created by forcing the liquid under high pressure through an elliptical orifice, bombarding a liquid stream with directed air jets, or a combination of these techniques. This process allows for a greater production rate and more uniform parts than hand lay-up.

Closed Molding means a grouping of processes for fabricating composites in a way that VOC containing materials are not exposed to the atmosphere except during the material loading stage. Processes where the mold is covered with plastic prior to resin application, and the resin is injected into the covered mold are also considered closed molding.

Compression Molding means a closed molding process for fabricating composites in which composite materials are places inside matched dies that are used to cure the materials under heat and pressure without exposure to the atmosphere.

Covered-Cure refers to an impervious film or barrier that is applied to the wet surface of the mold just after the application of the resin. This barrier may be applied immediately after roll-out phase, or just after the application phase without any subsequent roll-out.

Filament Application means an open molding process for fabricating composites in which reinforcements are fed through a resin bath and wound onto a rotating mandrel. The materials on the mandrel may be rolled out or worked by using non-mechanical tools prior to curing. Resin application to the reinforcement on the mandrel by means other than the resin bath, such as spray guns, pressure-fed rollers, flow coaters, or brushes are not considered filament application.

Fluid Impingement Technology means a spray gun that produces an expanding non-misting curtain of liquid by the impingement of low-pressure uninterrupted liquid stream.

Gel Coat is a specialized polyester quick-setting resin that is formulated to provide a cosmetic outer surface and to improve performance of the composite products. The "solvent" in gel coat is styrene monomer and/or methyl methacrylate (acrylic–MMA) which cross-links during curing.

Hand Lay-Up is the simplest fabrication in open mold process. Hand lay-up is a manual application technique of composite materials using a bucket and a brush or a roller, or other hand held method of application. Hand lay-up uses no mechanical spraying or chopping equipment for depositing the resin or glass reinforcement. The process continues until the desired thickness is achieved. The use of pressure-fed rollers and flow coaters to apply resin is not considered manual resin application.

Injection Molding means a closed molding process for fabricating composites in which composite materials are injected under pressure into a heated mold cavity that represents the exact shape of the product. The composite materials are cured in the heated mold cavity.

Methyl Methacrylate (MMA) is sometimes present as a secondary monomer added to the gel coat formulation to increase the UV-resistance, to improve the surface finish, and to impart greater toughness. The greater vapor pressure of MMA makes it much more volatile than styrene. Its emissions must be estimated separately from styrene emissions.

Non-Atomized Mechanical Application means the use of application tools other than buckets and brushes to apply resin and gel coat. Examples of non-atomized application include flow coaters, pressure-fed rollers, and fluid impingement spray guns.

Open Molding is a method of fabricating composite parts by applying gel coats, resins, fibers, and other composites materials on an open mold using either hand lay-up or spray-up applications.

Polymer (Marble) Casting means a process for fabricating composites in which composite materials are ejected from a casting machine or poured into an open, partially open, or closed mold and cured. After the composite materials are poured into the mold, they are not rolled out or worked while the mold is open, except for smoothing the material and/or vibrating the mold to remove bubbles.

Pultrusion means a continuous process for manufacturing composites that have a uniform cross-sectional shape. The process consists of pulling a fiber-reinforcing material through a resin impregnation chamber or bath and through a shaping die, where the resin is subsequently cured.

Robotic/Automated Spray means application of resin or gel coat with atomized mechanical equipment in a controlled setting either robotically and/or automatically.

Tooling resin means a resin that is used to produce molds. Tool resins generally have high heat distortion temperatures, low shrinkage, high hardness, and high dimensional stability.

Vapor Suppressant (VS) means an additive, typically a wax, which migrates to the surface of the resin during curing and forms a barrier to seal in the styrene and reduce styrene emissions.

Vapor Suppressed Efficiency (VSE) means the percent reduction of styrene emissions from the use of a resin containing a vapor suppressant added for the purpose of reducing styrene emissions during curing.

VOC EMISSIONS

VOC emissions from polyester resin operations occur when the cross-linking agent (monomer) contained in the liquid resin evaporated from fresh resin surfaces into air during application curing.

VOC emissions also come from the use of solvents for clean-up of hands, tools, molds, and application equipment. Styrene and methyl methacrylate are by far the principle and the most common monomers used in cross linking agents.

Since emissions result from evaporation of monomer from the uncured resin, they depend upon the amount of resin surface exposed to the air and the duration of exposure. Thus the potential for emissions varies with the manner in which the resin is mixed, applied, handled, and cured among the different fabrication processes. For example, the spray lay-up operation has highest potential for VOC emissions because the atomization of resin into spray creates an extremely large surface area from which volatile monomer can evaporate. In contrast, the emission potential in synthetic marble casting and closed molding operations is considerably lower, because of the lower monomer content in the casting resins and of the enclosed nature of the moldings.

VOC emissions from polyester resin operations can be reduced by the implementing the following:

- Switch to low VOC emitting application method;
- Improve resin transfer efficiency;
- Reduce styrene content in resin or use catalyzed resin;
- Use vapor suppressed resins; or
- Use add-on controls.

EMISSION FACTORS

The emissions from the polyester resin operations can be calculated using the factors provided in the attached tables and the following equation.

Emission = Throughput x Emission Factor *Equation 1*

The unit for annual throughput must be consistent with the unit of emission factor. For styrene and MMA emissions from polyester resin operations, the emission factors are determined using styrene and/or MMA contents in the resins and equations in Tables 1 or 2. Operators are encouraged to calculate emissions from the process using specific parameters that are applicable to its operations. ***Supporting documents must be submitted with the annual emission report to show the use of such parameters in calculating annual emissions.***

In addition to emissions from the monomers (styrene and/or MMA), emissions from other VOC solvents, commonly MEK, in the resin must also be calculated separately and combined with emissions from styrene and/or MMA. This calculation is illustrated in the examples section.

VOC emissions from polyester resin operations can be calculated using equation 1 with one of the following methods:

Method 1: Default Emission Factor

For simplicity, default emission factors for the common operations are provided in Emission Factors Tables of AER Help and Support Manual. These default emission factors have already incorporated the emissions from styrene, MEK, and MMA. This means operators don't have to separately

calculate the emissions from these materials. The default factors are developed using the average parameters applicable to conditions in the South Coast Air Basin.

Method 2: Specific Emission Factor

Alternatively, an operator can calculate VOC emissions from polyester resin operations using the specific styrene content with the equations listed in Tables 1 or 2 for the applicable emission factors in conjunction with the following restrictions:

1. For monomer (styrene and/or MMA) content, use information provided by the manufacturer, such as manufacturer's formulation data or material safety data sheet (MSDS), which must be included with the annual report as supporting documentation.
2. Monomer content should be entered as a fraction for equations in Table 1. For example, 35% should be entered as 0.35.
3. If the monomer contents are provided as a range, use the upper limit of the range for emissions calculation and compliance demonstration.
4. If the single value monomer content falls between the percentages in Table 2, the value of emission factor can be linearly extrapolated between the whole percents.
5. Include monomer content as supplied, plus any extra styrene monomer added, but before addition of other additives such as powders, fillers, glass, etc.
6. A default VSE of 0.50 (50%) is allowed and incorporated in the values in Table 2. For VSE of greater than 50%, the VSE must be ***officially certified in writing*** and must be submitted with the annual report to support the presence of VS and its VSE. **Note: Do not confuse vapor suppressed efficiency with add-on control efficiency. The VSE is imbedded into the emission factor for emission calculation; whereas, add-on control efficiency is for calculating emissions after further control by additional control equipment.**

INSTRUCTIONS AND EXAMPLES FOR CALCULATING AND REPORTING VOC EMISSIONS FROM POLYESTER RESIN OPERATIONS

This section contains instructions for calculating VOC emissions from polyester resin operations using the emission factors or emission factor equations. The resulted emission factors should be entered in proper places in the AER Reporting Tool. One set of data will be used in three examples to illustrate the levels of involvement and accuracy of VOC emissions.

ANNUAL DATA:

- The resin contains 33% - 36% styrene with vapor suppressant (VS) certified to be 65% efficient (VSE = 0.65). The MSDS also shows 1.5% MEK as solvent.
- The gel coat contains 41% styrene and 3% methyl methacrylate (MMA).
- 650,000 pounds of resin and 85,000 pounds of gel coat materials were used in making the products in the following areas:
  a) Manual Lay-up Resin = 450,000 lbs
  b) Mechanical Non-Atomized Spray Resin = 200,000 lbs

c) Gel Coat Non-Atomized Spray = 25,000 lbs

d) Gel Coat Atomized Spray = 60,000 lbs

Example 1 – Use of Default Factors: Facility A does not have complete supporting documents for detailed calculations, and calculates and reports VOC emissions using default factors as follows:

a) Manual Lay-up Resin = 450,000 lbs * 0.067 lb/lb = 30,150 lbs VOC

Throughput = 450,000 lbs ***Emission Factor = 0.067 lb/lb***

b) Mechanical Non-Atomized Spray Resin = 200,000 lbs * 0.05 lb/lb = 10,000 lbs VOC

Throughput = 200,000 lbs ***Emission Factor = 0.05 lb/lb***

c) Non-Atomized Spray Gel Coat = 25,000 lbs * 0.36 lb/lb = 9,000 lbs VOC

Throughput = 25,000 lbs ***Emission Factor = 0.36 lb/lb***

d) Atomized Spray Gel Coat = 60,000 lbs * 0.36 lb/lb = 21,600 lbs VOC

Throughput = 60,000 lbs ***Emission Factor = 0.36 lb/lb***

Total VOC emissions = 70,750 lbs or 35.38 tons VOC

Example 2 – Use of Emission Factors in Table 2: Facility B has MSDS for VS resin and gel coat. Facility cannot obtain VSE certification. The operator calculates and reports VOC emissions using Table 2 values, which include the default VSE of 50%, as follows:

a) Manual Lay-up VS Resin with 36% styrene, the emission factor is 0.038 lb/lb for styrene and 0.015 lb/lb for MEK

Emissions = 450,000 lbs * (0.038 lb/lb + 0.015 lb/lb) = 23,850 lbs VOC

Throughput = 450,000 lbs ***Emission Factor = 0.053 lb/lb***

b) Mechanical Non-Atomized Spray VS Resin, the emission factor is 0.031 lb/lb for styrene and 0.015 lb/lb for MEK

Emissions = 200,000 lbs * (0.031 lb/lb + 0.015 lb/lb) = 9,200 lbs VOC

Throughput = 200,000 lbs ***Emission Factor = 0.046 lb/lb***

c) Non-Atomized Spray Gel Coat with 41% styrene and 3% MMA, the emission factors are 0.134 lb/lb for styrene and 0.023 lb/lb for MMA

Emissions = 25,000 lbs * (0.134 lb/lb + 0.023 lb/lb) = 3,925 lbs VOC

Throughput = 25,000 lbs ***Emission Factor = 0.157 lb/lb***

d) Atomized Spray Gel Coat with 41% styrene and 3% MMA, the emission factor is 0.23 lb/lb for styrene and 0.023 lb/lb for MMA

Emissions = 60,000 lbs * (0.23 lb/lb + 0.023 lb/lb) = 15,180 lbs VOC

Throughput = 60,000 lbs ***Emission Factor = 0.253 lb/lb***

Total VOC emissions = 52,155 lbs or 26.08 tons VOC

Example 3 – Use of Emission Factor Equation in Table 1: Facility C has MSDS for resins and gel coats, and certification for VSE of 65%. The operator calculates and reports VOC emissions using specific equations with specific parameters as follows:

a) Manual Lay-up VS Resin with 36% styrene and VSE = 65%

Emission factor = [(0.286 * 0.36) – 0.0529]*[1 – (0.5*0.65)] = 0.034 lb/lb for styrene and 0.015 lb/lb for MEK

Emissions = 450,000 lbs * (0.034 lb/lb + 0.015 lb/lb) = 22,050 lbs VOC

Throughput = 450,000 lbs ***Emission Factor = 0.049 lb/lb***

b) Mechanical Non-Atomized Spray VS Resin with 36% styrene and VSE = 65%

Emission factor = [(0.157 * 0.36) – 0.0165]*[1 – (0.45*0.65)] = 0.028 lb/lb for styrene and 0.015 lb/lb for MEK

Emissions = 200,000 lbs * (0.028 lb/lb + 0.015 lb/lb) = 8,600 lbs VOC

Throughput = 200,000 lbs ***Emission Factor = 0.043 lb/lb***

c) Non-Atomized Spray Gel Coat with 41% styrene and 3% MMA

Emission factor = [(0.4506 * 0.41) – 0.0505] + (0.75 * 0.03) = 0.157 lb/lb

Emissions = 25,000 lbs * 0.157 lb/lb = 3,925 lbs VOC

Throughput = 25,000 lbs ***Emission Factor = 0.157 lb/lb***

d) Atomized Spray Gel Coat with 41% styrene and 3% MMA

Emission factor = (1.03646 * 0.41) – 0.195 + (0.75 * 0.03) = 0.252 lb/lb

Emissions = 60,000 lbs * 0.252 lb/lb = 15,120 lbs VOC

Throughput = 60,000 lbs ***Emission Factor = 0.252 lb/lb***

Total VOC emissions = 49,695 lbs or 24.85 tons VOC

TABLE 1 –EMISSION FACTOR EQUATIONS

OPEN MOLDING

RESINS APPLICATION

Manual

Lay-Up

Resins with Styrene Content S ≤ 32%:	EF = 0.126 * S
Resins with Styrene Content S ≥ 33%:	EF = (0.286 * S) – 0.0529
Resins Containing VS and Styrene Content S ≤ 32%:	EF = 0.126 * S * (1 – 0.5 * VSE)
Resins Containing VS and Styrene Content S ≥ 33%:	EF = [(0.286 * S) – 0.0529] * (1 – 0.5 * VSE)

Tooling

Resins with Styrene Content S ≤ 32%:	EF = 0.126 * S
Resins with Styrene Content S ≥ 33%:	EF = (0.286 * S) – 0.0529
Resins Containing VS and Styrene Content S ≤ 32%:	EF = 0.126 * S * (1 – 0.5 * VSE)
Resins Containing VS and Styrene Content S ≥ 33%:	EF = [(0.286 * S) – 0.0529] * (1 – 0.5 * VSE)

Mechanical

Atomized

Resins with Styrene Content S ≤ 32%:	EF = 0.169 * S
Resins with Styrene Content S ≥ 33%:	EF = (0.714 * S) – 0.18
Resins Containing VS and Styrene Content S ≤ 32%:	EF = 0.169 * S * (1 - 0.45 * VSE)
Resins Containing VS and Styrene Content S ≥ 33%:	EF = [(0.714 * S) – 0.18] * (1 - 0.45 * VSE)

Non-Atomized

Resins with Styrene Content S ≤ 32%:	EF = 0.107 * S
Resins with Styrene Content S ≥ 33%:	EF = (0.157 * S) – 0.0165
Resins Containing VS and Styrene Content S ≤ 32%:	EF = 0.107 * S * (1 - 0.45 * VSE)
Resins Containing VS and Styrene Content S ≥ 33%:	EF = [(0.157 * S) – 0.0165] * (1 - 0.45 * VSE)

Robotic/Automated Spray

Resins with Styrene Content S ≤ 32%:	EF = 0.130 * S
Resins with Styrene Content S ≥ 33%:	EF = 0.77 * [(0.714 * S) – 0.18]
Resins Containing VS and Styrene Content S ≤ 32%:	EF = 0.130 * S * (1 - 0.45 * VSE)
Resins Containing VS and Styrene Content S ≥ 33%:	EF = 0.77 * [(0.714 * S) – 0.18] * (1 - 0.45 * VSE)

Filament

Resins with Styrene Content S ≤ 32%:	EF = 0.184 * S
Resins with Styrene Content S ≥ 33%:	EF = (0.2746 * S) – 0.0298
Resins Containing VS and Styrene Content S ≤ 32%:	EF = 0.120 * S
Resins Containing VS and Styrene Content S ≥ 33%:	EF = 0.65 * (0.2746 * S) – 0.0298

GEL COATS APPLICATION

Gel Coats without Methyl Methacrylate (MMA)

Atomized

Gel Coats with Styrene Content S $\leq$ 32%:	EF = (0.445 * S)
Gel Coats with Styrene Content S $\geq$ 33%:	EF = (1.03646 * S) – 0.195

Non-Atomized

Gel Coats with Styrene Content S $\leq$ 18%:	EF = (0.185 * S)
Gel Coats with Styrene Content S $\geq$ 19%:	EF = (0.4506 * S) – 0.0505

Robotic/Automated Spray

Gel Coats with Styrene Content S $\leq$ 32%:	EF = (0.325 * S)
Gel Coats with Styrene Content S $\geq$ 33%:	EF = 0.73 * [(1.03646 * S) – 0.195]

Gel Coats with Methyl Methacrylate

Atomized

Gel Coats with Styrene Content S $\leq$ 32%:	EF = (0.445 * S) **+ [0.75 * MMA]**
Gel Coats with Styrene Content S $\geq$ 33%:	EF = (1.03646 * S) – 0.195 **+ [0.75 * MMA]**

Non-Atomized

Gel Coats with Styrene Content S $\leq$ 18%:	EF = (0.185 * S) **+ [0.75 * MMA]**
Gel Coats with Styrene Content S $\geq$ 19%:	EF = (0.4506 * S) – 0.0505 **+ [0.75 * MMA]**

Robotic/Automated Spray

Gel Coats with Styrene Content S $\leq$ 32%:	EF = (0.325 * S) **+ [0.75 * MMA]**
Gel Coats with Styrene Content S $\geq$ 33%:	EF = 0.73 * [(1.03646 * S) – 0.195] + **[0.75 * MMA]**

OTHER OPERATIONS

Closed Molding / Injection Molding / Polymer (Marble) Casting

Resins with Styrene Content S:	EF = 0.02 * S
Resins Containing VS with Styrene Content S:	EF = 0.015 * S

Pultrusion

Resins with Styrene Content S:	EF = 0.055 * S
Resins Containing VS with Styrene Content S:	EF = 0.03 * S

Covered-Cure after Roll-Out

Non-VS Resins in Manual Operations:	EF = 0.80 * Equation Listed Above
Non-VS Resins in Mechanical Operations:	EF = 0.85 * Equation Listed Above

Covered-Cure without Roll-Out

Non-VS Resins in Manual Operations:	EF = 0.50 * Equation Listed Above
Non-VS Resins in Mechanical Operations:	EF = 0.55 * Equation Listed Above

TABLE 2 –EMISSION FACTORS FOR COMMON STYRENE AND MMA CONTENTS (lb/lb)

Emission Rate in Pounds of VOC Emitted per Pound of Resin or Gelcoat Processed

Common Styrene Content in Resin/Gelcoat, %	33	34	35	36	37	38	39	40	41	42	43	44	45
Manual - Lay-Up	0.041	0.044	0.047	0.050	0.053	0.056	0.059	0.062	0.064	0.067	0.070	0.073	0.076
- Lay-Up with Vapor Suppressed Resin	0.031	0.033	0.035	0.038	0.040	0.042	0.044	0.046	0.048	0.050	0.053	0.055	0.057
- Tooling	0.041	0.044	0.047	0.050	0.053	0.056	0.059	0.062	0.064	0.067	0.070	0.073	0.076
- Tooling with Vapor Suppressed Resin	0.031	0.033	0.035	0.038	0.040	0.042	0.044	0.046	0.048	0.050	0.053	0.055	0.057
Mechanical - Atomized	0.056	0.063	0.070	0.077	0.084	0.091	0.098	0.106	0.113	0.120	0.127	0.134	0.141
- Atomized with Vapor Suppressed Resin	0.043	0.049	0.054	0.060	0.065	0.071	0.076	0.082	0.087	0.093	0.098	0.104	0.110
- Non-Atomized	0.035	0.037	0.038	0.040	0.042	0.043	0.045	0.046	0.048	0.049	0.051	0.053	0.054
- Non-Atomized with Vapor Suppressed Resin	0.027	0.029	0.030	0.031	0.032	0.033	0.035	0.036	0.037	0.038	0.040	0.041	0.042
- Robotic / Automated - Resin Spray	0.043	0.048	0.054	0.059	0.065	0.070	0.076	0.081	0.087	0.092	0.098	0.103	0.109
- Robotic / Automated - Resin Spray with VS Resin	0.033	0.037	0.042	0.046	0.050	0.054	0.059	0.063	0.067	0.072	0.076	0.080	0.084
Filament application	0.061	0.064	0.066	0.069	0.072	0.075	0.077	0.080	0.083	0.086	0.088	0.091	0.094
Filament application with VS Resin	0.040	0.041	0.043	0.045	0.047	0.048	0.050	0.052	0.054	0.056	0.057	0.059	0.061
Closed / Injection Molding / Polymer (Marble) Casting	0.007	0.007	0.007	0.007	0.007	0.008	0.008	0.008	0.008	0.008	0.009	0.009	0.009
Closed / Injection Molding / Polymer (Marble) Casting with VS	0.005	0.005	0.005	0.005	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.007	0.007
Pultrusion	0.018	0.019	0.019	0.020	0.020	0.021	0.021	0.022	0.023	0.023	0.024	0.024	0.025
Pultrusion with VS	0.010	0.010	0.011	0.011	0.011	0.011	0.012	0.012	0.012	0.013	0.013	0.013	0.014
Gelcoat - Atomized Application	0.147	0.157	0.168	0.178	0.188	0.199	0.209	0.220	0.230	0.240	0.251	0.261	0.271
- Non-Atomized Application	0.098	0.103	0.107	0.112	0.116	0.121	0.125	0.130	0.134	0.139	0.143	0.148	0.152
- Robotic / Automated Gelcoat Spray	0.107	0.115	0.122	0.130	0.138	0.145	0.153	0.160	0.168	0.175	0.183	0.191	0.198

Emission Rate in Pounds of Methyl Methacrylate Emitted per Pound of Gelcoat Processed

Common MMA content in Gelcoat, %	1	2	3	4	5	6	7	8	9	10	11	12	13
Emission Rate, lb/lb of Gel Coat	0.008	0.015	0.023	0.030	0.038	0.045	0.053	0.060	0.068	0.075	0.083	0.090	0.098