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June 25, 2012

Ms. Lynn Vendinello
Chief, Fibers and Organics Branch
Office of Pollution Prevention and Toxics
U.S. Environmental Protection Agency
1200 Pennsylvania Ave. N.W.
Washington, D.C. 20460

RE: New Data Supporting Critique of Frihart Study

Dear Ms. Vendinello,

On January 10, 2012 Georgia-Pacific Chemicals submitted a critique of the study entitled *Formaldehyde Emissions from ULEF and NAF Bonded Commercial Hardwood Plywood as Influenced by Temperature and Relative Humidity* ("Frihart study"). The critique was submitted on behalf of GP Chemicals, LLC, Momentive and Arclin, Inc., the three major formaldehyde-based resin producers in North America. The letter explained our concerns with the relevance and conclusions of the Frihart study and respectfully requested that EPA refrain from basing any rule-making decisions on the study's findings.

In further support of the concerns outlined in the January 10th critique, a new study was conducted by Arclin, Inc., *Particleboard Formaldehyde Emissions and Decay under Elevated Temperature and Humidity Conditions.* As detailed in the attached document, the new Arclin study uses accepted regulatory and industry testing practices and is thus far more relevant than the Frihart study. The Arclin research clearly shows under extreme environmental conditions that all panel emissions were generally 2-3 times greater than "standard conditions" for all adhesive types, and further that the emissions decayed significantly at a similar rate for all adhesive systems in both the extreme and the standard environmental conditions. Most significantly, panel emissions from all products under extreme conditions were well within California Air Resources Board Phase II emission levels within 25 days from date of panel making and exposure of the panels to an extreme environment did not adversely affect emissions when the panels were re-equilibrated to standard ASTM D-6007 conditions.

Based on the Arclin study findings, we recommend that the EPA maintain a performance based standard aligned with the California Air Resources Board (CARB) ATCM, including provisions that foster and open and unbiased competitive environment for both resin and panel producers, allow choices and availability to consumers, and enhance innovation of all adhesive types.

The Arclin and Frihart studies both attempted to better understand the impact on formaldehyde emissions from different adhesive systems when subjected to extreme environmental conditions. However, the Arclin study differs significantly from the Frihart Study in that it employs test methods, procedures and protocols that are more similar to actual in service conditions as well as consistent with

CARB approved and industry accepted practices. The new Arclin study addresses the deficiencies in the Frihart study as follows:

1. Emissions test method: The emissions data collected in the Frihart study used a modified EN 717-3 method. The EN 717-3 has not been approved by CARB nor is there an established correlation between the EN 717-3 method and the ASTM E-1333[1]. The Arclin study uses the ASTM D-6007 testing method which is approved for direct correlation to the ASTM E-1333.

2. Static versus dynamic equilibrium: The Frihart study used a static or stagnant testing environment which does not represent product emissions expected in normal use. The ASTM D-6007 method used by Arclin is a dynamic test method in which a state of equilibrium is reached using a designated number of air exchanges reflecting normal indoor environmental conditions.

3. Extreme conditions of testing: The Frihart study used unrepresentatively extreme "outdoor" temperature and humidity test conditions. The Arclin study used a temperature of 85°F and a relative humidity of 75%. The Arclin test conditions are also extreme, but were based on an actual worst case scenario. Specifically, the worst case city (Houston, Texas), which has an average summer temperature of 84°F and relative humidity of 76.5%. Since temperature and humidity vary cyclically throughout the day, the average of the daily low and high were used.

4. Ratio of edge to surface during testing: The Frihart study does not test products in a way that would be representative of how panel surfaces are exposed in actual use. In the Frihart study, there was extremely high edge exposure of the panels thus potentially exaggerating emission results. The Arclin study tested panels realistically in a manner they would be utilized as defined by worst case scenarios in manufactured homes for panel loading as well as edge exposure (correlation to ASTM E-1333).

5. Emission decay over time: The Frihart study had no long term VOC emission decay data. The only data provided showed cumulative emissions over a four day period leading to speculation regarding potential emission results from UF resins. In contrast, the Arclin study does an in-depth evaluation of how particleboard panels bonded with various types of adhesives perform over a much longer period of time. The Arclin data shows panel emissions from the moment of manufacturing through a 50 day period. Under extreme conditions, all panels regardless of adhesive technology, showed an initial 2-3 fold increase of emissions followed by a significant decay curve resulting in significantly low emissions by the end of 50 days. Additionally, when these same panels were equilibrated back to "standard" conditions at the end of 50 days, they behaved identical to panels which had been maintained at standard conditions showing there were no adverse or detrimental effects on panel emissions when exposed to extreme conditions. Panel emissions from all products under extreme conditions were well within CARB Phase II emission levels within 25 days from date of panel making and all panels were the same

[1] ASTM E-1333 is the primary CARB approved test method used for emulating performance of wood based panels within interior and the test method mandated in Section 601, Part (a)(7) and Part (a)(10) of the Public Law 111-199 for measuring formaldehyde emissions.

emission level (approximately 0.025 ppm or less) at standard conditions after a 45 day decay period.

6. Information on UF resin: The Frihart study provides no information on the ULEF-UF adhesive formulations or panel making procedures reducing Frihart conclusions regarding emission phenomena and hydrolysis concerns to nothing more than speculation. The Arclin formulations of the formaldehyde-based systems were known by the authors, and when possible CARB exempt "certified" ULEF adhesives were chosen for evaluation.

The Arclin study used responsible testing methods and parameters to better understand the emission characteristics of panels made with various adhesive types. The study showed the emission characteristics of panels made with various types of resins, when exposed to standard and extreme environmental conditions, respond in a similar and predictable manner.

Because of the similarities in performance of panels made with all adhesive types, we endorse an unbiased performance based product emissions standard for regulatory purposes for all panel producers and resin suppliers. Additionally, we request the EPA refrain from using the Frihart study as a basis for justifying any regulatory decisions.

Regards,

Tom C. Holloway
Technical Director
Decorative and Interior Resins
tom.holloway@arclin.com

Particleboard Formaldehyde Emissions and Decay under Elevated Temperature and Humidity Conditions

Darren Riedlinger, Pierre Martin and Tom Holloway

Arclin USA, 475 28th St. Springfield, OR 97477

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Abstract

Particleboard panels were prepared using four different resin chemistries: melamine-urea-formaldehyde, urea-formaldehyde, phenol-formaldehyde, and polymeric diphenylmethane diisocyanate. Matched panels of each chemistry where then exposed to either a control conditioning environment maintained at 77 °F, 50% RH or an elevated conditioning environment maintained at 85 °F, 75% RH. Emissions were monitored over 50 days and their respective decay rates were modeled as an exponential decay function. At the conclusion of the monitoring period panel physical properties were measured and compared.

Key words: Particleboard, formaldehyde emissions

Introduction

Product emission standards based on ASTM E1333 for composite panels have historically been tested at humidities and temperatures standardized to average indoor environmental conditions. This paper examines formaldehyde emissions from particleboard made with various adhesive types tested under extreme conditions over a 45-50 day period using a modified ASTM 6007 method. Environmental conditions during testing were based on high outdoor temperature and humidity conditions experienced during summer months in the Southeastern United States (1). Since temperature and humidity vary cyclically throughout the day, the average of the daily low and high experienced in the most extreme summer location was used for the experiment—corresponding to a relative humidity of 75% and a temperature of 85 °F.

Laboratory made particleboard panels, conditioned and tested for emissions, were bonded with four different adhesive types: a phenol-formaldehyde (PF) certified to meet California Air Resource Boards (ARB) ultra-low-emitting-formaldehyde (ULEF) standard, a polymeric diphenylmethane diisocyanate (pMDI), a urea-formaldehyde (UF) and a melamine-urea-formaldehyde (MUF).

Experimental

Panel Construction

Laboratory panels were made from wood furnish gathered from a particleboard plant which manufactures panels using only pMDI adhesives, ensuring the furnish would be free from panel recycle sources (mitigated as much as possible) that may have an influence on formaldehyde emissions. Sixteen panels total with four of each adhesive type were constructed. Panels were made with 50% surface material and 50% core material to a targeted density of 44.0 pounds per cubic foot. All panels were ½ inch nominal thickness with a targeted final thickness of 0.570 inches. Press temperatures were held constant at 345 °F for all adhesive types. The pMDI and amino resin systems were pressed with identical cycle-times;

however, the pMDI panels had slightly higher moisture contents to ensure cure. The only variance in press time was with the PF in which a longer cycle-time was used to ensure curing of the adhesive. None of the panels were sanded prior to formaldehyde testing.

Although exact adhesive and panel making recipes for these panels will not be revealed due to the proprietary nature of the adhesives and recipes, the MUF, PF, and pMDI represent a close approximation to recipes used in the composite particleboard panel industry. The UF was made at the same formaldehyde to urea ratio as the MUF and with the same panel making recipe, however, it has not been used commercially. Some panel making characteristics are presented in Table 1.

Table 1: Panel making details

Adhesive type	*Press temp. (°F)*	*Press time at position (sec)*	*Density (lbs./ft.^{3})*	*Thickness (in.)*
PF	345	240	43.15-43.80	0.572-0.573
UF	345	170	43.85-44.40	0.570-0.571
MUF	345	170	43.95-44.25	0.568-0.570
pMDI	345	170	44.00-44.65	0.566-0.568

Formaldehyde Emissions Testing

After removal from the hot press and cooling to ambient temperatures, one set of panels was cut into 6.75 x 6.75 inch samples and edge sealed using aluminum tape. They were then sealed in a polyethylene bag for later analysis in Arclin's Springfield, Oregon laboratory which had environmental conditions of 85 °F (29.44 °C) and 75% relative humidity. A duplicate set, treated similarly, were cut to a dimension of 7.87 x 9.06 inches and sent to Arclin's Ste. Therese, Quebec lab for testing using standard ASTM 6007 environmental conditions of 77 °F (25 °C) and 50% relative humidity for comparative purposes. Each testing environment consisted of an outer conditioning room containing one or more stainless steel testing chambers, capable of maintaining fixed airflow rates during emissions testing. Testing of all panels began once both labs received their samples and continued at periodic intervals thereafter. Because the two testing environments utilized in this study were located in different research laboratories--each with unique infrastructure and analytical capabilities, some slight differences existed in the respective methodologies.

For the control environment, a single Dynamic Micro-Chamber (DMC) was employed with an internal volume of 44 liters. The airflow rate was maintained at 3.60 L/min, resulting in ASTM D 6007 airflow-rate to sample-surface-area ratio (Q/A) of 1.173 m/h. Panels were stored in individual conditioning bays located within the conditioning environment between analyses and were transferred to the DMC between 10 and 30 minutes before sampling. During sampling, 1.0 L/min of the chamber make-up air was diverted into an impinger containing 20 ml of a 1% solution of sodium bisulfite for a period of 83 to 135 minutes. Immediately after sampling, two duplicate 4 ml aliquots of each impinger solution were reacted with chromotropic acid and analyzed using a Spectronic 301 spectrophotometer at 580nm, which had been previously calibrated using a series of formaldehyde solutions of known concentration ($R^2 = 0.999$). Background formaldehyde levels, tested periodically throughout the test were consistently below 7 parts per billion.

For the elevated temperature/humidity environment, four ASTM D 6007 small chambers were employed, each having an internal volume of 69.24 liters. Mass-flow controllers attached to the outlet port of each small chamber maintained an airflow rate of 1.152 L/min, resulting in an ASTM D 6007 Q/A ratio of 1.176 m/h. Panels were stored in individual conditioning bays located within the conditioning environment between analyses and were transferred to a randomly chosen small chamber five hours before analysis. Following equilibration, air sampling occurred over 60 minutes, during which time airflow was diverted from a bypass line to a Supelco S10 DNPH-

coated silica solid phase extraction column (sampled air volume equaled 69.2 +/- 0.1 liters). The cartridges were then sealed in Mylar bags, stored at 5 °C and analyzed by HPLC within one week. Both room and small chamber background formaldehyde levels were measured periodically throughout the experiment and were consistently below 3 parts per billion.

HPLC formaldehyde quantification was performed using an adaptation of NIOSH Method 2016. HPLC peak area response factors were calibrated for each analysis set using five DNPH-formaldehyde standards at concentrations between 0.1556 and 96.9 µg DNPH-formaldehyde per ml. Linear regression coefficients were greater than 0.9999 for all analyses.

Measured formaldehyde emissions are expressed in molar ppm, adjusted to correlate with the ASTM E1333 large chamber dynamic test method. This correlation was performed between Arclin's Springfield laboratory and the Composite Panel Association's E1333 large chamber using 12 sets of matched specimen whose emissions ranged between 0.01 and 0.15 ppm. A correlation factor of 0.7775 large-chamber ppm/small-chamber ppm was established with an R^2 equal to 0.987. A later correlation study was then performed between Arclin's Springfield and St. Therese laboratories using 12 specimens whose emissions ranged between 0.01 and 0.11 ppm. In this case, two-way linear regression of the two laboratories' measurements yielded a significant ($P < .0001$) intercept coefficient and the St. Therese values were adjusted using the following correlation equation ($R^2 = 0.9718$):

[1] Springfield E1333 ppm = (1.1441 x St. Therese ppm) – 0.01185

Results and Discussion

Control environment formaldehyde emissions:

Dynamic-airflow formaldehyde emissions for particleboard panels maintained at 77 °F and 50% RH are presented in Figure 1. Each panel set had been sealed in polyethylene immediately after pressing and initial measurements were taken less than one hour after unsealing. For all four resin chemistries, this initial emissions measurement was significantly elevated relative to subsequent samples and can likely be attributed to the release of entrained formaldehyde, which is typical when panels are sealed immediately after hot-pressing. For example, the MUF and UF-bonded panels initially generated emissions of 0.115 and 0.097 ppm, respectively, but had fallen to between 0.045 and 0.055 ppm after two days of conditioning and then declined steadily throughout the study. By the end the monitoring period, emissions from the MUF panel were 0.024 ppm and emissions from the UF panel were 0.013 ppm—both well below the ARB phase II limit. The PF and pMDI-bonded panels also exhibited relatively high emissions for the initial measurement and decayed to 0.014 and 0.023 ppm, respectively, after two days of conditioning. Ultimate emission levels after 50 days of monitoring were 0.003 ppm for the pMDI panels and near zero ppm for the PF panels. As pMDI contains no labile formaldehyde, the pMDI panels' emissions represent background levels arising solely from the wood furnish used in this study—either endogenous formaldehyde generated by wood itself (and possibly exacerbated by hot-pressing) **(2-4)**, or from formaldehyde containing recycle material in our source mill's furnish supply (despite our efforts to mitigate its presence). It is therefore noteworthy that the phenolic resin system, although not a non-added formaldehyde (NAF) system, consistently exhibited lower emissions than the pMDI system.

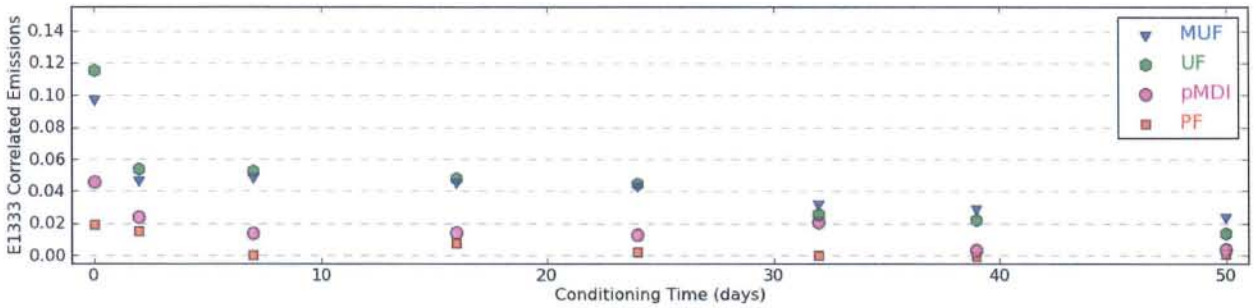


Figure 1: Particleboard emissions decay rate under standard temperature and relative humidity conditions

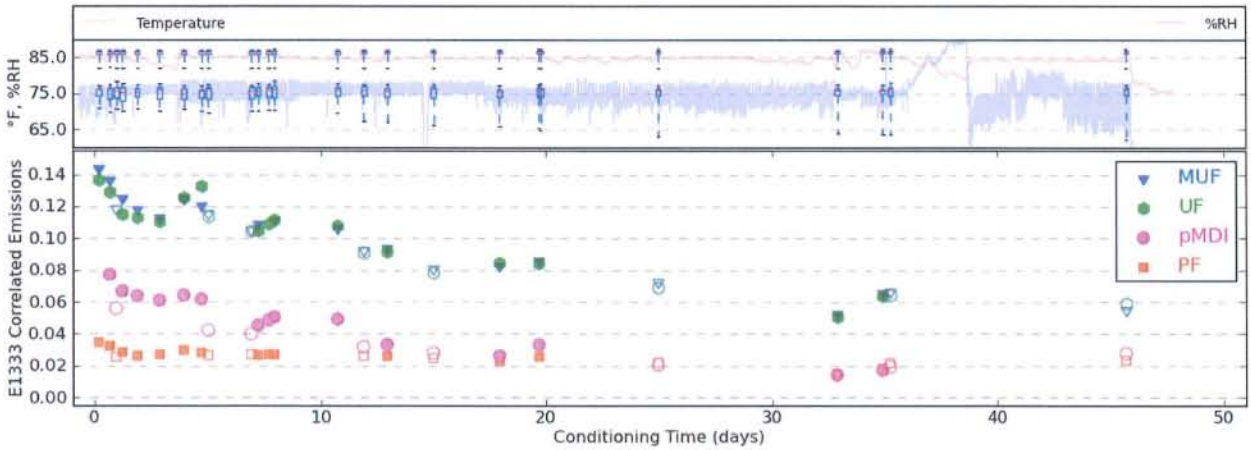


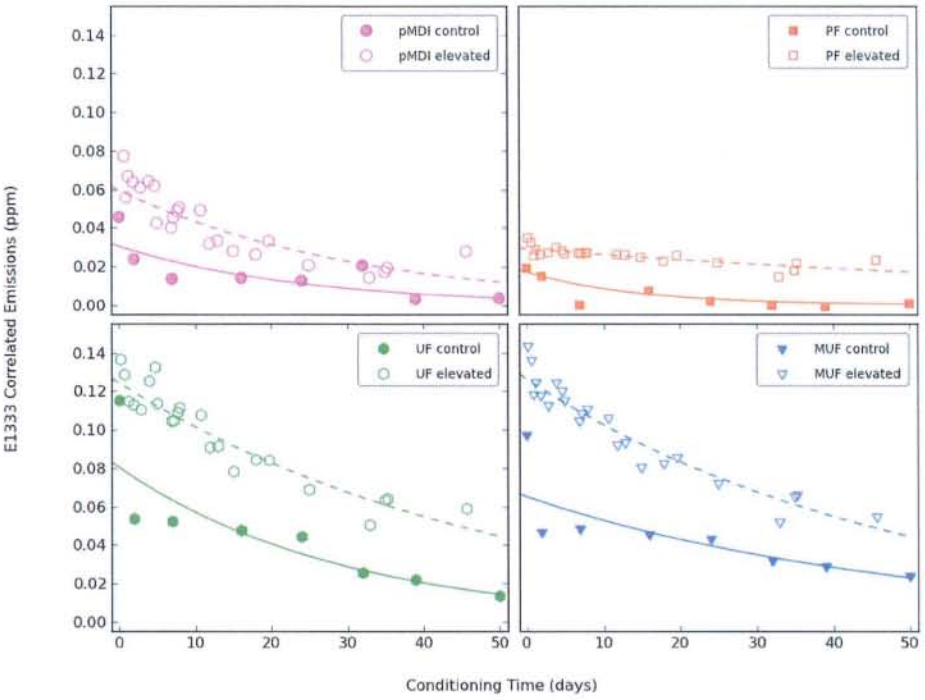
Figure 2: Particleboard emissions decay rate under elevated temperature and relative humidity conditions. Top: Room (solid lines) and small chamber (discrete box plots) temperature and humidity data. Box plots represent the minimum, lower quartile, median, upper quartile and maximum small chamber condition observed during each 60-minute board sampling. Bottom: E1333 correlated small chamber emissions for particleboard panels prepared using MUF, UF, pMDI or PF adhesives. 'Solid' versus 'open' data points distinguish between each of two replicate panels manufactured and analyzed for each resin type.

Elevated environment formaldehyde emissions:

Formaldehyde emission levels for those panels maintained at 85 °F and 75% RH are presented in Figure 2. Under these conditions our environmental controls were not as precise as those used for the 77 °F, 50% RH conditioning environment; therefore, actual temperatures and relative humidities of the room and small chamber are provided in the upper portion of Figure 2. Over the course of the entire monitoring period, the average conditioning room temperature was 84.1 °F (σ = 1.74) and the average room humidity was 73.6% (σ = 8.88). Unlike the temperature of the conditioning room, which could be maintained close to its average value with only occasional deviations, the conditioning room humidity oscillated regularly with approximately three cycles per hour. However, the small chambers buffered these oscillations and remained relatively constant: during sampling, the average conditions within the small chambers were 86.2 °F (σ = 1.03) and 74.7% RH (σ = 2.71).

As illustrated in Figure 2, although all panels (at least initially) generated higher emissions in the 85 °F, 75% RH elevated environment than in the 77 °F, 50% RH control environment, the relative trends were the same: the amino-based chemistries (MUF and UF) exhibited the highest emissions, the pMDI system was intermediate and the PF systems emissions were lowest. During the initial two days of conditioning the emissions from all panels declined. However, between days two

Figure 3: Comparisons of emissions in elevated and control environments, overlaid with exponential decay models



and four, emissions actually increased slightly in all panels—a phenomenon not observed in the control environment. In the 75% RH elevated environment, panels would likely take longer to approach their equilibrium moisture content than in the 50% RH control environment, and this may suggest that increasing panel moisture was counteracting an otherwise natural decay in emissions over time. Following day four, the emission levels from all panels again begin to decrease, with the magnitude of this decrease being greatest in the higher emitting systems. For example, at day four emissions from MUF and UF-bonded panels were both approximately 0.13 ppm and decreased steadily throughout the remainder of the 45-day monitoring, ultimately reaching levels below 0.06 ppm. Emissions from the pMDI panels were near 0.06 ppm at day four and decreased to approximately 0.027 ppm by the end of the study. Lastly, emissions from the PF panel, which were already below 0.03 ppm after four days conditioning, decreased to 0.023 ppm by the end of the study.

Emissions decay modeling and comparison:

From the raw data presented in Figures 1 and 2 alone it is difficult to make direct comparisons between emissions in the elevated environment and control environment at specific points in time, due to both noise in the datasets and a lack of measurements at identical conditioning times in the two environments. Panel formaldehyde emissions have generally been observed to decay exponentially with time (**5**). Each dataset was therefore fitted with an exponential decay function to average out measurement errors associated with any individual datapoint and allow us to interpolate emissions levels at arbitrary points in time. Model coefficients and fitting details are provided in Appendix A.

Emissions in the elevated and control environment are compared for each resin in Figure 3 and are overlaid with the fitted exponential decay models. Based on these models, emissions levels after 7, 30 and 45 days were calculated and are provided in Table 2. Relative emission differences for the MUF, UF

Table 2: Calculated emissions values based on the exponential decay models at various conditioning times. For each conditioning time the relative difference between the elevated and control models ('ratio') and absolute difference ('Δ') are provided.

Day:	7				30				45			
Resin	control	elevated	ratio	Δ	control	elevated	ratio	Δ	control	elevated	ratio	Δ
MUF	0.057	0.109	1.94	0.053	0.035	0.068	1.93	0.033	0.026	0.050	1.93	0.024
UF	0.063	0.108	1.71	0.045	0.029	0.067	2.35	0.039	0.017	0.050	2.88	0.032
PF	0.011	0.027	2.55	0.016	0.002	0.021	10.05	0.019	0.001	0.018	22.50	0.017
pMDI	0.023	0.048	2.10	0.025	0.009	0.023	2.63	0.014	0.005	0.014	3.02	0.009

and pMDI systems were similar, with emissions in the elevated environment being approximately two- to three-times higher than in the control environment, regardless of conditioning time. However, because emissions decayed exponentially over time, the actual magnitude of the emissions difference between the elevated and control environment (Δ) also tended to decrease exponentially. Unlike the MUF, UF and pMDI systems, the ratio between the elevated and control emissions for the PF system increased throughout the study, with a 22.5-fold difference in emissions after 45 days. Note, however, that emissions from the PF control system were extremely low; this unique trend observed for the PF panels could in part relate to greater measurement errors as emissions approached our analytical limits of detection.

Panel re-equilibration and physical properties:

Finally, after 50 days of conditioning our Springfield testing environment was adjusted back to the control conditions of 77 °F and 50% RH and those panels previously maintained in our St Therese control environment were shipped back to Springfield. These panels, along with the panels previously exposed to the elevated environment, were re-conditioning in Springfield for seven days and their emissions are presented in Table 3. The Springfield emissions measurements for the control panels (column *iii*) are similar to final measurements made in St. Therese (column *i*), indicating good agreement between the two laboratories. Furthermore, after equilibrating to 77 °F, 50% RH, emissions from those panels previously maintained in the elevated environment (column *iv*) were almost identical to the final emissions from the control panels (column *iii*), suggesting that exposure to elevated temperatures or humidities does not permanently alter a panels emissions characteristics.

Although panel emissions were not permanently affected, conditions in the elevated environment were severe enough to affect all the panels' physical properties. After re-equilibrating for 7 days at 77 °F and 50% RH, internal bond (IB) strengths were measured for both the control and elevated conditioning environment panels. IB values of those panels exposed to the control environment met M-2 grade ANSI standards, with the exception of the UF resin which only met ANSI M-1 grade. In contrast, IB values of all panel chemistries exposed to the elevated environment were 11-15% lower and exhibited some surface quality issues related to raised grain.

Table 3: Panel emissions in Springfield laboratory at 77 °F, 50% RH

	i	*ii*	*iii*	*iv*
Resin	St. Therese (control) final	Springfield (elevated) final	Control, re-tested in Springfield at 77 °F, 50% RH	Elevated, re-conditioned to 77 °F, 50% RH
PF	0.001	0.023	0.008	0.010
pMDI	0.003	0.028	0.009	0.010
UF	0.013	0.059	0.019	0.021
MUF	0.024	0.055	0.021	0.022

Conclusions

Particleboard panels were prepared using four different resin chemistries and their emissions were monitored over 50 days in both a 77 °F, 50% RH control conditioning environment and a 85 °F, 75% RH elevated environment. The elevated conditioning environment had moderate effect on panel physical properties, negatively impacting surface quality and slightly reducing internal bond strengths. While subjected to the elevated environment, emissions were generally 2-3x greater than what was observed in the control environment; however, in both environments panels emissions decayed exponentially throughout the study regardless of resin chemistry. Furthermore, the elevated conditioning environment did not appear to permanently impact emissions once these panels were re-equilibrated in a control environment.

References

1. *Formaldehyde Emissions from ULEF- and NAF-Bonded Commercial Hardwood Plywood as Influenced by Temperature and Relative Humidity.* **Frihart, Charles R, et al.** Geneva, Switzerland, 2010. Proceedings of the International Convention of Society of Wood Science and Technology and United Nations Economic Commission for Euorpoe. pp. 1-13.

2. *Formaldehyde emissions from solid wood.* **Myers, George E and Boehme, C.** Madison, WI : Forest Prod. J., 1997, Vol. 47, pp. 45-48.

3. *Volitile organic compounds and formaldehyde in nature, wood and wood based panels.* **Roffael, E.** s.l. : Holz Roh Werkst, 2006, Vol. 64, pp. 144-149.

4. *Wood-borne formaldehyde varying with species, wood grade, and cambial age.* **Weigl, M, et al.** s.l. : Forest Prod. J., 2009, Vol. 59, pp. 88-92.

5. **Versar Inc.** *Formaldehyde exposure model -- description and demonstration.* US Environmental Protection Agency, 1986. Contract No. 68-02-3968.

Appendix A: Formaldehyde emissions decay modeling

Panel emissions were modeled to the exponential decay function[†]: $Log_{10}(emissions) = M \cdot time + B$, resulting in the following model coefficients and regression values:

Treatment	Slope	Intercept	R^2
MUF elevated	-0.0091	-0.8976	0.923
MUF control	-0.0090	-1.1850	0.782
UF elevated	-0.0089	-0.9053	0.886
UF control	-0.0149	-1.0951	0.889
pMDI elevated	-0.0140	-1.2246	0.752
pMDI control	-0.0183	-1.5161	0.697
PF elevated	-0.0047	-1.5356	0.604
PF control	-0.0302	-1.7654	0.951

Model R^2 values are generally lower for those treatments that generated the lowest formaldehyde emissions, reflecting the greater relative error associated with emissions measurements as they approach background levels and suggesting the need to smooth such datasets before making reliable comparisons. Despite the low model R^2 values for some treatments, visual examination of Figure 3 suggests that the exponential decay model provides a good approximation of the overall emissions trend for each treatment without overfitting the data and modeling random variations associated with any individual data point.

[†] *In the case of the PF control emissions, three of the emissions measurements—after adjusting according to Equation 1—were slightly below zero (the minimum observed value was -0.00096 ppm) and could not be modeled by an exponential decay function. These three negative emissions values were excluded from the PF control emission model.*