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Formaldehyde Emissions from ULEF- and NAF-Bonded Commercial Hardwood Plywood as Influenced by Temperature and Relative Humidity

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Abstract

It is well documented in the literature that temperature and humidity can influence formaldehyde emissions from composite panels that are produced using urea-formaldehyde (UF) adhesives. This work investigates the effect of temperature and humidity on newer, ultra-low emitting formaldehyde urea formaldehyde (ULEF-UF) and no-added formaldehyde (NAF) adhesives. A modified version of the EN 717-3 method to collect formaldehyde coupled with the acetyl-acetone method to quantify formaldehyde emissions was used. Formaldehyde emissions from a commercial CARB phase II compliant hardwood-plywood panel bonded with a ULEF-UF resin increased greatly when panels were exposed to higher heat and humidity. Furthermore, the rate of emission for ULEF-UF panels increased with longer exposure at 100% humidity. In contrast, formaldehyde emissions from CARB phase II compliant hardwood-plywood bonded with a NAF resin were relatively stable at different temperature and relative humidity conditions and decreased over time. This work highlights the potential for long-term formaldehyde emissions from the new ULEF-UF, CARB phase II compliant resin systems.

Keywords soy, urea formaldehyde, formaldehyde emissions, heat, humidity, ULEF

Introduction

Increasing concerns over the quality of indoor air has led to recent changes in legislation and a general preference for more stringent limits on the quantity of formaldehyde that can be emitted from consumer products intended for indoor use. Wood composites bonded with urea-formaldehyde (UF) adhesive have been identified as an important source of indoor formaldehyde emissions (Battelle 1996). Formaldehyde release from interior wood composites has been a longstanding issue, leading in the 1980s to the adoption of voluntary standards in the United States and Europe that placed limits on formaldehyde emissions (ANSI 2009a,b, 2004; European Standard 2002). These voluntary standards led to lower formaldehyde-emitting wood composites, but in subsequent years, U.S. emissions from standard products stayed constant while products in Europe and Japan moved to lower emission levels.

Recent standards adopted by the California Air Resources Board (CARB) are intended to significantly reduce and regulate formaldehyde emissions in composite wood products (ATCM 2009). The CARB standard is also the basis for national legislation recently passed concerning the emission of formaldehyde in interior wood composites (TSCA 2010). The new standards have led to new UF adhesives with ultra-low formaldehyde emissions (ULEF-UF) (Dunkey 2005), and opened the door for no-added-formaldehyde (NAF) adhesives, such as soy-based adhesives (Allen et al. 2010, Wescott et al. 2010), polymeric diphenylmethane diisocyanate, and certain types of poly(vinyl acetate). Although both classes of adhesives, ULEF-UF and NAF, are capable of passing the CARB phase II formaldehyde emissions limits, there is a concern about the long-term emission potential of ULEF-UF adhesives when exposed to potentially higher temperature or humidity levels than specified in the current testing methodology for measuring formaldehyde emissions.

Although substantial progress has been made on ULEF-UF adhesives, the fundamental chemistry of urea formaldehyde is relatively unchanged and may remain susceptible to hydrolysis. The reaction of urea with formaldehyde first produces hydroxylmethyolated urea that then condenses to yield methylene and dimethylene ether bridged urea polymers (Pizzi 2003, Meyer 1979). Although these reactions are not unlike the steps to produce the other formaldehyde-containing wood adhesives, the UF polymers are distinct in that they are susceptible to hydrolysis under some normal use conditions (Myers 1986a). The reaction shown in Figure 1 for urea and formaldehyde illustrates the problem with depolymerization in that it can yield additional free formaldehyde, especially when free water is present.

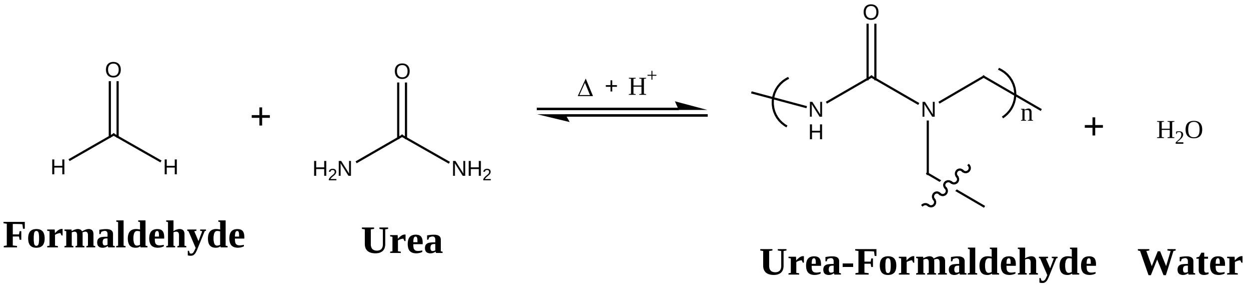

Figure 1. The reaction of urea with formaldehyde to form the urea-formaldehyde polymer.

The presence of free water in the composite panel, as in the case of higher humidity, tends to drive the reverse reaction, yielding more free formaldehyde. Myers showed that formaldehyde adsorbed onto wood reaches an emission plateau in about 7 days at 80% relative humidity (RH) and 27°C, as does phenol-formaldehyde-bonded particleboard. In contrast, UF-bonded particleboard emitted formaldehyde for over 30 days without reaching a plateau (Myers 1986b). In addition, Myers's own data and his analysis of the literature data showed that formaldehyde emissions increase from UF-bonded wood composites at higher humidity and temperature conditions (Myers 1985, Myers and Nagaoka 1981). This work was done with composites bonded with more traditional UF-based adhesives; it is unclear if the new ULEF-UF systems suffer from the same level of hydrolytic instability and subsequent high formaldehyde emissions.

Wood itself generates significant formaldehyde when exposed to certain conditions common to the composite panel manufacturing process (Schäfer and Roffael 2000, Roffael 2006). This so-called "native" formaldehyde has been shown to be transient and rapidly decreases to levels below those set by the standards (Birkeland et al. 2010). Production of formaldehyde from wood has been shown to occur at conditions of very high heat and would not be expected to be a significant source of formaldehyde in composite wood products during service.

Currently, the primary standard test method in the United States for measuring and regulating formaldehyde emissions in composite wood panels is the ASTM E 1333 (ASTM 2002) large chamber test. Secondary methods can be also used; however, all methods must prove equivalence to the primary method. In E 1333, samples are conditioned at 25°C and 50% RH for 7 days and then tested at the same temperature and RH conditions. Based upon the available literature, some questions arise regarding formaldehyde emissions from composite wood panels:

- Given that the standard test method, ASTM E 1333, uses 25°C (77°F) and 50% relative humidity, do these conditions represent all the exposure that interior composite wood products will experience in service?
- How do the formaldehyde emissions in CARB phase II certified composite wood products bonded with ULEF-UF adhesives compare to those bonded with NAF adhesives over a range of temperatures and relative humidity that they may reasonably experience in service?

This study focused on answering these questions, using a modified version of EN 717-3 to test the effects of temperature and relative humidity on commercial CARB phase II compliant plywood bonded with either ULEF-UF or NAF.

Methods

Samples

Plywood samples used for testing were 3/4-in.- (19-mm-) thick, seven-ply, hardwood plywood with maple face and back and mixed softwood cores obtained from a commercial collaborator. One plywood specimen was bonded with a ULEF-UF and one was bonded with a soy-based NAF adhesive. Samples from both plywood specimens were tested in a small chamber by the manufacturer and shown to be CARB phase II compliant (<0.05 ppm). Samples were wrapped and sealed in plastic within 24 h after hot-pressing and remained in plastic until testing by the modified EN 717-3 method.

Modified EN 717-3 (WKI Bottle Method)
A modified version of the EN-717-3 was conducted in this study; Table 1 defines the specific modifications used in this study. From other studies, the repeatability of this method gave a 4% coefficient of variation.

Relative humidity was controlled as follows: 30% RH (with saturated $MgCl_2$), 75% RH (with saturated NaCl), and 100% RH (RO H_2O) (Wexler 1961).

Table 1: Summary of modifications to EN-717-3

	EN-717-3	Our method
Temperature	40°C	25°C and 35°C
Test duration	3 h	1–4 days
Relative humidity (%)	100	30–100

Detailed Test Procedure
Using a Nalgene® 500-mL wide-mouth polypropylene bottle (Sigma Aldrich, Milwaukee, Wiscsonsin), with cap modified with epoxy and a paper clip, 50 mL (via burette) of either H_2O (100% RH), saturated $MgCl_2$ (30% RH), or saturated NaCl (75% RH) solution is placed in the bottom. Three 1- by -in. samples are weighed to 0.1 g, stacked on top of each other (faces together), and bound with a rubber band. The bound samples are then suspended above the solution in the bottle by attaching the rubber band to the paper clip. The bottle is then kept in a temperature/humidity controlled room (25°C) or in a water bath (35°C) for the allotted time (24, 48, or 96 h). The test bottles are then cooled in an ice water bath for 30 min, the samples removed carefully, and the solution collected for analysis. The samples are analyzed for formaldehyde on the same day using the acetyl-acetone method.

Acetyl-Acetone Method (ONORM 1992, Nash 1953, Belman 1963)
A calibration curve was generated using a standard formaldehyde solution prepared from 37% formaldehyde (Sigma Aldrich, Milwaukee, Wisconsin) titrated to determine formaldehyde level. A six-point calibration curve was generated using concentrations of 0 to 5.6 µg/mL formaldehyde and yielding an $R^2 = 0.9998$. The standards were analyzed as described below to obtain the formaldehyde response. Equal parts (2 mL) of 0.4% acetyl-acetone (Fisher Scientific, Fair Lawn, New Jersey), 20% ammonium acetate (Daigger Chemical, Vernon Hills, Illinois), and sample solution were combined in a test tube. The mixture was heated to 40°C for 15 min in a water bath, then cooled to 25°C. The cooled solution was placed in the dark for 1 h. The mixture was then analyzed for absorbance with a spectrophotometer at a wavelength of 412 nm. The formaldehyde concentration of the sample was determined based on the calibration curve as described above. The results were converted to micrograms of formaldehyde emitted per gram of wood. Standard solutions were run at 1, 10, and 30 µg/mL to cover the range of formaldehyde

concentrations measured. Controls were run using the acetyl-acetone method with standard formaldehyde levels in the presence of $MgCl_2$ and NaCl to ensure no interference from the salts.

Figure 2: Sample set-up for modified EN-717-3 method

Results and Discussion

A static formaldehyde emissions technique was employed to assess changes in emissions for composite wood products as a function of temperature and humidity. The method was a modified version of the EN 717-3 method. The modifications to this method are outlined in Table 1. The purpose of the modifications was to allow the test to be run at various temperatures, relative humidities, and durations to better understand the formaldehyde emission potential of composite panels under a variety of possible exposures. The 100% humidity was higher than typical, but accelerated tests are generally run under more severe conditions than normal exposures due to shorter times under those conditions.

Two commercially produced decorative hardwood plywood specimens were evaluated in this study. Both specimens were of the same construction, and the only variable was the adhesive used to bond the veneers together to produce the final product. One specimen was bonded with a ULEF-UF adhesive; the other specimen was bonded with a NAF soy-based system. Samples from both specimens were tested by the manufacturer in a small chamber correlated to ASTM E 1333 prior to our testing, and both were shown to be CARB-phase II compliant.

The ASTM E 1333-96 “Large Chamber Method” and any correlated “Small Chamber Method” per ASTM D 6007-02 must be run at 25°C and 50% relative humidity. It is likely that these conditions may be typical for many homes in the United States, in particular, those that contain and operate an air conditioning system. However, there are many instances when these panels are used within the interior of a home that they may be subjected to extended periods of time at temperatures higher than 25°C and/or relative humidity levels higher than 50%. The data in Figures 3a (www.weather.com) and 3b (www.cityrating.com/relativehumidity.asp) show that the majority of the United States, in fact, is actually much higher than 50% RH. Most notably, during the summer months, the southeastern region has substantially higher RH and temperature than the test conditions (Table 2). It is this finding that led us to evaluate composite panel emissions as a function of temperature and humidity.

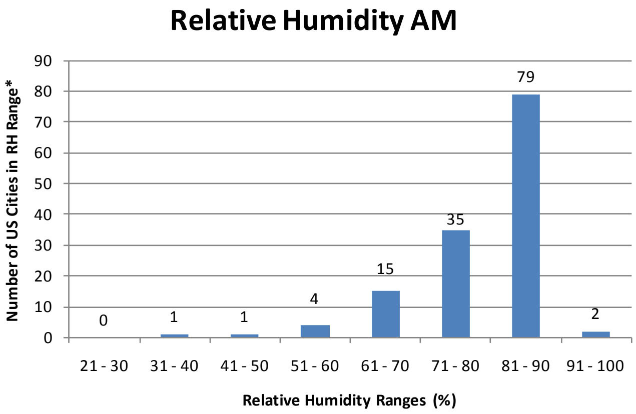

Figure 3a: AM relative humidity distribution of 137 U.S. Cities (Average = 79%)

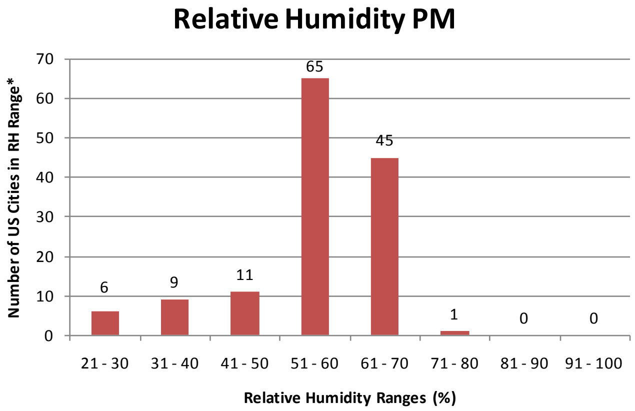

Figure 3b: PM relative humidity distribution of 137 U.S. cities (Average = 55%)

Table 2: Summer temperature and relative humidity averages for select U.S. cities

	Ave. low temp. Jun–Aug (°F (°C))	AM RH (%)	Ave high temp Jun–Aug (°F (°C))	PM RH (%)
Chicago, IL	64 (18)	80	82 (28)	62
Fargo, ND	57 (14)	81	80 (27)	64
Houston, TX	75 (24)	90	93 (34)	63
Kansas City, MO	70 (18)	81	88 (31)	63
Las Vegas, NV	76 (24)	39	102 (39)	21
Los Angeles, CA	64 (18)	79	83 (28)	65
Miami, FL	76 (24)	83	91 (33)	61
New York, NY	66 (19)	72	80 (27)	56
Raleigh-Durham, NC	67 (19)	85	86 (30)	54
Seattle, WA	55 (13)	83	73 (23)	62

Impact of Relative Humidity

In this section of the study, we used water (100% RH) and saturated solutions of $MgCl_2$ (30% RH) and NaCl (75% RH) to control the relative humidity inside the sample bottles. (See the experimental section for details.) These experiments were run at both 25°C (77°F) and 35°C (95°F). Table 3 shows the results.

Table 3: Formaldehyde emissions in (μg CH2O/g wood) via modified EN-717-3 method

		ULEF-UF			**NAF**		
	Temp.	**% Relative Humidity**			**% Relative Humidity**		
Days	(°C)	30	75	100	30	75	100
1	25	1.8	3.6	5.8	0.7	0.7	1.6
2	25	4.2	6.0	16.7	1.2	1.6	2.9
4	25	5.6	11.4	50.8	1.4	2.4	4.0
1	35	3.1	8.9	24.0	0.5	2.4	4.5
2	35	5.2	15.5	54.2	0.7	2.7	5.0
4	35	9.1	31.3	178.1	2.1	4.4	5.3

To better analyze the data, several charts were constructed from the data shown in Table 3. Figures 4a and 4b show emissions as a function of relative humidity for both the 25°C and 35°C data sets. These results clearly show that the ULEF-UF panel emitted significantly higher formaldehyde levels when subjected to higher relative humidity levels and that this was further exacerbated by a concomitant increase in temperature.

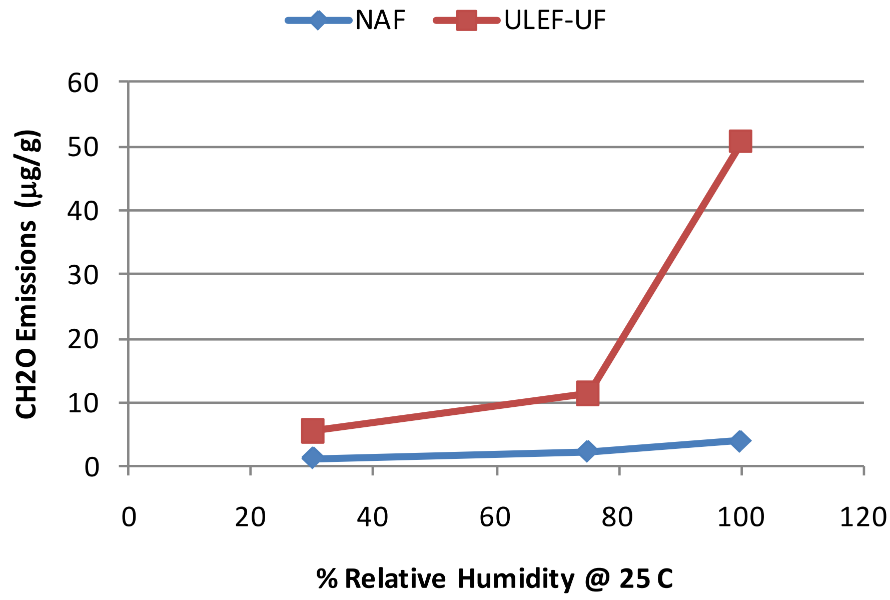

Figure 4a: Formaldehyde emissions at various relative humidity levels at 25°C (4 day samples)

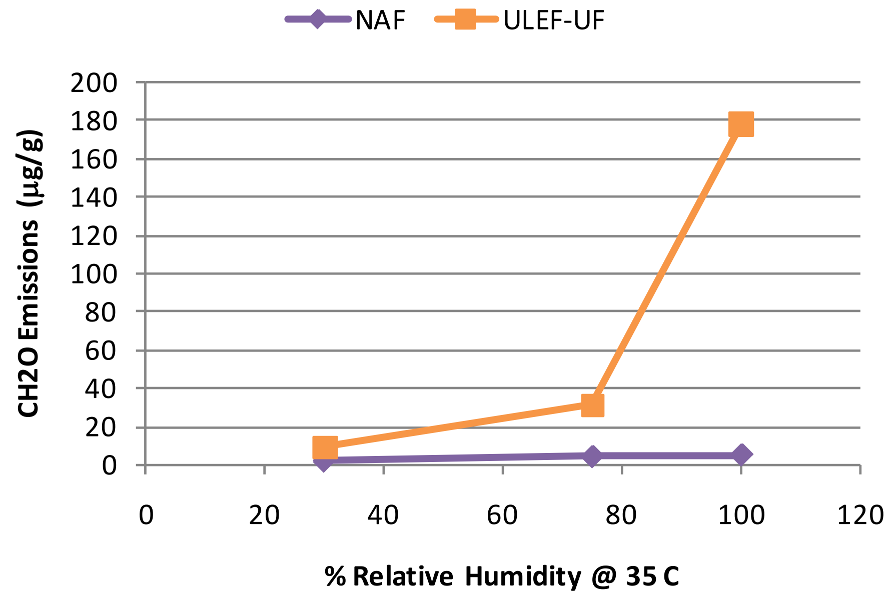

Figure 4b: Formaldehyde emissions at various relative humidity levels at 35°C (4 day samples)

Although it was expected that emission levels of panels produced with ULEF-UF adhesive would increase more than those produced with NAF adhesive at increasing temperature and humidity, the fact that the ULEF-UF panel emitted >33 times the amount of formaldehyde than the NAF panel at 100% RH/35°C and the ULEF-UF panel's emissions within its own set would increase by >31 times (100% RH/35°C vs 30% RH/25°C) was quite surprising to us.

We were also interested in rate of emissions in this study. To assess rate of emissions, individual samples were tested at 1-, 2-, and 4-day increments. Results of this study are shown in Figures 5 and 6 (note differences in scale for each set of figures). These results show that for all the NAF samples, regardless of temperature or relative humidity, rate of formaldehyde emissions decreased over time. This is a desired feature as this would suggest that emission levels will only improve (reduce) over the life of the product. Interestingly, the ULEF-UF produced panel did not show this behavior when subjected to the 100% relative humidity level, and even at the lower humidity levels emission rates were either relatively flat or only slightly decreasing. The trends were the same regardless of temperature, that is, emissions rate was roughly double at 4 days what if was after only 1 day. This could be the result of scavenger consumption or possibly sample equilibration and/or diffusion rates.

Another interesting aspect of these data is the apparent limited or fixed amount of "native" formaldehyde present in these panels. With the NAF panels, this native formaldehyde appeared to be released faster when the temperature was higher and the relative humidity was higher, hence the emissions only increased from 4.5 to 5.3 from day 1 to day 4 within the 100% RH/35°C sample set. It appears that once the native formaldehyde was extracted from the moist panel, there was virtually no formaldehyde left in the panel, thus the total formaldehyde emitted did not change substantially when the test duration was extended. The ULEF-UF panel was produced from UF resin, and these resins are well known to hydrolyze and produce additional formaldehyde; the NAF panel did not show this behavior.

The effect of temperature and humidity on formaldehyde emission reported in Table 3 is similar to the effects seen by Myers and Nagaoka (1981). Using a dynamic chamber method and UF-bonded particleboard, they showed that moving from 25°C and 30% RH to 25°C and 75% RH resulted in an approximate two-fold increase in formaldehyde emissions. An examination of the data in Table 3 shows that at 25°C, the increase from 30% to 75% RH yields a 2.0-, 1.4-, and 2.0-fold increase in emissions for the 1-, 2-, and 4-day data, respectively.

Furthermore, when Myers and Nagaoka changed both temperature (from 25°C to 40°C) and RH (from 30% to 75%), the resultant increase in formaldehyde emission was approximately six-fold. An analysis of data from Table 3 shows that moving from 25°C and 30% RH to 35°C and 75% RH yields a 4.9-, 3.7-, and 5.6-fold increase in emissions for the 1-, 2-, and 4-day data, respectively.

Although Myers and Nagaoka (1981) did not conduct analyses at relative humidity levels above 75%, in a comprehensive literature survey, Myers was able to derive quantitative temperature and relative humidity factors at a wide range of temperature and relative humidity conditions (Myers 1985). Based on these equations, the move from 30% to 90% RH at 25°C is predicted to yield a three-fold increase in formaldehyde emissions. The data in Table 3 show that moving from 30% to 100% RH at 25°C yields increases in formaldehyde emissions of 3.2, 4.0, and 9.1 fold for the 1-, 2-, and 4-day data, respectively. The 1-day data agree well with Myers prediction; however, the longer test periods present increasing rates of formaldehyde emission. The mechanism for this increase is currently unknown.

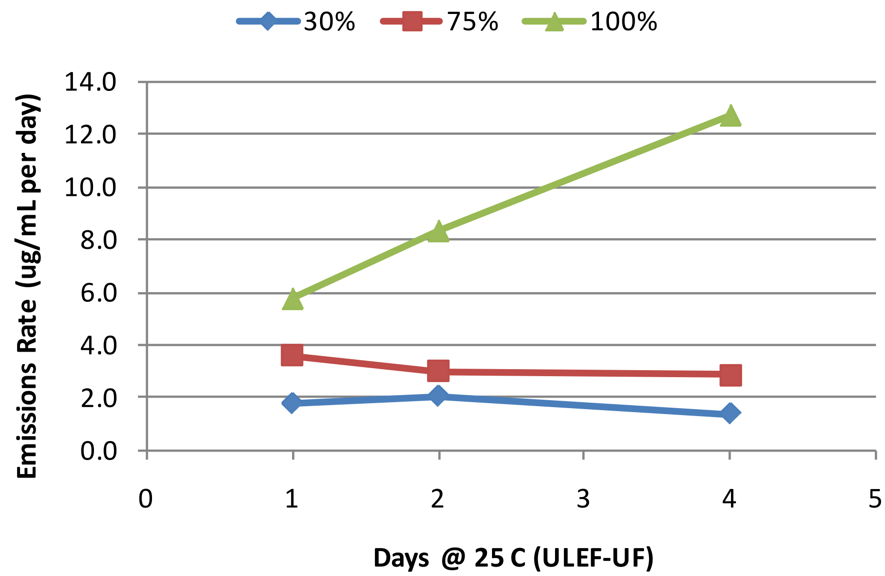

Figure 5a: Emissions rate as a function of % relative humidity for ULEF-UF panel at 25°C.

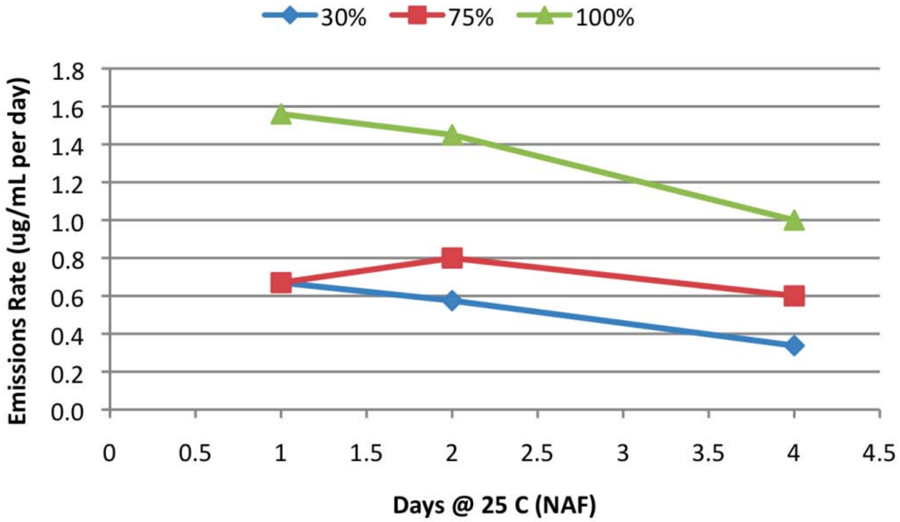

Figure 5b: Emissions rate as a function of % relative humidity for NAF panel at 25°C.

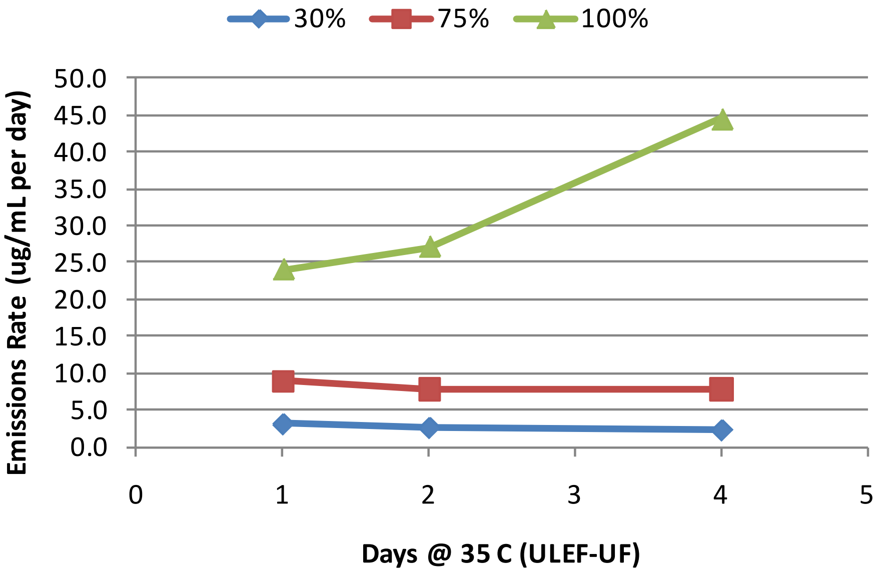

Figure 6a: Emissions rate as a function of % relative humidity for ULEF-UF panel at 35°C.

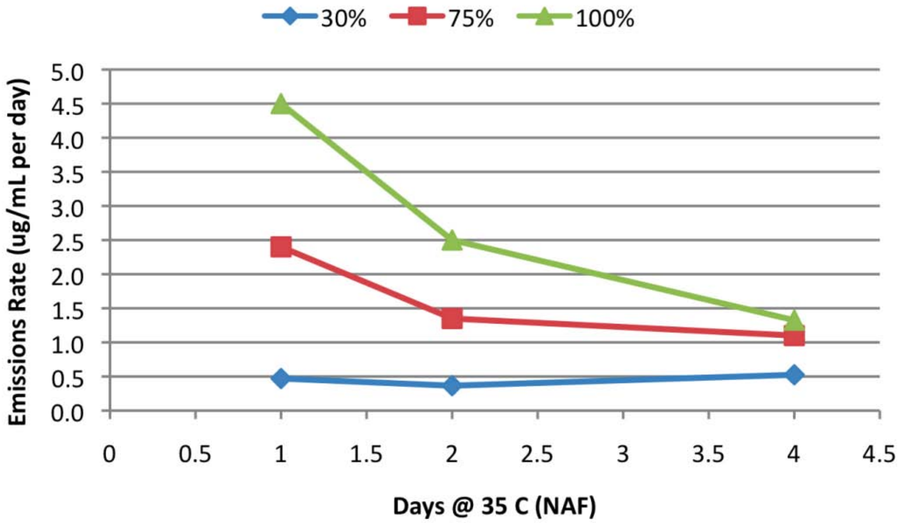

Figure 6b: Emissions rate as a function of % relative humidity for NAF panels at 35°C.

Conclusions

Testing of formaldehyde emissions from CARB II compliant plywood panels using an ultra-low emitting formaldehyde (ULEF) UF resin and a no-added-formaldehyde (NAF) resin carried out at six different conditions (25°C at 30%, 75%, and 100% relative humidity, and 35°C at 30%, 75%, and 100% relative humidity) using a modification of EN 717-3 has shown the following: (1) The

ULEF-UF product emitted more formaldehyde as the temperature and relative humidity increased; at 100% humidity, there was an initial delay in this rise probably due to the consumption of the scavenger. (2) The NAF plywood product showed that the total formaldehyde emissions reached a plateau and decreased rapidly after only a few days under all test conditions. Thus, neither the wood nor the NAF are providing any significant potential source of long-term formaldehyde as a result of these increased heat and moisture conditions.

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