

## Mass Balance Determination of Emission Factors for the Production of Sheet Molding Compound

By

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### Abstract

Sheet molding compound (SMC) is made by dispensing a mixture of resins, fillers, maturation agents, catalysts, mold release, and other additives onto two sheets of carrier film. The lower film, containing a thin layer of paste covered by chopped roving, is joined by the top film sandwiching the fibers between the two layers of paste. SMC manufacturing facilities in Ohio and Indiana are required to conduct volatile organic compound (VOC) emission tests to determine compliance with Title V permit conditions of the United States Environmental Protection Agency (USEPA) Clean Air Act. The purpose of this research is to determine if the styrene emission rates obtained by method 204D, "Volatile Organic Compounds Emissions in Uncaptured Stream from Temporary Total Enclosure," can be predicted by laboratory mass balance models. Data on how emission rates are influenced by airflow, paste temperature, styrene and glass content led to a model that accurately predicted the styrene emission rate of one SMC machine. More data on operating variables and SMC machine set-ups will need to be collected to determine if the model holds true across the industry.

### Introduction

SMC manufacturing facilities are required by the EPA to conduct VOC emission tests. The results from the laboratory mass balance model were compared to the results obtained by method 204D conducted at a processing facility. The primary purpose of this research was to determine if mass balance could be used as an alternative method for determining the styrene emission factor for an SMC machine at a local processing facility. The secondary goal was to collect data on production

variables and SMC machine set-ups to determine if the mass balance model could be used across the industry.

### Experiment

Airflows across all areas of the SMC machine were recorded along with paste temperature, machine dimensions, styrene content, and glass percentage.

A small, low-velocity wind tunnel equipped with a scale that resolves to 0.1mg was designed. Airflows, sample weights, and paste temperatures were monitored throughout the experiment.

Before conducting the experiment, scale noise due to airflow was examined. Noise determination was conducted on the same pan used for all experimental runs and a solid weight. Airflows of 0, 50, 75, 100, 130, 160, and 230 feet per minute (fpm) were tested (Exhibit 1 and 2).

All runs were conducted on a round metal pan with an area of 0.16379 ft<sup>2</sup>. The samples were prepared even with the pan rim to eliminate turbulence across the paste surface. The pan was placed in the wind tunnel with the surface of the paste flush to the tunnel bottom (Exhibit 3).

The mix formulation used for the laboratory experiment was the same formulation used during the method 204D test run at the production facility. The formulation was altered for the styrene content tests. For these tests, pure styrene was added to the paste to obtain the desired styrene content. The range of styrene contents tested was restricted by paste viscosity. Usable paste viscosities are often dependent on SMC glass content, but typical paste viscosity for the production facility was in the range of 5,000 cP to 65,000 cP measured on a Brookfield DV-II viscometer with spindle 4 at 20 rpm. The standard paste had a viscosity of 61,000 cP at 90°F. The viscosities of the paste used in this experiment ranged from 3,120 cP to 74,240 cP (Exhibit 4).

The paste was made within 12 hours of use. Each sample was individually heated to temperature in a water bath directly before use. The paste temperature was recorded immediately before the beginning of each run. The paste temperature was within  $\pm 1^\circ\text{F}$  of the target temperature.

Airflows were stabilized before each run. After the airflow was set, it was blocked while the sample was inserted into the wind tunnel. An additional airflow reading was taken at the end of each

run to ensure that the intended flow rate was obtained. The scale was allowed to settle for approximately eight to ten seconds before removing the air block. This lag time allowed for the initial starting weight to be determined. Since SMC paste continuously releases styrene, time zero was calculated as the time when the air block was removed, exposing the sample to the desired airflow.

Initial experimentation indicated that the scale took approximately five seconds to reach equilibrium. It was also concluded that it took approximately two seconds for the airflow to reach the desired flow rate after the air block was removed. In order to exclude this system noise, the first few seconds of data for tests with airflow was removed and the best-fit regressions were extrapolated back to zero.

A data acquisition unit that collected ten readings per second was used. Six or more sets of each test were collected for evaluation. The cumulative weight loss,  $Y$ , in grams was plotted against the cumulative exposure time,  $X$ , in seconds to determine the best-fit regression equation. The 95% confidence intervals of the mean weight loss were plotted versus the variable of interest. Basic statistics were evaluated for each variable.

## Results

The effect airflow had on standard paste was examined at flow rates of 0, 50, 100, 130, 160, and 230 fpm (Exhibits 5-7).

The effect of paste temperature on styrene emission was examined by conducting tests with zero airflow at 74.1°F, 82.7°F, 90°F, 100°F, and 110°F (Exhibits 8-10). The combined effect of temperature and airflow was also examined with 90°F, 100°F, and 110°F standard paste at airflows of 50, 100 and 130 fpm (Exhibits 11-19).

Glass was placed on the surface of the paste at 49 grams per square foot. Styrene loss was determined for airflow of zero and 70 fpm (Exhibits 20-22).

The effect of styrene content was examined with and without airflow. Samples containing 13.59%, 15%, 18%, and 30% styrene were run without airflow (Exhibits 23-25). The tests were repeated with 160 fpm of airflow (Exhibits 26-28).

## Discussion

Trends were found in the experimental data that explained how exposure time, airflow, styrene content, glass, and paste temperature influenced the emission rate of styrene during SMC production. Exposure time (length of exposed area /line speed) has a weak and variable impact on the emission rate. Temperature also had a weak impact on the emission of styrene. Airflow and glass cover had a significant effect on the emission rate. Styrene content did not influence the rate of styrene loss at zero airflow. The only samples affected by the 160 fpm of airflow was the paste containing 30% styrene.

The experiments indicated that the mass of styrene emissions per unit area may be predicted by the power equation  $Y = aX^b$ . As  $b$  approaches 1, the areal emission rate (mass / time-area) becomes less dependent on exposure time. At  $b = 1$  (linear function), the areal emission rate is constant across measured exposure times. In no case did  $b$  exceed 1 for the best-fit regression line.

The emission of styrene was effected by airflow. The  $a$  and  $b$  values in the regression equation,  $Y = aX^b$ , were both effected when the airflow rate was increased. The trend can be seen in the graph of weight loss versus airflow of standard 90°F paste (Exhibit 5). Increased airflow increased the  $a$  values and decreased the  $b$  values. The effect airflow has on the styrene emission is confirmed by the 95% confidence intervals of the mean weight loss versus airflow (Exhibit 6). The emission rate of styrene from standard 90°F paste was 0.044 lb/hrft<sup>2</sup> with a typical exposure time of 3 seconds. The emission rate increased to 0.474 lb/hrft<sup>2</sup> at 230 fpm of airflow.

The data on airflow was not easily collected. airflow on the analytical scale caused the system noise to increase as the flow of air increased. Extensive time was taken to assure that the scale was isolated from as many unnecessary air currents as possible. Different pan sizes and shapes were tested to determine which would have the least impact on system noise. Even with all of the precautions taken, the noise added to the system by high velocity airflows prevented loss determinations for airflows beyond 230 fpm.

Emission rates increased with temperature at zero airflow (Exhibit 8). At 74.1°F the paste emitted 0.024 lb/hrft<sup>2</sup> of styrene. If the temperature was increased to 110°F the paste would emit 0.063 lb/hrft<sup>2</sup>. Raising the airflow to 50 fpm did not significantly change the emission rates of the 90°F, 100°F or 110°F samples. With 100 fpm airflow the styrene loss at all three temperatures increased. The regressions of the 100°F and 110°F pastes were in the form of a power function while the regression

of the 90°F paste remained linear over the 60 second exposure time (Exhibit 14). The 95% confidence intervals of the mean weight loss verses temperature of the 100°F and 110°F samples overlapped at 100 fpm of airflow (Exhibit 15). At 130 fpm the regression of all three paste temperatures were power functions (Exhibit 17). The 95% confidence intervals of the 100°F paste overlapped both the 90°F and 110°F pastes (Exhibit 18). At 130 fpm airflow and an exposure time of 3 seconds, the emission of styrene at 90°F was 0.179 lb/hrft<sup>2</sup>. If the temperature was increased to 110°F the emission rate would increase to 0.280 lb/hrft<sup>2</sup>.

When the surface of the paste was covered by glass, the styrene emission rate dropped. Several glass percentages at various airflows would need to be tested to determine the relationship between glass percentage and styrene emission.

Varying the percentage of styrene in the paste did not affect the emission rate at zero airflow (Exhibit 23). The 95% confidence intervals for the mean weight loss verses styrene content of pastes containing 13.59%, 15%, 18%, and 30% overlapped (Exhibit 24). With 160 fpm of airflow the 95% confidence intervals of mean weight loss at 13.59%, 15%, and 18% overlapped. At this airflow, a 120% increase in styrene content increased the emission rate by 29% for an exposure period of 3 seconds. It is not known at this time how much of this emission rate increase is due to the change in paste viscosity and how much can be contributed to the styrene content of the paste.

The power function equations derived during this study were used to model (predict) emissions of a 48" SMC machine that was tested by Method 204D. The model considered average airflows measured across three open portions of the line, area and exposure time for each of those sections, paste temperature, as well as glass and styrene content of the paste run during the test ("Standard Paste").

The maximum hourly styrene emission rate as determined by method 204D was 3.94 lb/hr with a standard deviation of 0.38 lb/hr. The maximum hourly styrene emission rate predicted by the mass balance model was 4.20 ± 0.39 lb/hr (Exhibits 29-32).

## Conclusion

The emission of styrene during the production of SMC was viewed as an evaporative process. Different factors that may have impacted the rate of styrene loss during the SMC production process were examined. This study indicated that the emission of styrene was a process driven by evaporation. Contrary to popular belief, the emissions were not driven by the styrene content of the SMC or the throughput of the SMC machine. Correlation of the mass balance model and field test results suggests that a well-designed mass balance experiment may be an alternative to the total temporary enclosure for the derivation of a styrene emission factor. This mass balance model could be modified to generate emission factors for other similar processes that may not be as easily tested by EPA method 204D. If this model is used to determine emissions in areas with 100 fpm or less of airflow less, the experimental error will be in the range of 1.5%.

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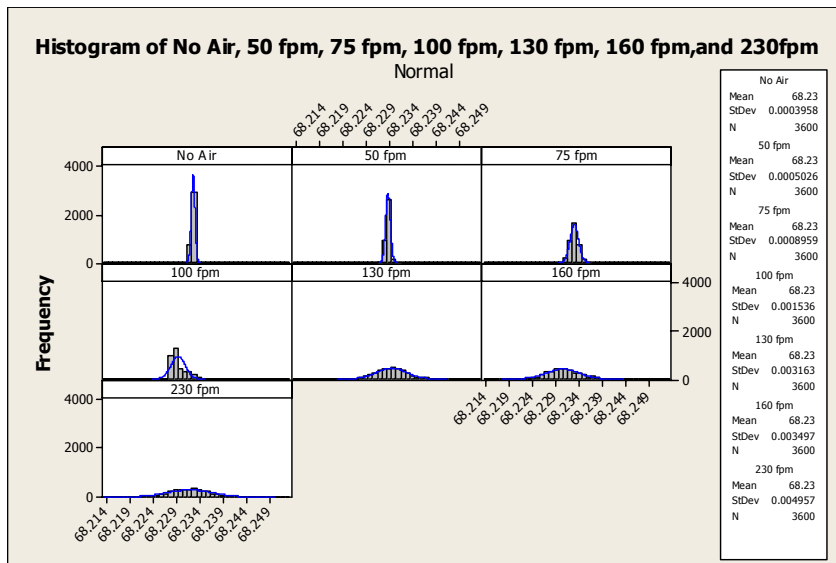
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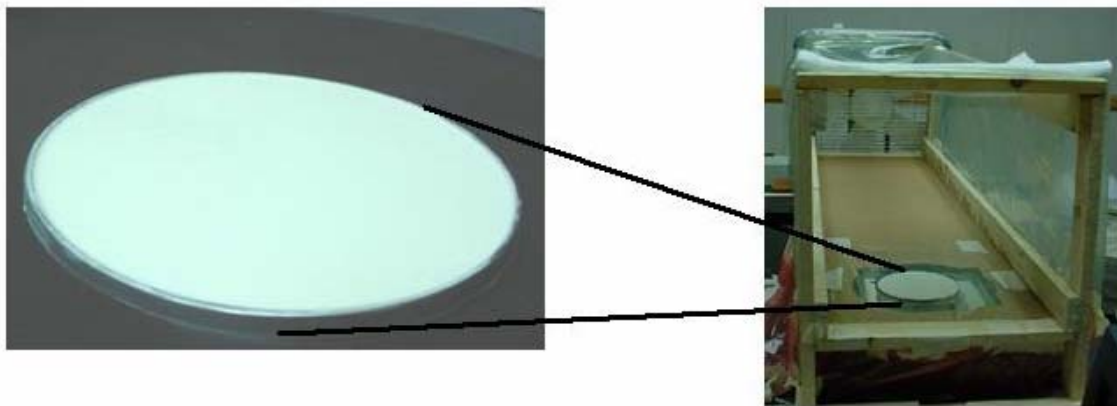
**Exhibit 1: Solid weight test under various airflows. Weight measurements made in grams.**

Variable	N	Mean (g)	SE Mean	ST Dev	Min	Median	Max	Range
No Air	3600	68.233	0.000007	0.000396	68.232	68.233	68.233	0.00100
50 fpm	3600	68.234	0.000008	0.000503	68.232	68.234	68.236	0.00400
75 fpm	3600	68.233	0.000015	0.000896	68.231	68.233	68.236	0.00500
100 fpm	3600	68.235	0.000026	0.00154	68.225	68.229	68.234	0.00700
130 fpm	3600	68.235	0.000053	0.00316	68.225	68.235	68.246	0.0210
160 fpm	3600	68.230	0.000058	0.0350	68.216	68.230	68.246	0.0300
230 fpm	3600	68.232	0.000083	0.00496	68.214	68.232	68.253	0.390

**Exhibit 2: Histogram of a solid weight with various airflows.**



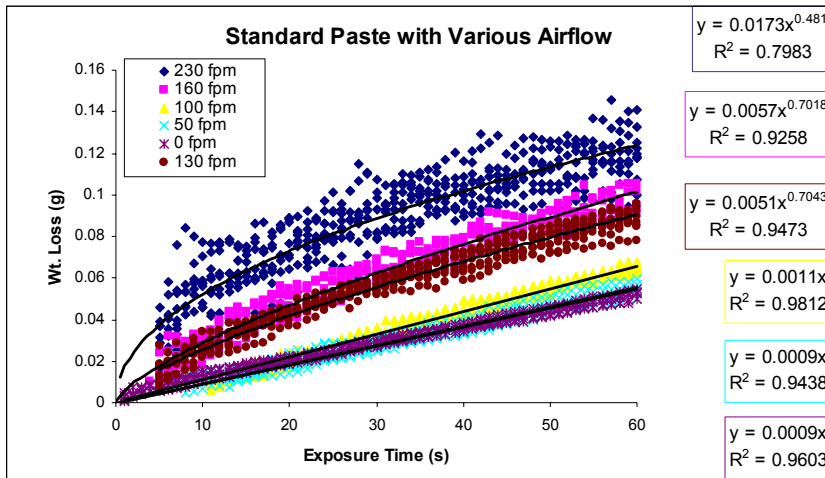
**Exhibit 3: Location of sample pan in wind tunnel and distribution of paste onto pan.**



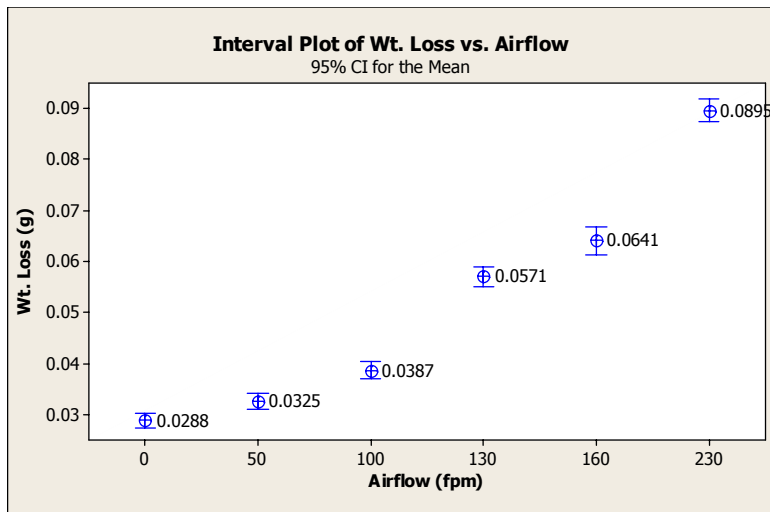
**Exhibit 4: Paste viscosities taken on a Brookfield DV-II viscometer at 20 rpm.**

Paste	Temp (°F)	Spindle	Viscosity (cP)
Standard 13.59%	74	4	74,240
Standard 13.59%	82	4	65,440
Standard 13.59%	90	4	61,000
Standard 13.59%	100	4	36,480
Standard 13.59%	110	4	31,440
15%	90	4	19,920
18%	90	4	14,160
30%	90	2	3,120

**Exhibit 5: Weight loss vs. exposure time of standard paste at 90°F under various airflows.**



**Exhibit 6: 95% confidence intervals for the mean weight loss vs. airflow of standard 90°F paste.**

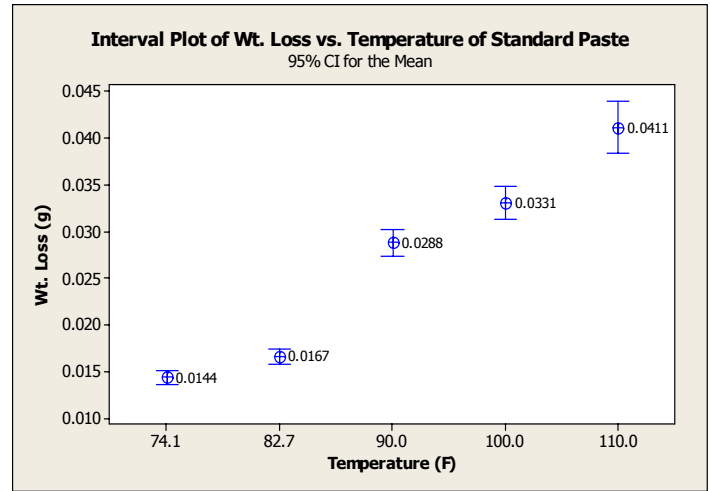
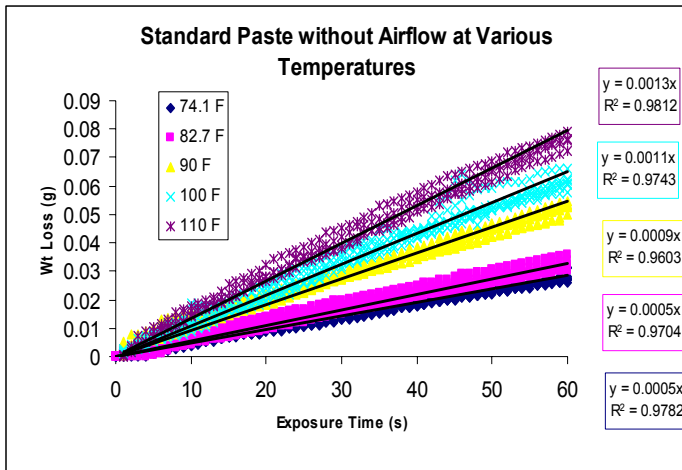


**Exhibit 7: Descriptive statistics of weight. loss vs. airflow of standard 90°F paste.**

Airflow (fpm)	Mean (g)	SE Mean	StDev	Variance	Median	Range	95% CI intervals
0	0.0288	0.0007	0.0139	0.0002	0.0291	0.0542	0.0274, 0.0303
50	0.0325	0.0008	0.0135	0.0002	0.0291	0.0543	0.0310, 0.0340
100	0.0387	0.0009	0.0166	0.0003	0.0402	0.0615	0.0369, 0.0404
130	0.0571	0.0010	0.0213	0.0005	0.0594	0.0898	0.0551, 0.0591
160	0.0642	0.0014	0.0235	0.0006	0.0664	0.0950	0.0614, 0.0669
230	0.0895	0.0011	0.0253	0.0006	0.0933	0.1299	0.0873, 0.0917

**Exhibit 8 (left): Weight loss vs. exposure time of standard paste at various temperatures with zero airflow.**

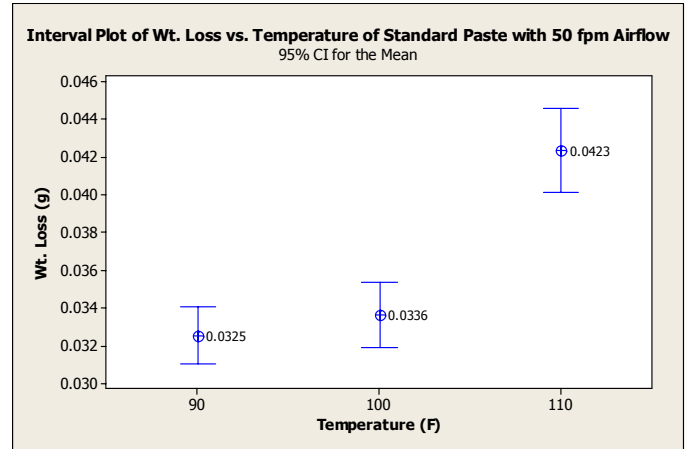
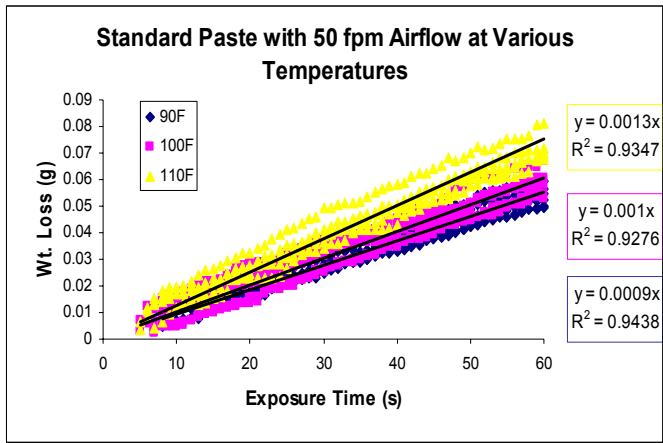
**Exhibit 9 (right): 95% confidence interval of the mean weight loss vs. temperature of standard paste with zero airflow.**



**Exhibit 10: Descriptive statistics of weight. loss vs. temperature of standard paste without airflow.**

Temp (F)	Mean (g)	SE Mean	StDev	Variance	Median	Range	95% CI intervals
74.1	0.0144	0.0004	0.0084	0.0001	0.0145	0.0311	0.0137, 0.0151
82.7	0.0167	0.0004	0.0094	0.0001	0.0170	0.0359	0.0158, 0.0175
90	0.0288	0.0007	0.0139	0.0002	0.0291	0.0543	0.0274, 0.0303
100	0.0331	0.0009	0.0182	0.0003	0.0339	0.0543	0.0313, 0.0349
110	0.0412	0.0014	0.0219	0.0005	0.0418	0.0789	0.0384, 0.0439

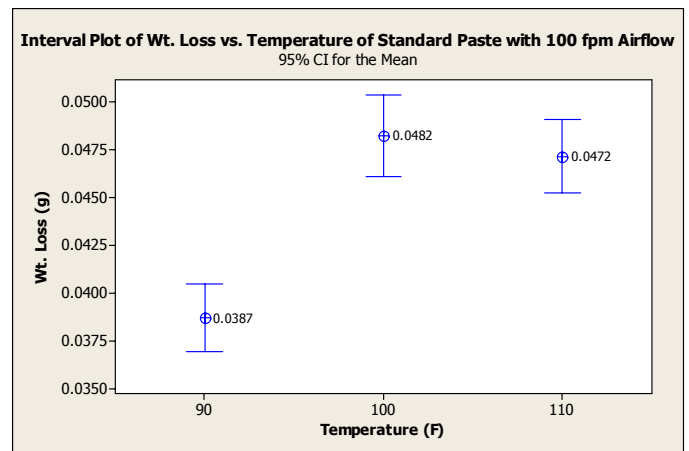
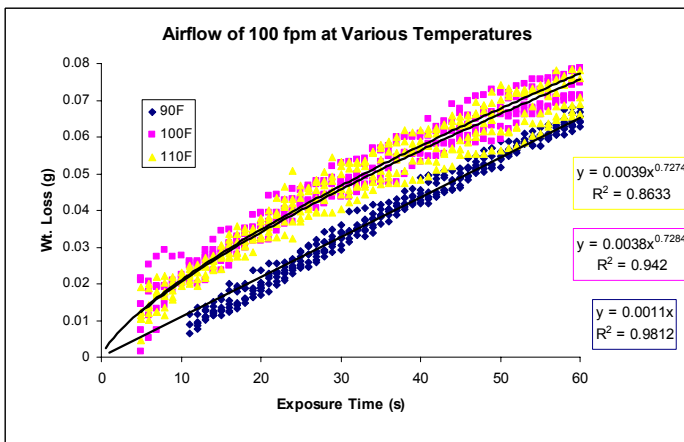
**Exhibit 11 (left):** Weight loss vs. exposure time of standard paste at 90°F, 100°F, and 110°F with 50 fpm airflow.  
**Exhibit 12 (right):** 95% confidence interval of the mean weight loss vs. temperature of standard paste with 50 fpm of airflow.



**Exhibit 13:** Descriptive statistics of weight. loss vs. temperature of standard paste with 50fpm of airflow.

Temp(F)	Mean (g)	SE Mean	StDev	Variance	Median	Range	95% CI intervals
90	0.0325	0.0008	0.0135	0.0002	0.0321	0.0547	0.0310, 0.0340
100	0.0336	0.0009	0.0159	0.0003	0.0345	0.0647	0.0319, 0.0354
110	0.0423	0.0011	0.0187	0.0004	0.0425	0.0778	0.0401, 0.0446

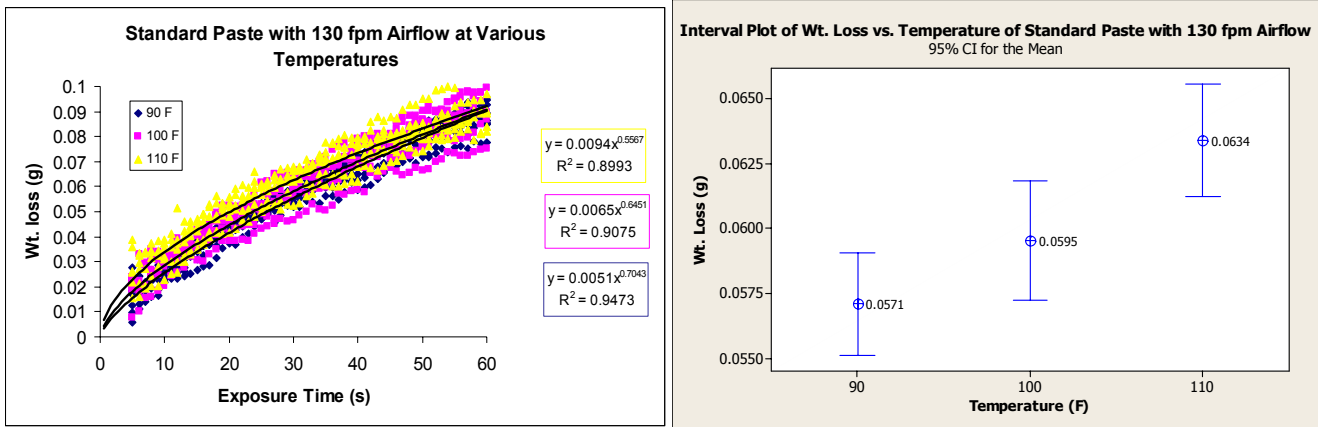
**Exhibit 14(left):** Weight loss vs. exposure time of standard paste at 90°F, 100°F, and 110°F with 100 fpm airflow.  
**Exhibit 15 (right):** 95% confidence interval of the mean weight loss vs. temperature of standard paste with 100 fpm of airflow.



**Exhibit 16:** Descriptive statistics of weight loss vs. temperature of standard paste with 100 fpm of airflow.

Temp (F)	Mean (g)	SE Mean	StDev	Variance	Median	Range	95% CI intervals
90	0.0387	0.0009	0.1661	0.0003	0.0402	0.0615	0.0369, 0.0404
100	0.0482	0.0011	0.0180	0.0003	0.0486	0.0774	0.0461, 0.0504
110	0.0472	0.0010	0.0180	0.0003	0.0490	0.0762	0.0452, 0.0491

**Exhibit 17 (left):** Weight loss vs. exposure time of standard paste at 90°F, 100°F, and 110°F with 130 fpm airflow.  
**Exhibit 18 (right):** 95% confidence interval of the mean weight loss vs. temperature of standard paste with 130 fpm of airflow.

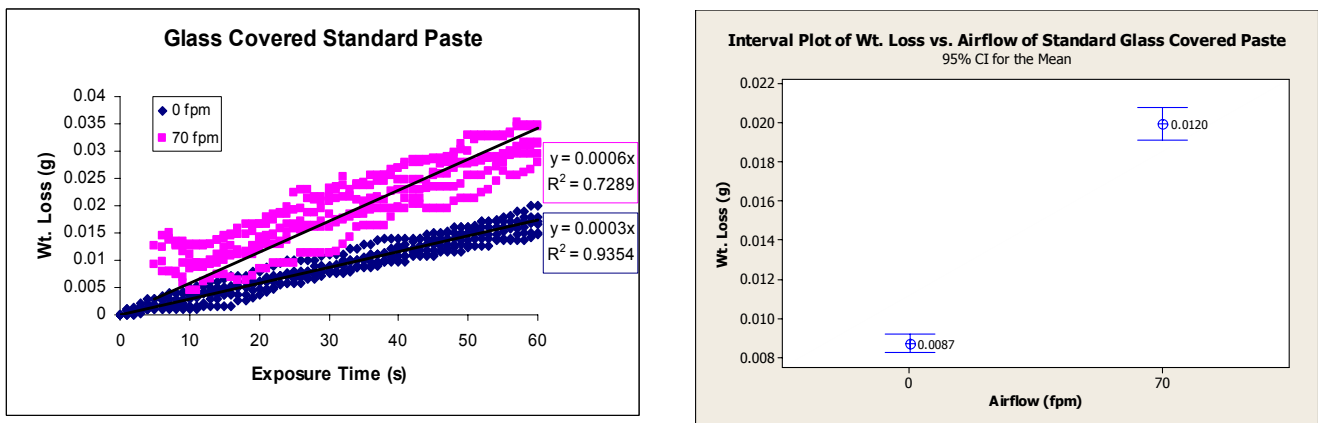


**Exhibit 19: Descriptive Statistics of weight loss vs. temperature of standard paste with 130 fpm of airflow.**

Temp (F)	Mean (g)	SE Mean	StDev	Variance	Median	Range	95% CI intervals
90	0.0571	0.0010	0.0213	0.0005	0.0594	0.0898	0.0551, 0.0591
100	0.0595	0.0012	0.0214	0.0005	0.0622	0.0929	0.0572, 0.0618
110	0.0634	0.0011	0.0202	0.0004	0.0652	0.0912	0.0612, 0.0656

**Exhibit 20 (left):** Weight loss vs. exposure time of standard paste covered with 49 g per ft<sup>2</sup> of glass at 90°F with zero and 70 fpm of airflow.

**Exhibit 21 (right):** 95% confidence interval of the mean weight loss vs. airflow of standard 90°F paste covered with 49 grams per ft<sup>2</sup> of glass.

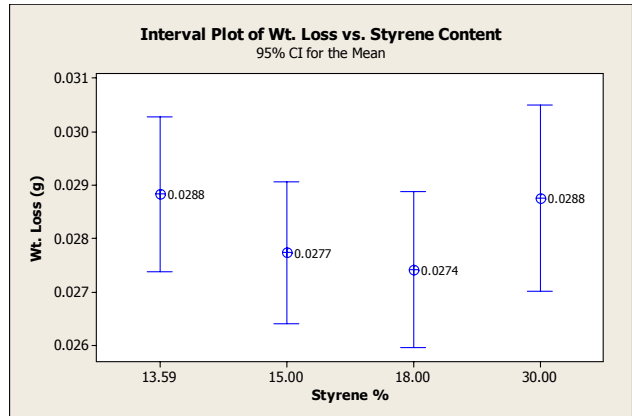
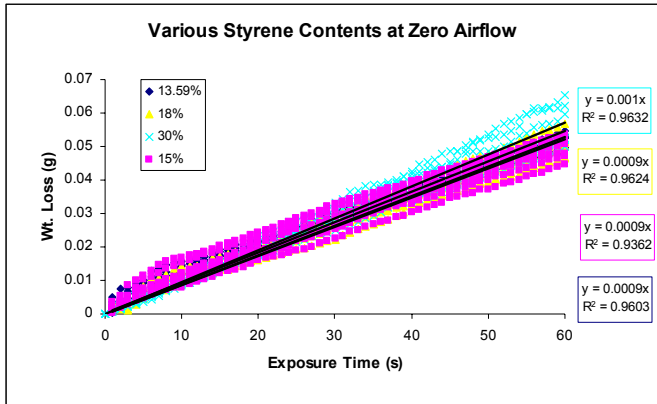


**Exhibit 22: Descriptive Statistics of weight loss vs. airflow of standard 90°F paste with 49 grams per ft<sup>2</sup> of glass.**

Airflow (fpm)	Mean (g)	SE Mean	StDev	Variance	Median	Range	95% CI intervals
0	0.0087	0.0002	0.0051	0.0000	0.0087	0.0200	0.0082, 0.0092
70	0.0200	0.0004	0.0077	0.0001	0.0196	0.0308	0.0191, 0.0208

**Exhibit 23 (left):** Weight loss vs. exposure time of 13.59%, 15%, 18%, and 30% styrene paste at 90°F with zero air-flow.

**Exhibit 24 (right):** 95% confidence interval of the mean weight loss vs. styrene content with zero airflow.

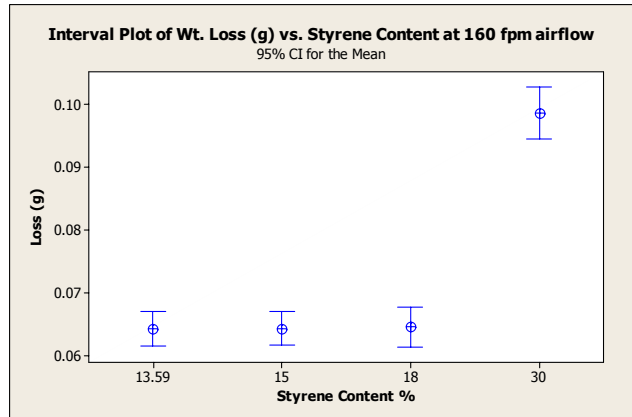
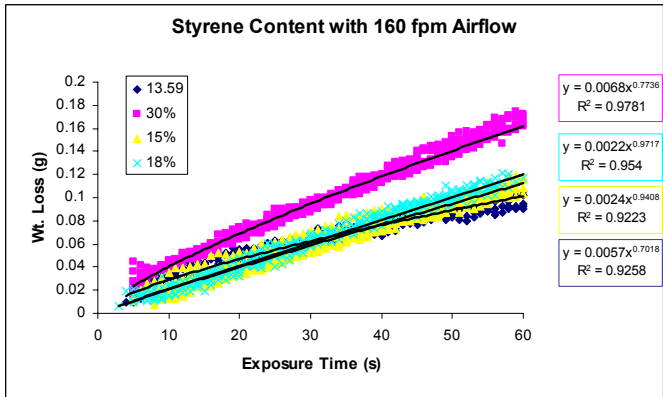


**Exhibit 25: Descriptive Statistics of weight loss vs. styrene content with zero airflow.**

Styrene %	Mean (g)	SE Mean	StDev	Variance	Median	Range	95% CI intervals
13.59	0.0288	0.0007	0.0139	0.0002	0.0291	0.0543	0.0274, 0.0303
15	0.0277	0.0007	0.0139	0.0002	0.0291	0.0533	0.0264, 0.0291
18	0.0274	0.0007	0.0139	0.0002	0.0275	0.0557	0.0260, 0.0289
30	0.0288	0.0009	0.0170	0.0003	0.0290	0.0654	0.0270, 0.0305

**Exhibit 26 (left):** Weight loss vs. exposure time of 13.59%, 15%, 18%, and 30% styrene pastes at 90°F with 160 fpm of airflow.

**Exhibit 27 (right):** 95% confidence interval of the mean weight loss vs. styrene content with 160 fpm of airflow.



**Exhibit 28: Descriptive statistics of weight loss vs. styrene content with 160 fpm of airflow.**

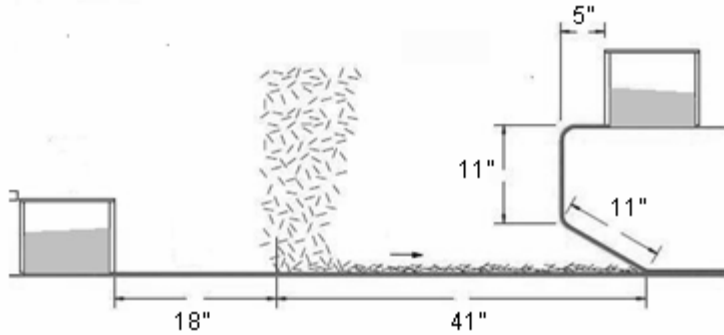
Styrene %	Mean (g)	SE Mean	StDev	Variance	Median	Range	95% CI intervals
13.59	0.0642	0.0014	0.0235	0.0006	0.0664	0.0950	0.0614, 0.0669
15	0.0643	0.0014	0.0289	0.0008	0.0655	0.1122	0.0616, 0.0671
18	0.0645	0.0016	0.0308	0.0010	0.0660	0.1157	0.0614, 0.0677
30	0.0986	0.0021	0.0414	0.0017	0.0978	0.1577	0.0945, 0.1027

**Exhibit 29: 48” SMC Machine Dimensions**

SMC Sheet Width = 46"

Bare Wet Paste Area = (18" + 11" + 11" + 5") \* 46" / 144 = 14.38 ft<sup>2</sup>

Glass Fiber Covered Wet Paste Area = 41" \* 46" / 144 = 13.10 ft<sup>2</sup>



**Exhibit 30: Mass balance model**

For each area of the machine

$$\text{emission factor} = \frac{\text{line fit at exposure time} * \left( \frac{3600}{\text{exposure time}} \right)}{\text{pan area} * 453.59}$$

maximum emission per hour = (emission factor a \* wet area a) + (emission factor b \* wet area b)...

**Exhibit 31: Predicted Maximum Emission**

**Exposure Time Wet Area Without Glass**

Lower	2	sec
Upper	3	sec

**Exposure Time Glass Covered Wet Area**

4.6 sec

**Wet Area**

Glass Covered	13.1	sq ft
Bare Paste Lower	5.75	sq ft
Bare Paste Upper	8.625	sq ft
	<u>27.475</u>	sq ft

**Line Fit Standard Paste 90F, g emitted/sample-sec**

230 fpm (lower bare)	0.0173x <sup>0.481</sup>	x=exposure time
100 fpm (upper bare)	0.0011x	

**Line Fit Standard Paste Glass Covered 90F**

70 fpm	0.0006x
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**Emissions Factor**

Lower Bare	<b>0.59</b>	lb/hrft <sup>2</sup>
Upper Bare	<b>0.05</b>	lb/hrft <sup>2</sup>
Glass Covered	<b>0.02</b>	lb/hrft <sup>2</sup>

**Predicted Emission** **4.20** lb/hr

<b>Actual Test Emission</b>	4.33	lb/hr
	3.93	lb/hr
	3.57	lb/hr

Average **3.94** lb/hr

Standard Deviation **0.38**

**Exhibit 32: Experimental Error Determination**

$$\text{Experimental error} = \left( \text{a\% contribution of emission} * \frac{\text{residual error ss}}{\text{total ss}} \right) + \left( \text{b\% contribution of emission} * \frac{\text{residual error ss}}{\text{total ss}} \right) ..$$

Sum of squares designated by ss