

POLYESTER RESIN & FIBERGLASS REINFORCED PLASTIC OPERATIONS

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PROCESS DESCRIPTION: Many products are manufactured from polyester resin and fiberglass reinforced plastic (FRP). During the manufacturing process, liquid polyester resins are mixed with cross-linking agents and catalysts to initiate polymerization reaction which produces a “cured”, hard plastic part of the desired shape. Chopped glass fiber may be mixed with the resin for additional structural strength. Materials may be vapor suppressed in two ways: chemically or physically. Chemical suppression is achieved by using a vapor suppressed resin (VSR) and only reduces styrene emissions, while physical suppression is accomplished by placing an impervious barrier film over the material prior to curing. This type of physical suppression is known as “covered-cure,” which includes vacuum-bagging and press-molding, which reduces emissions from styrene and potentially reduces emissions from other volatile HAPs. The variety of manufacturing operations using polyester resins can be categorized as follows.

Manual	Pultrusion
Mechanical Atomized	Filament Winding
Mechanical Non-Atomized	Marble Casting
Gelcoat	Closed Mold Casting (Polyester Resin)
Continuous Lamination	

Organic emissions occur during the manufacturing process. Emissions typically consist of clean up solvents, volatile catalysts, and some portion of the cross-linking agent / monomer. District emission estimation procedures for polyester resin / fiberglass reinforced plastic operations are as follows.

For styrene, methyl styrene (from mechanical non-atomized operations) and methyl methacrylate (from gelcoat operations):

$$E_a = U_a \times D \times C_i \times MEF \times e_{capture} \times (1 - e)$$

$$E_h = U_h \times D \times C_i \times MEF \times e_{capture} \times (1 - e)$$

For methyl styrene (except from mechanical non-atomized operations) and methyl methacrylate (except from gelcoat operations) and all other pollutants:

$$E_a = U_a \times D \times C_i \times e_{capture} \times (1 - e)$$

$$E_h = U_h \times D \times C_i \times e_{capture} \times (1 - e)$$

Where:

E_a = Annual emissions of each listed toxic air contaminant, (lbs/year)

E_h = Maximum hourly emissions of each listed toxic air contaminant, (lbs/hour)

U_a = Annual usage of each material, (gals/year)

U_h = Maximum hourly usage of each material, (gals/hour)

D = Density of each material used, (lbs/gal)

C_i = Concentration of each listed substance in each material used, (lbs/lb)

For manual, mechanical atomized, mechanical non-atomized and gelcoat:

MEF = $UEF / (C_i \times 2000 \text{ lbs/ton})$

UEF = Unified emission factor, if applicable, (lbs released/ton material used)

UEF can be found in EF Table 1 of ANSI/ACMA (10/2011) document using the individual specific weight percent of styrene, methyl styrene and methyl methacrylate (MMA).

For continuous lamination, pultrusion, filament winding, marble casting and closed molding:

MEF = Monomer emission factor, if applicable, (lbs released/lb monomer used)

MEF found in Table 4.4-2 of AP-42, Section 4.4

e_{capture} = Capture efficiency of control device, (%)

e = Control device control efficiency, (%)

EMISSIONS INFORMATION:

Information regarding material composition can usually be obtained from SDS documentation. The fraction of free monomer emitted is based on emission factors from EPA AP-42 (2/2007), Section 4.4, and the American National Standard Institute (ANSI) and the American Composites Manufacturers Association (ACMA), "Estimating Emission Factors from Open Molding and Other Composite Processes" (10/2011), EF Table 1. Additional factors and assumptions were obtained from "Technical Discussion of the Unified Emission Factors for Open Molding of Composites" by Robert A. Haberlein, Ph.D., QEP (4/1999). All volatile solvents used in clean-up activities or as catalysts are assumed to be emitted.

To quantify methyl styrene emissions from mechanical non-atomized operations, the UEF is determined by multiplying 0.55 by the equivalent styrene UEF listed on EF Table 1 from the ANSI/ACMA (10/2011) document.

To quantify methyl methacrylate emissions from gelcoat operations, the UEF is determined by

using the methyl methacrylate weight percent on EF Table 1 of the ANSI/ACMA (10/2011) document.

Weight percent of styrene monomer (not the total styrene weight percent) should be used for calculation purposes. If only the total styrene weight is provided, that value may be used for conservative emission calculations.

For vapor suppressed resins (VSR), the VSR reduction factor should be based on the test found in EPA MACT Rule, Appendix A to Subpart WWWW of Part 63 – Test Method for Determining Vapor Suppressant Effectiveness.

Covered-cure factors for styrene reduction vary based on when the barrier film is applied and whether the material was applied using a manual or mechanical application. These factors, which are from Haberlein (4/1999), are defined in Table A, as shown below.

Table A

When Barrier Film was Applied	Manufacturing Operation Type	Covered-cure Factor
Post-application	Manual Application	0.50
	Mechanical Application	0.55
Post-roll-out	Manual Application	0.80
	Mechanical Application	0.85

A linear relationship was developed using the data on EF Table 1 the ANSI/ACMA (10/2011) document to determine the styrene UEF if the styrene weight percent range is between 33-50%, unless otherwise noted.

VOC content should not be used to calculate VOC emissions since only some of the styrene, MMA and/or methyl styrene is emitted.

ASSUMPTIONS / LIMITATIONS:

- Site specific monomer test data may be more representative of actual emissions than the AP-42 default values and should be used when appropriate. Emissions of volatile solvents should always be based on mass balance procedures when possible.
- Some monomers and cross-linking agents are solids or non-volatile liquids (e.g., diallyl phthalate, acrylamide, 2-ethyl hexylacrylate, etc.). Emissions of these substances are assumed negligible.
- The emission factors described in this document do not include emission factors for volatile monomers and cross-linking agents other than styrene, methyl methacrylate, and methyl styrene. These emission factors will be used to estimate emissions of other volatile monomers and cross-linking agents like vinyl toluene, vinyl acetate, etc. until

more accurate information becomes available.

- Emissions of the polyfunctional alcohols used in the polyester resin manufacturing process are assumed to be negligible during casting.
- Emissions of fiberglass particulates must be calculated separately from the organic releases and should be based upon site specific information. Default particulate emission factors do not exist and cannot be developed due to the highly unique nature of each manufacturing operation.
- Lesser Atomized Gelcoat Application (LAGA) equipment is designed to apply a spray plume with less atomization than older equipment designs, which results in lower styrene emissions. For LAGA equipment, the UEF for atomized gel coat has been found to over predict gel coat emissions, while the non-atomized gel coat factor has been shown to under predict gel coat emissions.
- Used UEF method if AP-42 calculation method had a rating that was less than B and there was an available UEF method.
- The AP-42 calculation methods with a rating of B or better were used (i.e., calculation methods for both continuous lamination and marble casting).
- The AP-42 calculation methods with a rating less than B were used, because the UEF was not available (i.e., the calculation methods for pultrusion, marble casting, and closed mold).
- For covered-cure operations, once the impervious barrier is applied, the barrier is assumed to be 100% effective at preventing the evaporation and emission of styrene (or other Toxic Air Contaminants) vapor from the uncured material.