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EDITORS

Alfred W. Christiansen

and

Anthony H. Conner

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Forest Products Society
2801 Marshall Court
Madison, WI 53705-2295
phone: 608-231-1361
fax: 608-231-2152

PREFACE

The manuscripts in this book are based on presentations from the symposium *Wood Adhesives 1995* held in Portland, Oregon, June 29-30, 1995. This is the sixth in a series of symposia organized by the Wood Adhesives Science and Technology Work Unit at the Forest Products Laboratory and held every five years. The symposia are dedicated to the exchange of information and ideas about research on wood adhesives, adhesion to wood, and new bonded wood products. We hope that these proceedings will further stimulate the exchange of needs, ideas, and information on research and development of wood adhesives among researchers, producers, and consumers,

The symposium was organized into sessions: The Customer in Global Markets, Surface Chemistry and Modifications for Enhanced Adhesion, Greening of Bonded Wood Products—VOCs, and New Developments in Conventional and Renewable Adhesive Systems. In addition to the oral presentations devoted to these topics, a number of presentations were given in a poster format. Both the oral and the poster presentations have been included in these proceedings. With the exception of the papers from the first session, because the subjects did not lend themselves to independent assessment, the papers were reviewed before acceptance into the proceedings.

The Planning Committee thanks all the authors for their work in preparing their oral presentations and posters; the success of the symposium was due to their thorough preparations and excellent presentations. We also greatly appreciate the scientists who reviewed the papers, thus providing guidance in achieving the quality seen in this book. We thank Art Brauner, Susan Rutter, Julie Lang, Ann Messing, and Doris Robertson of the Forest Products Society for making the site arrangements, and Susan Stamm for final editing and preparation of this typeset copy of the proceedings. We thank the Session Chairs who guided these sessions: Michael Hoag, Alan L. Lambuth (now deceased), Richard W. Hemingway, and Cynthia D. West.

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Analysis of Volatile Organic Chemical Emissions from particleboard

Melissa G.D. Baumann, Stuart A. Batterman, Guo-Zheng Zhang, and Anthony H. Conner

Abstract

The emission of volatile organic chemicals (VOCs) from building materials has been of increasing concern over the last two decades. In wood, VOCs include chemicals naturally present as well as chemicals added during processing. Very little information is available on the types and quantities of VOCs that are emitted, and current methods of air analysis have not been validated for these compounds. We examined different methods for preparing mixtures of standard VOC compounds emitted from wood. We found that typical methods for preparing gas-phase standards worked poorly with the compounds (terpenes and aldehydes) expected from wood products. This indicates that special care must be taken when working with emissions from wood products and when preparing appropriate calibration curves. VOC emissions from particleboard samples were tested using an automated system designed for that purpose. The results showed the emission of a wide variety of chemicals; the main constituents were terpenes and aldehydes. Because the emission rates of these compounds change greatly with time, caution must be taken in the design of experiments to assure that all samples are evaluated within the same timeframe.

Introduction

Over the past several decades, air pollution in homes and office buildings has become a matter of increasing concern. Formaldehyde emission has been the major concern associated with bonded wood products. Recently, interest has turned to other volatile organic chemicals (VOCs) that may be emitted from wood products. The VOCs include chemicals naturally present in the wood as well as those added during processing. In new,

Melissa G.D. Baumann, USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin, Stuart A. Batterman and Guo-Zheng Zhang, Environmental and Industrial Health, University of Michigan, Ann Arbor, Michigan, and Anthony H. Conner, USDA Forest Service, Forest Products Laboratory Madison, Wisconsin.

Keywords: volatile organic compound, VOC, terpenes, particleboard, The Forest Products Laboratory is maintained in cooperation with the University of Wisconsin. This article was written and prepared by U.S. Government employees on official time, and it is therefore in the public domain and not subject to copyright.

energy-efficient buildings air exchange rates are low, permitting concentrations of VOCs to accumulate to detectable and possibly harmful levels. Adverse health effects associated with these increased VOC concentrations include eye and respiratory irritation, irritability inability to concentrate, and sleepiness.

Formaldehyde emissions from wood products have been extensively studied (7) and are currently limited by U.S. Department of Housing and Urban Development standards for manufactured homes (5) and by statutes in Minnesota (4). However, few studies have addressed the emission of other VOCs from wood and wood products. Studies of non-formaldehyde emissions from wood products have investigated only a limited number of wood products (3,8,9). Moreover, since these studies used different testing conditions and methods, it is difficult to compare the results. These studies reported a wide variety of compounds emitted from wood (Table 1); however, the source of some of these compounds is not clear.

To address these concerns, we initiated a long-term effort to develop and validate test methods for wood emissions and to use these methods to analyze the emissions from a wide variety of composite wood products. We developed an automated system for collecting and analyzing VOC emissions from composite wood products. Several sorbent materials commonly used for collecting VOCs from air samples were evaluated to determine the best sorbent material for collecting VOCs from wood products (2). We also evaluated the stability of aldehydes and terpenes, typical wood product VOC emissions, in stainless steel SUMMA® canisters* (12).

Table 1. VOCs reported from wood products.

•Acetone	•Hexanal
•Benzaldehyde	•Methylene chloride
•Benzene	•Propanal
•Butanone	•Terpenes
•Ethanol	•Toluene
•Ethyl acetate	•Xylenes
•Formaldehyde	

* Tradenames listed in this report are for information only and do not represent the endorsement of the U.S. Department of Agriculture of any product or service.

Information about the stability of terpenes in stainless steel canisters and initial data on the VOC emissions from particleboard are presented here.

Canister Stability of Terpenes

Background

In addition to cellulose, hemicellulose, and lignin, wood contains up to approximately 10-percent extractable components, depending upon the species. The extractives are thought to be the origin of a large portion of the VOCs that are emitted from wood. Many extractives, especially in coniferous species, are terpenoid compounds. Current methods of air analysis have not been validated for these somewhat reactive compounds.

Experimental

Sample Preparation

High and low concentration gas samples containing aldehydes (butanal, pentanal, hexanal, heptanal, octanal, nonanal, *trans*-2-octenal, and benzaldehyde), terpenes (α -pinene, β -pinene, and 3-carene), and benzene (as a control) were prepared and stored in spherical 6-L electropolished stainless-steel canisters (Andersen Samplers, Inc., Atlanta, Georgia). Prior to use all canisters were cleaned by repeated cycles of pressurization with humidified zero-grade air, followed by heating to 120°C and evacuation to < 0.1 torr. A high concentration standard was prepared at room temperature (20°C to 22°C) by syringe injection of 140 μ L of HPLC-grade water and 5.8 μ L liquid of each neat compound into a clean canister. The canister was then pressurized to 1 atm with ultra-pure nitrogen (Scott Specialty Gases, Troy, Michigan). The water added to this canister gave a relative humidity of approximately 50 percent, and concentrations of the target compounds were between 68 and 133 ppmv. A canister containing toluene, to be used as a control and

for preparation of internal standards, was prepared by injecting 140 μ L of HPLC-grade water and 5.8 μ L of toluene into a clean canister to give a concentration of 110 ppmv and a relative humidity of 50 percent.

Low concentration samples were prepared to represent concentrations and conditions likely in indoor air. Five canisters were humidified at room temperature (20°C to 22°C) by adding 140 μ L of HPLC-grade water. Using a gas-tight syringe, 500 μ L of the high concentration sample was withdrawn and added to each canister. Each canister was then filled with dry zero-grade (< 0.1 ppm VOCs expressed as methane) air to a pressure of 1 atm. The low concentration samples had relative humidities near 50 percent and concentrations of individual VOCs from 2.9 to 5.6 ppbv. Toluene from the toluene canister was added to several canisters containing VOC mixtures as an internal standard.

Sample Analysis

Gas samples from the canisters were analyzed after 1 h, 2 h, 1 day, 2 days, 4 days, 8 days, and 16 days. For each analysis, a 320-mL gas sample was bled from the canister to a cryogenic trapping system (CDS Analytical, Peakmaster EV). For samples that did not already contain toluene as an internal standard, toluene was introduced onto the trap at the same time. The trap was then heated and the gas sample was analyzed by gas chromatography (GC) (Hewlett Packard, 5890E, Series II) and mass spectrometry (Hewlett Packard, 5972). Details of the analytical procedure are presented elsewhere (12). To determine concentrations, the integrated counts of the several fragmentation ions of each peak were summed, multiplied by the appropriate response factor, and divided by the sample volume. Response factors for each of these compounds were determined from the high concentration standard and confirmed by liquid injections of target compounds diluted in pentane.

Results and Discussion

Figure 1 displays recoveries for terpenes prepared in canisters containing humidified air. Percentage of recovery was based on the initial reading for the compounds and was averaged over the five canisters. The average decrease during the first day was 21 percent for α -pinene and 17 percent for β -pinene and 3-carene. This decrease was typical of all the compounds tested in the canisters, both aldehydes and terpenes. Over a period of 16 days, the recoveries of most compounds decreased to about 50 percent.

The loss of the compounds over the course of the study can be explained by several mechanisms, including adsorption on the canister walls, dissolution in condensed water in the canisters, homogeneous gas-phase reactions, and heterogeneous reactions occurring on the

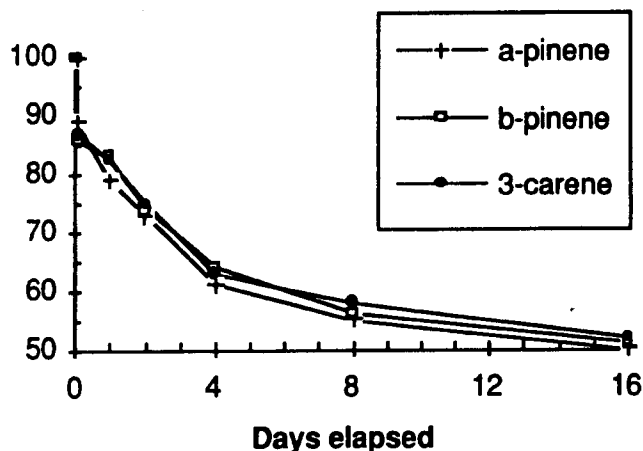


Figure 1. Percent recovery of terpenes from stainless steel canister containing mixture of terpenes and aldehydes in clean air at 50-percent relative humidity.

canister walls. Information collected in this study was insufficient to determine the mechanism of compound loss.

Emissions From Composite Wood Samples

Background

Emissions from composite wood products may potentially arise from various sources. The source most commonly investigated is the adhesive used to bond the products. However, it is also known that wood contains a variety of chemical materials that occur naturally, some of which could be emitted to the indoor environment. Other sources of chemical emissions from wood are the breakdown products resulting from reactions that occur when the wood is heated to drying and pressing temperatures, additives that are used in composite wood products, and contamination from exterior sources such as machine oils and petroleum fuels.

A list of target compounds for this study was compiled from compounds known to be present in wood and other components of composite wood products and compounds that have been identified in the literature as being emitted from wood products. The target compounds are given in Table 2, and the structures of the target terpenes are shown in Figure 2. These compounds served as the initial compounds to be identified and quantified in wood product emissions.

Experimental

Sample Preparation

Samples of 16-mm (5/8-in.) Southern Pine industrial particleboard (SPPB) and 16-mm (5/8-in.) mixed western softwood particleboard (WPB) were cut into 250- by 250-mm (10- by 10-in.) pieces at the mill within 4 h of sanding. The test samples were sandwiched between two similar boards and wrapped in aluminum foil for shipping. Upon receipt at the laboratory, samples were stored

at 4°C (39°F), wrapped in the original packaging, until shortly before testing.

Before testing, pieces from the center of the test board were cut into 102- by 102-mm (4- by 4-in.) samples; edges of the samples were sealed by applying a saturated solution of sodium silicate. After the first application, samples were allowed to dry at room temperature for 15 min. A second coat of sodium silicate was then applied, and the samples were left at room temperature to dry for 1 h.

Prior to loading the samples in the test chamber, the 50-L electropolished stainless-steel chamber was flushed for 12 h at 20°C to 22°C with zero-grade air humidified to 50-percent relative humidity. Airflows in and out of the chamber were such that the chamber was maintained at a slight positive pressure relative to atmospheric pressure. A blank sample was withdrawn from the chamber and analyzed as described in the following text. After the blank sample was withdrawn, an edge-sealed wood sample was placed near the center of the chamber, and the chamber was sealed. Air flow through the chamber was adjusted to 1 air change per hour, and sampling began 2 h after loading.

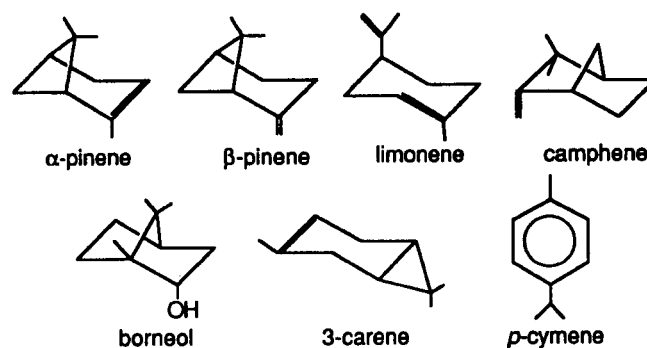


Figure 2. Structures of target terpenes.

Table 2. Target compounds.

Acids and Esters	Alcohols	Aldehydes and Ketones	Aliphatic Hydrocarbons	Aromatic Hydrocarbons
Acetic acid	Borneol	Acetaldehyde	Camphene	Benzene
Methyl acetate	Isopropanol	2-Butanone	Octane	<i>p</i> -Cymene
	1-Pentanol	Nonanal	3-Carene	Toluene
		Acetone	Pentane	Xylenes
		Heptanal	Heptane	
		Octanal	α -Pinene	
		Benzaldehyde	Limonene	
		Heptanones	β -Pinene	
		1-Octenal		
		Butanal		
		Hexanal		

Sample Analysis

For sampling, 320 mL of exhaust from the chamber was directed to a cryogenic concentrator (CDS Analytical, Peakmaster EV) where it was trapped at -100°C (-148°F). The sample was then heated to 150°C (302°F) and flushed to the head of a gas chromatography (Hewlett-Packard, 5890E Series 2) equipped with electronic pressure control. The gas flow from the concentrator was split using a ratio of 12:1 before being cryofocused at the GC column head. The fused silica capillary column was 30 m by 0.25 mm (id.) with a $0.25\ \mu\text{m}$ film thickness (98 ft. by 0.98×10^{-3} in. (id.) with a 0.98×10^{-5} in. film thickness) (Hewlett Packard, HP-5). The cryofocused sample was then heated to 150°C (302°F) and the GC temperature program initiated. The GC oven was initially held at -20°C (-4°F) for 5 min. The oven was then heated to 120°C (248°F) at a rate of $25^{\circ}\text{C}/\text{min}$ ($77^{\circ}\text{F}/\text{min}$) and held at 120°C (248°F) for 5 min.

A quadrupole mass selective detector (Hewlett Packard, 5972A) and workstation (Hewlett Packard, G1034 C Chemstation) were used for sample detection, data acquisition, and data manipulation.

Table 3. VOCs in Southern Pine particleboard (SPPB) and western softwood particleboard (WPB).

Compound	SPPB		WPB	
	2 h	17 h	2 h	16 h
Benzaldehyde	x	x	x	x
Benzene	x	x	x	x
Butanal	x	x		
Camphene	x	x	x	
3-Carene			x**	x
<i>p</i> -Cymene			x	
Heptanal	x	x	x	x
Hexanal	x	x	x	x
Limonene	x	x	x***	x
1-Nonanal	x	x	x	x
Octanal	x	x	x	x
<i>trans</i> -2-Octenal		x		
Pentanal	x	x	x	x
1-Pentanol	x	x		
α -Pinene	x	x	x	x
β -Pinene	x	x	x	x
Toluene	x			
<i>p</i> -Xylene, 2- and 3-heptanone*	x	x	x	
Number of unknowns	13	9	9	7

* *p*-Xylene, 2-heptanone, and 3-heptanone eluted together.

** Other peaks overlapped with 3-carene.

*** Two other compounds were also eluted with limonene.

Results and Discussion

Compounds identified in the emissions from SPPB and WPB are listed in Table 3. After 2 h in the chamber, more than 22 compounds were found in SPPB and 28 compounds in WPB. For SPPB, 13 compounds were among the target compounds; the remainder were unidentified. For WPB, 15 compounds were target compounds and 13 were unidentified. Identified compounds included several terpenes (α -pinene, β -pinene, limonene, camphene, 3-carene, and *p*-cymene), aldehydes (butanal, pentanal, hexanal, benzaldehyde, 2-octenal, and others), and hydrocarbons (toluene and benzene). For both SPPB and WPB, acetone and methylene chloride were present in the blank sample that was run prior to loading the test sample. Therefore, the presence or absence of these compounds could not be confirmed.

The presence of benzene in both wood samples and toluene in the SPPB sample indicates that these wood samples did emit these compounds. Neither of these compounds was present in the air sample withdrawn from the chamber immediately before loading the wood samples, indicating that the compounds were not contributed by the analysis system. Further work is necessary to determine whether benzene and toluene come from the wood furnish, the resin, or the additives used in the manufacture of the products. It is also possible that they are introduced after manufacture.

Although quantitative results were not obtained in this study, chromatograms clearly showed that the major components of the emissions were terpenes and aldehydes, including α - and β -pinene, limonene, pentanal, and hexanal. It is interesting that the homologous series of aldehydes from pentanal to nonanal was present in both samples. The SPPB sample, which contained higher concentrations of all aldehydes, also contained butanal. The dominance of the terpenes and aldehydes was not unexpected; terpenes are natural components of wood extractives, and various lower molecular weight aldehydes have been identified in wood that has been thermally treated (6) and in building materials that have been subjected to microbiological degradation (11).

Samples of emissions gathered at 2 h and 16 or 17 h after loading the wood into the chambers showed a significant decrease in the concentrations of the emitted compounds. This was particularly noticeable for the pines, indicating that the emission rates of these compounds may decrease more rapidly than the emission rates of the other compounds. Further work is needed to adequately characterize the decrease in emission rates of the various compounds over time,

Conclusions

It is clear from this research that extreme care must be taken in the preparation and analysis of emissions from composite wood products. The physical and chemical characteristics of the compounds found in wood emissions have not been studied sufficiently to assure that standard methods for air sampling and analysis will be adequate for these compounds.

Initial evaluations of emissions from particleboard showed terpenes and aldehydes as the main constituents. Because the emission rates of these compounds change greatly with time, caution must be taken in the design of experiments to assure that all samples are evaluated within the same timeframe. Additional research will be needed to determine the source of some emissions from particleboard, including aldehydes, benzene, and toluene. Future work will be aimed at evaluating emissions from particleboard samples obtained from manufacturers representing a wide cross-section of the industry

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