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Determination of native (wood derived) formaldehyde by the desiccator method in particleboards generated during panel production

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Abstract

Hot-pressing wood, particularly in the production of wood composites, generates significant ''native'' (wood-based) formaldehyde (FA), even in the absence of adhesive. The level of native FA relates directly to the time and temperature of hot-pressing. This native FA dissipates in a relatively short time and is not part of the long-term FA emission issue commonly associated with hydrolyzing urea-formaldehyde bonds. This paper demonstrates that the common desiccator/chromotropic acid method is very specific for FA and is not influenced by other volatile compounds set free from wood during hot-pressing. Furthermore, it is shown that particleboard produces native FA at high levels even in the absence of adhesives or in the presence of one type of no-added formaldehyde (NAF) adhesive. Soy-based adhesives suppress native FA emission and provide low FA emission levels in both the short and long term. This study highlights an often overlooked aspect that should be considered for emission testing: standardizing the time and conditions employed immediately after pressing and prior to the onset of emissions testing. Addressing this issue in more detail would improve the reliability of correlation between data obtained by rapid process monitoring methods and emission measurements in large chambers.

Keywords: adhesives; environmental analysis; formaldehyde emission; no-added formaldehyde (NAF) adhesive; soy-based adhesives; wood adhesion.

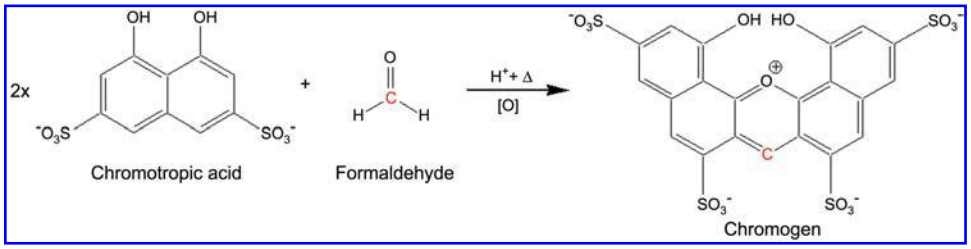
Introduction

Emission of formaldehyde (FA) from composite wood products for interior applications has been a topic of concern for many years. The widespread use of urea-formaldehyde (UF) adhesives in these products and their presence within the home aggravate this problem (Meyers 1984a). The acceptable emission level of FA from composite wood materials used in the interior has decreased as defined by the current American National Standard (ANSI) voluntary standards: ANSI A208.1-2009 (particleboard), ANSI A208.2-2009 (fiberboard), and ANSI/HPVA HP-1-2004 (hardwood plywood) (ANSI 2009a, 2009b, 2004). In 2008, the California Air Resources Board (CARB) passed a regulation concerning any interior composite wood products sold in California. This requires low FA emission and a Third Party Certification system (TPC) with much tighter quality controls than have typically been employed in the industry (ATCM 2009). The ANSI standards have since been modified to be aligned with the CARB standards, and currently there is national legislation up for consideration that will probably also adopt the CARB emission standards.

A variety of test methods for determining FA emissions from wood products have evolved over time. Each method has its own unique set of board conditioning and test conditions that possess both positive and negative attributes. The ANSI standards, specifically A208.1-2009 (ANSI 2009a), call for a large chamber test ASTM E 1333 (ASTM 2002) and most of the industry uses this method for demonstrating compliance to the standard. CARB also requires the large chamber test for certification, but could also allow other approved secondary methods if reliable correlation to the large chamber method is proven. The large chamber test is expensive, time-consuming, and needs a large amount of samples. Thus, it is impractical for quality assurance in commercial production.

The desiccator test as described in ASTM D 5582-00 (ASTM 2006) is widely used for rapid FA determination. It is simple and ideal for commercial production control because it provides a reasonable correlation to the large chamber test (Meyers 1983; Que and Furano 2007). In all methods, FA content is ultimately determined by colorimetry based on chromotropic acid (1,8-dihydroxynaphtalene-3,6-disulfonic acid) (Eegriwe 1937) or acetyl acetone (Nash 1953; Czech 1973), with the former being more common. The chemistry of the chromophoric acid method for the analysis of FA is well described by Georghiou and Ho (1989) and the authors established the structure of the chromotropic acid-FA chromogen. The chromogen is detected at 580 nm for maximal absorbance reading (Scheme 1).

It is obvious that the FA emission directly correlates with the amount of free FA in UF resins (Meyers 1986). Accordingly, typical FA/urea ratios in UF resins have been lowered significantly, and FA scavenger and catalyst technologies have been developed (Meyers 1984b; Elbert 1995) to reduce FA emissions. As FA emission regulations are tightening, questions arise about the FA emission from wood itself (Meyer and Boehme 1997; Funch 2002; Roffael 2006; Weigl et al. 2009). According to the quoted studies, FA emission



Scheme 1 Reaction of chromotropic acid (1,8-dihydroxynaphtalene-3,6-disulfonic acid) with formaldehyde to form the active chromogen.

from wood is inferred to be insignificant in comparison to FA emitted from the UF moiety of traditional composite wood panels. However, within the new CARB limits, the wood derived FA emission is a more significant part of the total FA emissions.

Schäfer and Roffael (2000) demonstrated that FA emission of wood increases at elevated temperatures and prolonged heating times. The authors also proposed reaction mechanisms about FA formation from wood. Emissions of FA and other volatile organic compounds (VOCs) have been measured during pressing (Carlson et al. 1995; Baumann et al. 2000; Jiang et al. 2002) and it was found that FA arises even in the absence of any resin in the wood. Although there is evidence in the literature that FA is produced from wood during hot-pressing of composite panels, it is generally accepted that FA from wood is an insignificant contributor to the total measurable level of FA in a composite wood product.

In the present study, the performance of the desiccator test on particleboard and hardboard samples is revisited. It is clearly shown that FA from wood (native FA) is produced at significant levels and retained within the board when exposed to typical hot-pressing conditions. The native FA requires a certain time to migrate to the surface via diffusion and be dissipated from the bulk of the board. Against this background, one of the goals was to demonstrate the influence of the time elapsed between pressing of the boards and FA determinations.

Materials and methods

Resins

The polyamidoamine-epichlorohydrin resin (PAE-NAF) is commercially available (ChemVisions™ CA1000) and was obtained from Ashland, Inc. (formerly Hercules Inc., Wilmington, DE, USA). The Soyad® NAF adhesive is a proprietary blend of soy flour and other non-reactive ingredients with a solids content of 45–60% and a pH value of 5.5. It was obtained from the same company. Wood furnish for particleboards and hardboards was obtained from a variety of industrial collaborators around North America. Furnish A: northwest US; Furnish B: southeast US; Furnish C: western US; Furnish D: northeast Canada; Furnish E: southeast US; Furnish F: northern Canada. The UF adhesive was provided by an industrial collaborator (65% solids; face F/U ratio 1.05:1.00, core F/U ratio 1.15:1.00). In the core, 1.0% v/v NH_4Cl (Sigma-Aldrich, Milwaukee, WI, USA) was used as an accelerator. Scavenger: 40% urea solution at 20% (wt/wt) to UF in the face and 15% (wt/wt) in the core. Materials for chromotropic acid analysis and control testing of the method were obtained from Sigma Aldrich, Inc. (Milwaukee, WI, USA). The volatile organic compounds tested, FA, formic acid, acetaldehyde, acetone, propanaldehyde, acrolein, glyoxal, glutaraldehyde, benzaldehyde, and methanol, were chemically pure and purchased from Sigma-Aldrich.

Hardboard

Particleboard face furnish (Furnish B: southeast US) was dried to 3.0±0.5% moisture content (MC). For the board without adhesive, the pH of the water was adjusted to match that of the adhesive (pH 2.5) and applied such that the final MC of the furnish was 10.7% (on dry basis). Adhesive was sprayed in a rotating drum blender such that the MC of the final furnish was 10.7% (on dry basis) and the resin/wood load was 2.0% (wt/wt). The material was then formed into two boards 0.56 m×0.56 m and pressed for either 180 s or 300 s at 170°C in a 0.91 m×0.91 m oil-heated press. After removing from the press, the board was allowed to cool for 30–60 min and wrapped in plastic. Boards were stored at 30% RH and 27°C until samples could be cut for desiccator tests. The samples remained in plastic until the first desiccator test and were then conditioned at 50% RH and 23°C for further desiccator testings.

Particleboard-UF and Soyad-NAF

Face and core material (Furnish F: northern Canada) were dried to 3.0±0.5% MC. Urea-formaldehyde (face F/U=1.05:1.00 and core F/U=1.15:1.00) and Soyad-NAF adhesive was applied with an atomizing spray nozzle at a face load of 10.8% (wt/wt) and a core load of 7.25% (wt/wt). The material was formed into a 0.86 m×0.86 m face-core-face board with a face/core ratio of 40:60. Boards were pressed for 300 s at 170°C in a 1.27 m×1.27 m steam-heated press. The boards were allowed to cool for 30–60 min and wrapped in plastic. Boards were stored at 30% RH and 27°C and kept in plastic until desiccator samples could be cut. The samples remained in plastic until the first desiccator test and were then conditioned at 50% RH and 23°C for further desiccator testing.

Particleboard-PAE-NAF

Face and core material (furnishes A–F) were dried to 3.0±0.5% MC. PAE-NAF adhesive was applied by an atomizing spray nozzle at a face load of 1.75% (wt/wt) and a core load of 2.5% (wt/wt). The material was formed into a 0.86 m×0.86 m face-core-face board with a face/core ratio of 40:60. Boards were pressed for 300 s at 170°C in a 1.27 m×1.27 m steam-heated press. The boards were allowed to cool for 30–60 min and wrapped in plastic. The further procedure was the same as described above.

Formaldehyde analysis

Desiccator testing was conducted as described in ASTM D 5582-00 (ASTM 2006) with eight samples (6.99 cm×12.7 cm). However, the edges of the samples were not sealed with paraffin wax. Chromotropic acid analysis was done according to ASTM D 5582-00 (ASTM 2006). For control samples, stock solutions of FA and each possible interference compound were prepared and diluted as necessary to obtain absorbance readings within instrumental capabilities.

Results and discussion

Revisiting of the chromotropic method

Early in the commercialization process, experiments with Soyad-NAF adhesives had produced remarkably high FA emissions as measured both by the desiccator and dynamic microchamber methods when samples were evaluated within days of coming out of the press (results not shown). To exclude false identification, a variety of control compounds – known to be emitted from hot-pressed wood (Wang and Gardner 1999) – with similar structures and functionalities to FA – were tested using the chromotropic acid analysis. A solution of known concentration was prepared for each of the compounds and subjected to chromotropic acid analysis.

Figure 1a and b show the results. In Figure 1a, the absorbance of all samples was normalized on the basis of FA concentration at 1.96 μg/ml. Figure 1b shows the same absorbances with an elongated *y*-axis in the low absorbance range between 0 and 0.0007. It is clear that the compounds indicated do not significantly influence FA detection. Moreover, the spectral fingerprint of FA is so specific that an interference with other compounds can be excluded. Although the reliability of the method has been shown previously (MacFayden 1945), research was focused only on detection at 580 nm and did not provide the highly specific spectral fingerprint of the FA-chromogen leaving open the possibility of interference from high levels of other VOCs from wood.

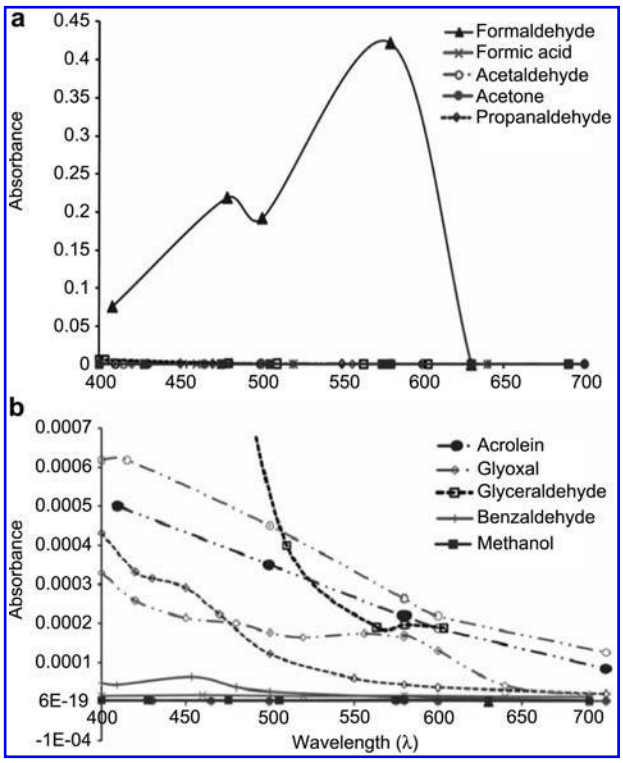


Figure 1 Formaldehyde determination by the chromotropic acid method. (a) Spectra of solutions of formaldehyde and potential interference compounds at equivalent concentrations of 1.96 μg ml^{-1}. (b) The same spectra with expanded *y*-axis.

Results of board tests

Although the board with PAE-NAF does not contain any FA, a possible FA release was tested. The first control board contained 2.0% PAE-NAF (final MC 10.7%). One board from this batch was pressed for 180 s and the other for 300 s at 170°C. A second set of panels was also prepared under the same pressing conditions, but this time by spraying only water that had been pH adjusted to 2.5 to match that of the PAE-NAF (final MC was again 10.7%).

The panel without adhesive, although somewhat weak, had enough integrity for sample preparation suited to the desiccator test. Figure 2a shows the FA emissions obtained with no conditioning of the samples. In both panels, little to no detectable FA evolved from samples pressed at 180 s but the FA emission is elevated for panels pressed for 300 s. Surprisingly, the water-only panel actually yielded higher levels of FA than did the PAE-NAF containing board. This difference could have been due to a slight FA scavenging ability of the free amines in PAE-NAF or to the slightly elevated density of the PAE-NAF boards, which could reduce FA diffusion rate (Christensen et al. 1987). Figure 2a is clear evidence that FA is released from wood under hot and wet conditions, typical to composite pressing.

The PAE-NAF and water-only samples were tested again 10 and 17 days later after conditioning them at 23±1.7°C and 50% RH. After 10 days of conditioning (Figure 2b), the native FA produced during the hot-press had completely dissipated.

To quantify the relative level of native FA observed in an NAF panel to the FA produced in a UF containing panel, a series of four particleboards were prepared: (1) commercial UF without scavenger, (2) commercial UF with scavenger, (3) Soyad-NAF non-scavenging, and (4) Soyad-NAF scavenging. All panels produced had similar strength properties in the range of M2 particleboard as defined by ANSI A208.1-2009 (data not shown). This was targeted to ensure that the structure of panels is similar.

Based on Figure 3, which presents the FA release, it is clear that native FA is produced at significant levels, actually showing higher initial FA levels for the non-scavenged Soyad-NAF than in the scavenged UF panel. Although the Soyad-NAF non-scavenged board initially yields more FA than the scavenged UF board, the FA dissipates rather rapidly from the board and the detectable level of FA goes to background level. In the case of the scavenged UF board, there

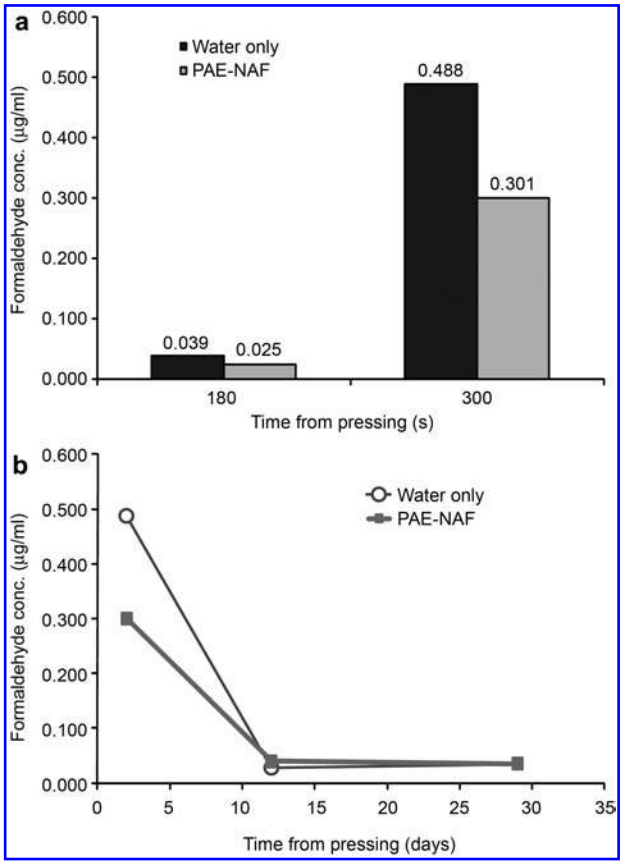


Figure 2 (a) Formaldehyde levels of hardboard samples pressed for 180 and 300 s as measured by the desiccator method described in ASTM D 5582-00 (2006). (b) Formaldehyde levels for hardboard samples pressed at 300 s measured over time by the desiccator method, ASTM D5583-00 (2006). PAE is polyamidoamine-epichlorohydrin and NAF is for no-added-formaldehyde.

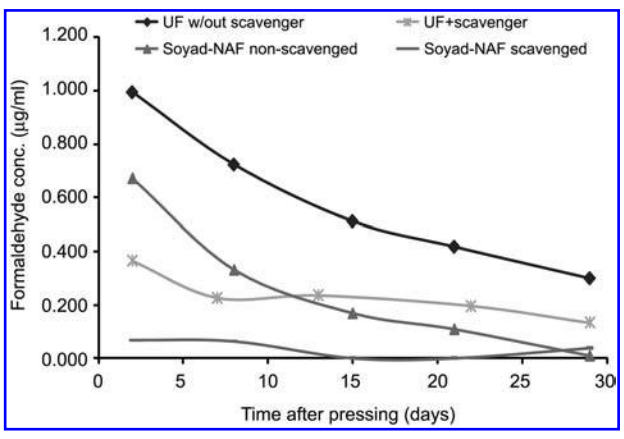


Figure 3 Comparison of FA emissions from boards prepared by scavenged and non-scavenged UF and Soyad-NAF adhesives measured over time by the desiccator method, ASTM D5583-00 (2006).

is a small initial drop in FA concentration followed by a sustained level of detectable FA concentration.

Based on these data, we suggest that the scavenger in the UF is probably scavenging significant amounts of native FA

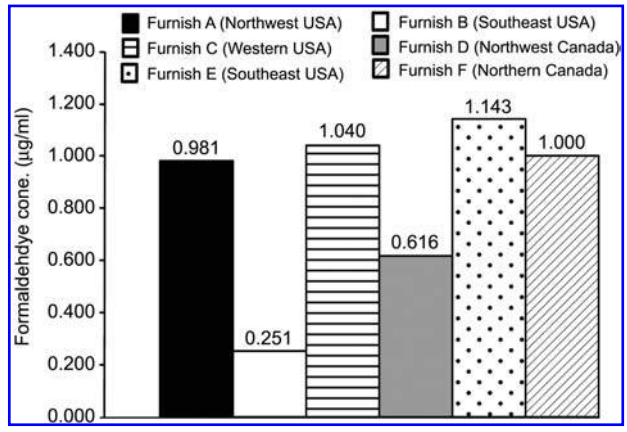


Figure 4 Formaldehyde emissions of particleboards prepared by PAE-NAF and a variety of furnishes obtained from the mills indicated. Formaldehyde was measured using the desiccator method, ASTM D 5583-00 (2006).

as well as FA coming from the free FA in the UF. The detectable FA is produced by the UF adhesive as it releases FA over time at equilibrium. This concept is supported by the data of non-scavenged UF board because the FA concentration is tending toward a similar equilibrium value as that of scavenged UF board. The data of Soyad-NAF adhesive indicate that once the native FA has dissipated, the board will remain at low background levels as the adhesive does not provide a long-term FA source as in UF board. It is also obvious that in the Soyad-NAF adhesive board with scavenger, the native FA is also captured. In such a case one can report a true zero-emission composite.

To eliminate the possibility that the high yield of native FA was due to an unusual wood furnish source described in the above studies, PAE-NAF particleboards were prepared with furnishes obtained from six other mills located around North America (see materials and methods section). FA emissions after hot-pressing of boards at 170°C for 300 s (Figure 4) revealed that all the samples produced significant FA emissions, although the FA level was somewhat furnish-dependent.

Conclusions

Boards produced with PAE-NAF, Soyad-NAF, and without adhesive (only with water) provide strong evidence about native (wood-derived) FA release. FA arises from wood under conditions of hot-pressing. Native FA is retained in the panel for a certain time after production. It is detectable within the standard time period typical for testing under commercial certification. It was demonstrated that the chromotropic method is reliable and not influenced by other potential interfering compounds released from wood. The native FA is transient and dissipates within a short time. The press time and temperature play an important role on the amount of native FA.

The discovery that native FA in hot-pressed composite wood panels has the potential to yield significant FA readings

even for panels produced using NAF adhesives certainly requires review and discussion about the best way to preserve the spirit of the CARB ruling. Improving indoor air quality and lowering FA emissions is important given our current knowledge of the risks of FA exposure. Careful testing using well-defined and appropriate procedures is crucial for the ability of producers to consistently achieve the low FA targets with minimal disruption in day-to-day manufacturing or inventory control.

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