

Emission Factors for Non-Atomized Application of Gel Coats used in the Open Molding of Composites

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July 17, 2001

Introduction

A new process for applying gel coat has been developed by the equipment manufacturers since the UEF factors were released in April 1999. Traditional gel coat spray application uses a high-pressure mechanical fluid delivery system to apply gel coat to the open mold surface. This traditional process employs a pressurized spray gun to coat the mold with a fine mist of catalyzed gel coat aerosol droplets. The new gel coat process uses specialized equipment that can apply gel coat to the open mold surface with little or no atomization of the gel coat material. For this reason, the new process is called “non-atomized gel coat application.”

Non-atomized gel coat application is fundamentally different than traditional atomized gel coat spray application. In order to determine the proper emission factors for this new gel coating process, the CFA engaged the Clean Manufacturing Technology Institute (CMTI) located in West Lafayette, Indiana to determine the styrene emission rates for non-atomized gel coat application. The same test procedures and methodologies employed by the CFA in the earlier emission test programs were used by CMTI. The goal of the testing by CMTI is the development of a non-atomized gel coat factor equation for inclusion as an update to the CFA UEF equations. These new factors are described in this report.

The new emission factors are shown in **Table 3** on page 13. Non-atomized gel coat application shows an average 43% emission reduction compared to atomized application, although the exact reduction depends on the monomer content of the gel coat.

Background

From 1996 through 1998, the Composites Fabricators Association (CFA) conducted extensive styrene emissions testing at the Dow Chemical facility at Freeport, Texas. The CFA testing program consisted of three test phases, which investigated the effects of various process parameters on the styrene emissions from the open molding of composite parts. The emission test protocol used in the CFA testing was described in the November 1998 CFA report entitled “*Styrene Emissions Test Protocol & Facility Certification Procedures, Revision 2.1.*” The results of the CFA Phase I testing were detailed in the September 1996 CFA report entitled “*Phase I - Baseline Study; Hand Lay-up, Gel Coating, Spray Lay-up including Optimization Study.*”

On February 28, 1998, Engineering Environmental Consulting Services (EECS), on behalf of the CFA, released a report entitled “*CFA Emission Models for the Reinforced Plastics Industries.*” This report detailed a set of equations and factors developed from the CFA emission test data. These equations and factors predicted the styrene emission rates from typical open-molding lamination processes employed by the reinforced plastics industry. The report was subsequently posted on the EPA CHIEF web site as an acceptable replacement for the obsolete AP-42 factors that had been developed by the EPA for reinforced plastics.

In 1997, the National Marine Manufacturers Association (NMMA) also conducted emission testing using the CFA emission test protocol. The NMMA testing focused on the emissions from the open molding of large composite boat parts. The results of this testing are described in the August 1997 NMMA report entitled “*Baseline Characterization of Emissions from Fiberglass Boat Manufacturing.*” The NMMA report was also posted on the EPA CHIEF web site.

In November 1998, the CFA and NMMA tentatively agreed to merge the emissions data from their respective test programs. The merged data set was then used to develop a new set of equations and factors that “unified” the methodology employed by boat builders and non-boat builders for estimating the emissions from the open molding of composite parts. For this reason, the new emission factors were named the Unified Emission Factors (UEF). The UEF factors were described in an April 7, 1999 EECS report entitled *Technical Discussion of the Unified Emission Factors for Open Molding of Composites*, which was published by the CFA and posted on the CFA website.

Styrene Emissions Testing at the CARL Facility

CMTI operates a comprehensive research and development facility named the Coatings Application Research Laboratory (CARL), which is located in West Lafayette, Indiana next to the local airport and near Purdue University. The purpose of the CARL facility is to investigate new and existing coating technologies. The CARL facility site has a small research building, which houses a small spray booth enclosure that is ventilated through a small exhaust stack. The spray booth enclosure meets the EPA Method 204 criteria for a permanent total enclosure, so 100% capture of the emissions released inside the enclosure can be assumed. A detailed discussion of the equipment and procedures at the CARL facility is provided in the next section.

A CFA technical representative visited the CARL facility in May 2000. During this visit, the emissions test equipment setup and testing procedures in place at the CARL facility were thoroughly inspected. A series of calibration runs to verify the capture efficiency of the test enclosure and the quantitative accuracy of the sampling equipment for measuring styrene vapor were also performed during the visit. Based upon the field observations and results of the calibration runs, the CARL facility was recommended as a certified emissions test facility for measuring styrene emissions from open-molding processes.

A series of non-atomized gel coat application emissions test runs were performed at the CARL facility from March 16 through April 6, 2001. Jim Noonan, assistant director at CMTI, and Jean Hall, process engineer at CMTI, conducted this testing. Larry Craigie, the CFA Technical Services Manager, observed the testing. Experienced gun operators on loan from the equipment suppliers applied the gel coat test materials. Two different operators were employed during the testing.

Test Procedures and Methods at the CARL Facility

The CMTI personnel adhered to the formal styrene emission test protocol developed by CFA in November 1998 in nearly all aspects, with two minor exceptions:

Exhaust flow measurement - CMTI conducted Method 1 and Method 2 flow traverses before and after each test run, and also continuously measured and recorded the velocity pressure at a fixed point in the exhaust stack using a permanently mounted pitot tube during each of the test run

Variable FID response at low styrene concentrations - CMTI confirmed that the FID instruments had a variable response to styrene vapor at low styrene concentrations. CMTI verified this characteristic by repeatedly challenging the FID instrument with bag samples of known volume and styrene mass contents. CMTI used the collected data to derive a response factor equation that was applied to the FID output to correct for the variable FID response to styrene. After applying the correction factor equation, CMTI was able to show near perfect sample recovery during the styrene mass balance calibration runs.

CMTI personnel used the following test methods during the testing periods at the CARL facility:

Method 1 and Method 2 were used to measure the exhaust flow rate through the test enclosure at the CARL facility. These methods utilize a standard pitot tube and precision micromanometer to measure the average airflow velocity inside the test enclosure exhaust duct.

EPA Method 3 is often used to determine the CO₂ and O₂ concentrations and dry molecular weight of the exhaust streams from large industrial combustion processes, such as steam boilers and process ovens. However, the exhaust flow stream at the CARL facility was not the byproduct of a combustion process, and was essentially ambient moist air with a trace of styrene vapor. Therefore, CMTI did not use Method 3, but instead computed the air density correction factor from the moist air properties published by the American Society of Heating, Refrigeration & Air Conditioning (ASHRAE). The ASHRAE correction factor was based upon the barometric pressure, elevation, temperature, and relative humidity of the exhaust airflow. These parameters were measured by CMTI during each test run and were used to correct the measured exhaust flow rate to the corresponding exhaust flow rate at standard conditions.

EPA Method 4 is frequently used to measure the moisture content in the exhaust streams from large industrial combustion processes. This method passes a known volume of gas through a pre-weighed amount of silica gel sorbent, and measures the increase in sorbent weight caused by to the moisture contained in the gas. As mentioned above, the exhaust stream at the facility is not the byproduct of a combustion process and was essentially nominal ambient moist air. Hence, Method 4 was not used by CMTI.

EPA Method 25A was used to measure the total hydrocarbon concentration (THC) in the exhaust stream. Only styrene was assumed to be present in the gel coat materials applied to the “standard CFA mold” during the test runs, so styrene was assumed to be the only hydrocarbon species contained in the exhaust air. Hence, the Method 25A results were converted to styrene emission rates for each test run.

The capture efficiency of the test enclosure at the CARL facility was compared to the Method 204 criteria for a permanent total enclosure to determine its capture efficiency. The test enclosure met all of the Method 204 criteria, so the perfect (100%) capture of all test run emissions was assumed in the enclosure exhaust stream.

A portable personal computer (PC) was stationed next to the test enclosure. This PC recorded and processed the experimental data for each test run. Various sensors, which are discussed below, were connected to an analog-to-digital signal converter card that was installed in this PC. This data converter changed the voltage and current signals from the sensors into digital data. Data collection software produced by Labview was used to collect and store this data. A specialized MS Excel spreadsheet program developed by CMTI was used to process the data and report the experimental results in real-time.

The dry standard exhaust airflow rate through the exhaust stack was calculated by measuring the following test enclosure parameters:

Dry bulb air temperature - by means of an air temperature sensor in the stack.

Relative humidity - using a solid-state humidity sensor in the ambient air.

Static pressure - by use of a micromanometer pressure sensor in the stack.

Velocity pressure at fixed point in the exhaust stack - was monitored by a differential micromanometer pressure sensor connected to a “L-type” pitot tube. CMTI assumed a 1.00 factor but changed the factor to the more commonly accepted value of 0.99 during the May visit. A full Method 1/Method 2 velocity pressure traverse is conducted inside the stack both before and after each test run to verify the correspondence of the fixed pitot velocity pressure reading to the exhaust flow rate. After repeated measurements, CMTI discovered that the fixed-point measurement seemed to be an extremely reliable measure of the exhaust flow rate. CMTI developed a special laser-collimated pitot tube to ensure a consistent traverse path for each traverse. A small laser was attached to the pitot tube, and the laser beam was pointed at pre-positioned target plates attached to the roof trusses. The pitot tube followed the same path so long as the laser beam remained inside the target “bulls-eye.”

Flow rate conversion algorithm - CMTI developed an algorithm based upon the ASHRAE equations of state for moist air and the ASHRAE correction equation for local barometric pressure at the local elevation to calculate the equivalent standard flow rate in the exhaust stack in units of dry standard cubic feet per minute (dscfm). This algorithm used the dry bulb temperature, relative humidity, static pressure in the stack, fixed-point velocity pressure, and local barometric pressure values at each sample interval.

Flow stream conditioning to eliminate airflow vorticity - CMTI placed a bundle of flow straightening tubes inside the exhaust stack immediately down stream from the tube-axial exhaust fan outlet and just upstream from the pitot traverse path and fixed-pitot location. The tubes in this bundle were 24 inch long sections of aluminum gutter down spout that were tightly packed together to form a series of longitudinal flow channels. The flow channels dampened the turbulence caused by the axial fan motion and forced the swirling air flow motion caused by the rotating fan blades to straighten out and form a smooth parabolic velocity pressure profile at the outlet of the tube bundle. Flow vorticity at the flow measurement location inside the exhaust stack was practically eliminated, which allowed Method 1 and Method 2 flow measurement techniques to be used to measure the exhaust flow rate through the test enclosure.

Styrene Concentration

CMTI used two flame ionization detector (FID) instruments to measure the background styrene concentrations inside the CARL facility building and inside the test enclosure exhaust stack duct. The stack concentration was measured downstream from the axial fan, so well mixed conditions existed inside the stack at the sample point.

The response signals from the FID instruments were sent to the analog-to-digital converter and the data was recorded in the PC. The FID response to styrene was determined prior to the testing by challenging the instrument with known styrene-in-air concentration samples that were prepared at the facility. The samples were made by injecting a small, known quantity of pure styrene liquid into a Tedlar bag that contained a known volume of pure air. The styrene was allowed to evaporate and mix with the air, and then the bag contents were passed through the FID instrument while the corresponding signal level was noted.

CMTI passed twenty-six (26) styrene samples through the FID instrument to calibrate the styrene response. These samples had styrene concentrations that ranged from 5 to 200 ppmv. Based upon the data from these samples, CMTI developed the following styrene response factor equations:

linear	$Y = 0.4265 X - 1.1627$	$R^2 = 0.9979$
polynomial	$Y = 4E-05 X^2 + 0.4101X - 0.1992$	$R^2 = 0.9981$
power	$Y = 0.3603 X^{1.028}$	$R^2 = 0.9986$

where X is the FID instrument signal level in centivolts and Y is the volumetric styrene concentration in parts per million (ppmv).

CMTI selected the power equation as the best fit for the FID response to styrene. Note that most researchers assume a constant FID response factor for styrene, which proved to be an incorrect assumption for the FID equipment at the CARL facility.

Capture Efficiency Tests (Styrene)

The capture efficiency of the enclosure was further measured by evaporating an open pan of laboratory-grade styrene monomer placed on a small table inside the test enclosure. Initially these styrene capture efficiency test runs resulted in higher-than-possible sample recovery results that could not be explained by simple experimental error. These early tests consistently returned an average of about 108% capture of the styrene mass released in the test enclosure (the average of several runs should have been no more than 100%).

CMTI devoted several months of investigation to solve this mystery prior to the test period. CMTI finally discovered that the variable response of the FID instrument at lower styrene concentrations was the major cause of the higher-than-possible recovery results. When the response factor equation discussed previously was applied to the test data to correct for the variable FID response, the collection efficiency values were nearly perfect (very close to 100%).

Capture Efficiency Tests (Propane)

CMTI obtained several small cylinders of pure propane calibration gas that were carefully weighed by the gas supplier. These cylinder samples were then used to verify the capture efficiency of the test enclosure and setup. Since propane was used instead of styrene, the variable response of the FID instruments to styrene was not a factor. The propane tests resulted in near perfect capture efficiencies, ranging from 98% to 104% of the propane mass that was released inside the enclosure. These near-perfect results for propane strongly supported CMTI's belief that the earlier capture efficiency test results using styrene had been skewed due to the variable response of the FID instrument to different styrene concentration levels. This was especially noticeable at relative low styrene concentrations.

Test Run Results

CMTI conducted sixty-six (66) test runs at the CARL facility during the test period from March 16 through April 6, 2001. Thirty-seven (37) of the test runs involved non-atomized gel coat application. Two different non-atomizing applicators, produced by different equipment manufacturers, were used to apply gel coat to the mold during the non-atomized gel coat test runs. One test runs was aborted due to mechanical difficulties. The other twenty-eight (28) test runs involved an air-assisted airless spray gun, which atomized the gel coat during spray application. Fourteen (14) of these runs incorporated the controlled spray technique developed by CFA to reduce the emission rate from an atomizing gel coat spray gun. The remaining fourteen (14) test runs were uncontrolled, which meant that the controlled spray technique was not employed.

Eight different types of gel coat material were applied to the standard CFA test mold during the test program. These gel coat materials had the following styrene contents:

Description	% Styrene by wt. as Analyzed by Gas Chromatography
Gel coat #1	40.8%
Gel coat #2	19.2%
Gel coat #3	52.0%
Gel coat #4	40.9%
Gel coat #5	29.7%
Gel coat #6	27.7%
Gel coat #7	24.5%
Gel coat #8	30.0%

Two different types of non-atomized gel coat applicators were used during the testing. Two different operators applied gel coat during the testing.

The test data values for all sixty-six experimental test runs are listed in **Table 1** on the following page. The thirty-seven non-atomized gel coat test runs, which were used to develop the non-atomized gel coat emission factor equation, are listed in **Table 2**, which follows **Table 1**.

Table 1 - Raw Experimental Data

Test Type	Test Run (#)	Test Code	Styrene Content (% wt)	Styrene Emission Rate (% available styrene)	Styrene Emission Rate (% gel wt)
Uncontrolled	1	Unc	52	54.45%	28.31%
Uncontrolled	2	Unc	52	52.19%	27.14%
Uncontrolled	3	Unc	52	56.32%	29.29%
Uncontrolled	4	Unc	24.5	42.60%	10.44%
Uncontrolled	5	Unc	24.5	41.28%	10.11%
Controlled AAA	6	Con	24.5	38.35%	9.40%
Controlled AAA	7	Con	24.5	38.78%	9.50%
Controlled AAA	8	Con	24.5	33.18%	8.13%
Controlled AAA	9	Con	30	32.04%	9.61%
Uncontrolled	10	Unc	30	35.21%	10.56%
Controlled AAA	11	Con	40.9	42.06%	17.20%
Uncontrolled	12	Unc	40.9	47.28%	19.34%
Uncontrolled	13	Unc	29.7	36.35%	10.79%
Controlled AAA	14	Con	29.7	27.83%	8.27%
Controlled AAA	15	Con	27.7	27.00%	7.48%
Controlled AAA	16	Con	27.7	29.61%	8.20%
Uncontrolled	17	Unc	27.7	43.67%	12.10%
Controlled AAA	18	Con	40.8	36.29%	14.81%
Uncontrolled	19	Unc	40.8	46.19%	18.85%
Controlled AAA	20	Con	40.9	35.66%	14.59%
Non-atomized	21	Non-A	40.8	29.72%	12.12%
ABORTED	22		NA	NA	NA
Non-atomized	23	Non-A	40.8	30.62%	12.49%
Non-atomized	24	Non-A	29.7	24.83%	7.37%
Non-atomized	25	Non-A	29.7	24.31%	7.22%
Non-atomized	26	Non-A	52.0	37.25%	19.37%
Non-atomized	27	Non-A	52.0	33.26%	17.30%
Non-atomized	28	Non-A	52.0	35.45%	18.44%
Non-atomized	29	Non-A	24.5	32.14%	7.87%
Non-atomized	30	Non-A	24.5	30.35%	7.44%
Non-atomized	31	Non-A	40.9	29.56%	12.09%
Non-atomized	32	Non-A	40.9	32.83%	13.43%
Non-atomized	33	Non-A	30	26.76%	8.03%
Non-atomized	34	Non-A	30	26.17%	7.85%

Table 1 - Raw Experimental Data, continued

Test Type	Test Run (#)	Test Code	Styrene Content (% wt)	Styrene Emission Rate (% available styrene)	Styrene Emission Rate (% gel wt)
Non-atomized	35	Non-A	19.2	15.29%	2.94%
Non-atomized	36	Non-A	19.2	17.46%	3.35%
Non-atomized	37	Non-A	19.2	18.38%	3.53%
Non-atomized	38	Non-A	27.7	23.55%	6.52%
Non-atomized	39	Non-A	27.7	24.63%	6.82%
Controlled AAA	40	Con	52.0	45.18%	23.49%
Non-atomized	41	Non-A	52.0	39.98%	20.79%
Non-atomized	42	Non-A	52.0	37.87%	19.69%
Non-atomized	43	Non-A	19.2	19.21%	3.69%
Non-atomized	44	Non-A	19.2	19.90%	3.82%
Controlled AAA	45	Con	19.2	24.03%	4.61%
Controlled AAA	46	Con	19.2	23.75%	4.56%
Uncontrolled	47	Unc	19.2	32.47%	6.23%
Uncontrolled	48	Unc	19.2	30.77%	5.91%
Uncontrolled	49	Unc	30	38.02%	11.41%
Non-atomized	50	Non-A	30	31.18%	9.35%
Non-atomized	51	Non-A	30	31.92%	9.58%
Non-atomized	52	Non-A	30	32.88%	9.87%
Controlled AAA	53	Con	24.5	34.57%	8.47%
Uncontrolled	54	Unc	24.5	41.42%	10.15%
Non-atomized	55	Non-A	24.5	29.67%	7.27%
Non-atomized	56	Non-A	24.5	30.96%	7.58%
Non-atomized	57	Non-A	27.7	26.09%	7.23%
Non-atomized	58	Non-A	27.7	25.22%	6.99%
Non-atomized	59	Non-A	40.9	33.43%	13.67%
Non-atomized	60	Non-A	40.9	32.49%	13.29%
Non-atomized	61	Non-A	40.9	33.02%	13.51%
Non-atomized	62	Non-A	40.8	28.60%	11.67%
Non-atomized	63	Non-A	40.8	30.41%	12.41%
Non-atomized	64	Non-A	29.7	27.84%	8.27%
Non-atomized	65	Non-A	29.7	26.32%	7.82%
Non-atomized	66	Non-A	29.7	24.46%	7.26%
	66a		29.7	14.73%	4.38%

Table 2 - Non-Atomized Gel coat Test Data

Test Run	Test Code	Styrene Content	Styrene Emission Rate
(#)		(% wt)	(% gel wt)
21	Non-A	40.8	12.12
23	Non-A	40.8	12.49
24	Non-A	29.7	7.37
25	Non-A	29.7	7.22
26	Non-A	52	19.37
27	Non-A	52	17.30
28	Non-A	52	18.44
29	Non-A	24.5	7.87
30	Non-A	24.5	7.44
31	Non-A	40.9	12.09
32	Non-A	40.9	13.43
33	Non-A	30	8.03
34	Non-A	30	7.85
35	Non-A	19.2	2.94
36	Non-A	19.2	3.35
37	Non-A	19.2	3.53
38	Non-A	27.7	6.52
39	Non-A	27.7	6.82
41	Non-A	52	20.79
42	Non-A	52	19.69
43	Non-A	19.2	3.69
44	Non-A	19.2	3.82
50	Non-A	30	9.35
51	Non-A	30	9.58
52	Non-A	30	9.87
55	Non-A	24.5	7.27
56	Non-A	24.5	7.58
57	Non-A	27.7	7.23
58	Non-A	27.7	6.99
59	Non-A	40.9	13.67
60	Non-A	40.9	13.29
61	Non-A	40.9	13.51
62	Non-A	40.8	11.67
63	Non-A	40.8	12.41
64	Non-A	29.7	8.27
65	Non-A	29.7	7.82
66	Non-A	29.7	7.26

Non-Atomized Gel Coat Emission Factors

Both a linear equation and a power equation were derived for the experimental non-atomized gel coat test data using a standard least-squares approximation curve-fitting routine. The resulting emission factor equations have the following forms:

Linear Equation

$$\text{Styrene emission rate (\% gel coat wt.)} = 0.4506 \times [\% \text{ styrene}] - 0.0505$$

Power Equation

$$\text{Styrene emission rate (\% gel coat wt.)} = 0.5442 \times [\% \text{ styrene}]^{1.5838}$$

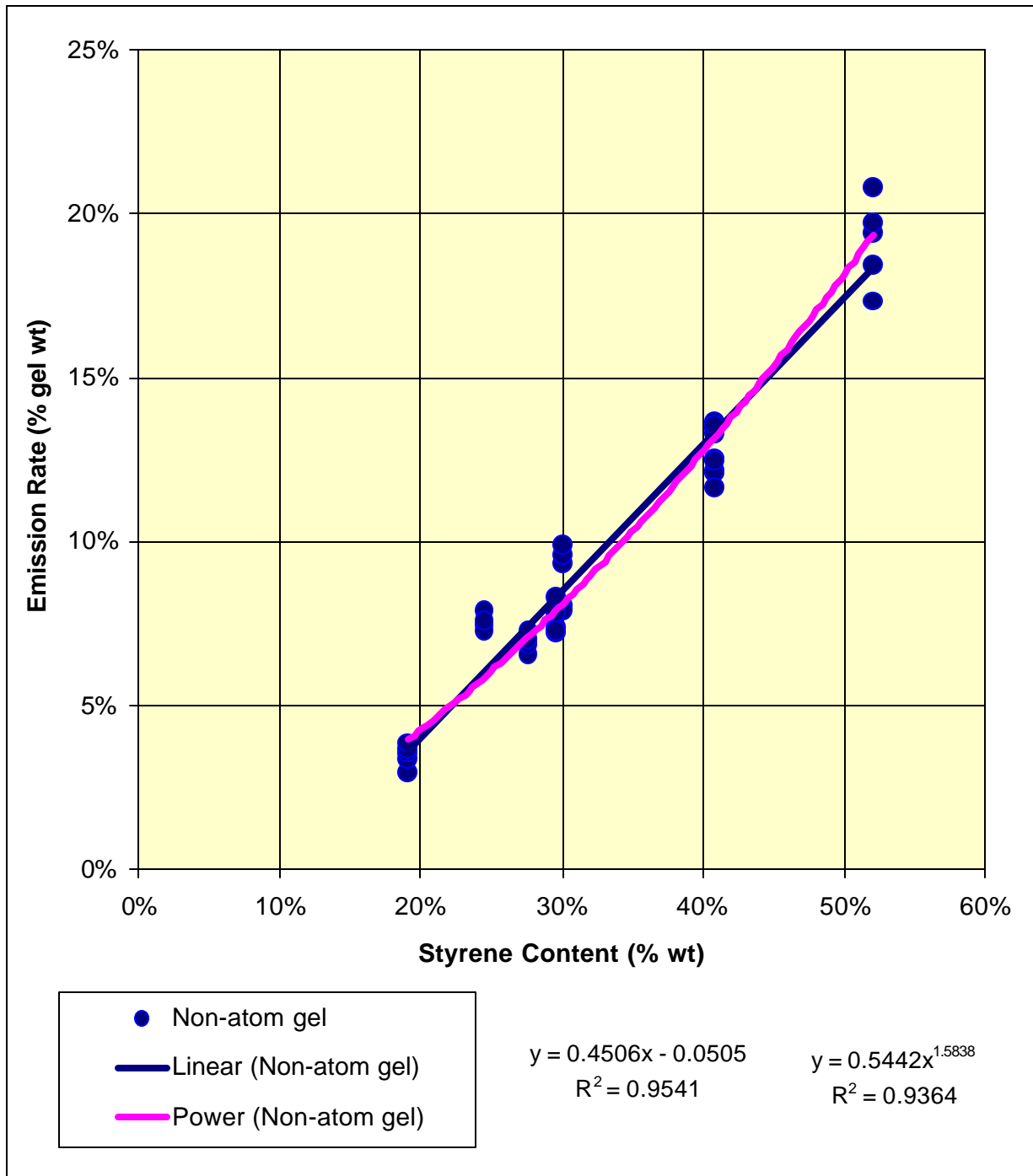
These equations compare the styrene content of a particular gel coat to the corresponding styrene emission rate expressed as a percentage of the gel coat weight. Both the styrene content and the emission rates are input as fractional numerical values (i.e., a 44% styrene content is input as the value 0.44, not as 44). These parameters and units were selected to remain consistent with numerical approach used in the derivation of the current UEF factor equation for gel coat spray application.

The linear equation has a slightly better fit to the experimental data ($R^2 = 0.9541$) than the power equation ($R^2 = 0.9364$). Therefore, the linear equation is selected as the UEF factor equation for estimating styrene emissions from the non-atomized gel coat application process.

The lowest styrene content for the experimental data was 19.2% styrene by weight of gel coat. Hence, a value of 19% was set as the lowest bound of the available experimental data. Based upon the linear equation, the emission rate for non-atomized application of a 19% styrene content gel coat is 3.5% (or 0.035) of the gel coat weight. The equivalent emission rate expressed as a percentage of the available styrene content in the gel coat is 18.5% (or 0.185) of the styrene monomer. In order to remain consistent with the approach used in the current UEF factor equations, a fixed emission rate of 18.5% of the available styrene monomer is assumed for any gel coat with a styrene monomer content less than 19%. This provides a conservative estimator for the lower styrene content gel coats and also causes the resulting emission factor equation to pass through zero emissions at zero styrene content (an important requirement for EPA acceptance).

A plot of the non-atomized gel coat emission factor equation is shown in **Figure 1** on the following page. This plot shows the individual experimental data values, and both the linear and the power equation curve-fits.

Figure 1 - Non-Atomized Gel coat Emission Factor Equations



A comparison of the non-atomized gel coat factor equation to the UEF gel coat spray factor equation is detailed in **Table 3** below. A comparison plot of the two equations is shown in **Figure 2** on the following page.

Table 3 - Comparison of Non-Atomized and Atomized (Spray) Gel Coat Factors

Styrene Content in Gel Coat	UEF Emissions Factors	
	Pounds of Styrene Emitted Per Ton of Gel Coat Applied	
	Atomized	Non-Atomized
19%	169	70
21%	187	88
23%	205	106
25%	223	124
27%	240	142
29%	258	160
31%	276	178
33%	294	196
35%	336	214
37%	377	232
39%	418	250
41%	460	268
43%	501	286
45%	543	304
47%	584	322
49%	626	340
51%	667	359

This data indicates a 43% average reduction in emissions by using the non-atomizing application equipment, although the exact reduction depends on the monomer content of the gel coat.

Figure 2 - Comparison of Non-Atomized and Atomized Gelcoat Emission Factors

