TECHNOLOGY SUMMARIES

In an effort to increase benefits to all CELL division members. including those who are not able to attend the national meeting we will feature Technology Summaries in the division newsletters. These summaries are written by experts in their respective fields and are intended to be a brief overview of the state-of-the-art in a specific topical area. If you have specific technical areas that you would like to see reviewed or if you are willing to write a brief technology summary please contact Tor P. Schultz, Forest Products Lab, Mississippi State University, Mississippi State, MS 39762-9820, Phone (601) 325-3136. E-mail: schultz@fpl.msstate.edu.

Two reviewers are given; both are in the area of air emissions and possible environmental problems:

VOLATILE ORGANIC CHEMICAL EMISSIONS FROM COMPOSITE WOOD PRODUCTS: A REVIEW

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INTRODUCTION

Over the past several decades, air quality in homes and office buildings has become a matter of increasing concern. Most people spend 80 to 90 percent of their time indoors, where chemical concentrations are usually significantly higher than outdoors. This problem was exacerbated as a result of the energy crisis in the 1970s, when homeowners and builders worked to increase the energy efficiency of their buildings by decreasing air exchange rates. Decreased exchange rates permit volatile organic chemicals (VOCs) emitted by building materials, furnishings, and occupant activities to accumulate to detectable and possibly harmful concentrations. Adverse health effects associated with increased VOC concentrations include eye and respiratory irritation (including asthma), irritability, inability to concentrate, and sleepiness. Trätek, the Swedish Institute of Wood Technology Research, estimates that 7 to 10 percent of the Swedish population has suffered ill health as a direct result of poor indoor air quality, caused in part by VOCs emitted by building materials and furnishings.

A result of increased emphasis on indoor air quality is the need for accurate information regarding the amounts and types of VOCs that are emitted from building materials, furnishings, cleaning products, and other materials found or used in the indoor environment. This information is needed not only by building occupants, but also by product manufacturers, building designers and contractors, and regulatory and public health agencies. Product manufacturers are increasingly advertising “low VOC” materials or materials suitable for use by people with chemical sensitivities. Outperforming a competing product on indoor air tests may impart a significant competitive advantage. Building designers and contractors are now being asked to certify that new buildings will meet standard indoor air quality requirements. They need emissions information to make decisions on which materials will best meet those requirements while fulfilling structural and aesthetic needs.

The Washington State East Campus Plus project provides an example of how these requirements affect planning. During the design and construction of four state office buildings, indoor air quality specifications were established that limited VOC emissions from building materials and furnishings. To be sure of meeting the emissions specifications, many of the building and furnishing materials had to be tested for VOC emissions prior to installation. For example, office furniture systems were required to emit no more than 0.05 ppm formaldehyde and 0.50 ppm total VOCs to be considered for installation.

In the United States no federal regulations govern VOC concentration in indoor air. However, regulatory agencies such as the Environmental Protection Agency (EPA) and the Occupational Safety and Health Administration have shown interest in ensuring that people are not adversely affected by the indoor air in their homes and offices. Development of indoor air VOC standards by these agencies is complicated by several factors: correlations between product test methods and indoor concentrations are not straightforward; many VOCs are a result of occupant activities, including smoking, use of cleaning products or perfumes, and cooking; and the detection of specific VOCs at low concentrations does not indicate whether they will have long-term negative health effects.

Composite wood products such as particleboard, plywood, and medium density fiberboard (MDF) are widely used in indoor products such as subflooring, door cores, cabinets, paneling, and furniture. In 1994, combined shipments of particleboard and MDF were almost 5.4×10^8 square meters (19 mm basis).[2] With the broad use of wood products in modern homes and offices, there are concerns that emissions from these products could have a significant impact on indoor air quality.

WOOD PRODUCTS AND FORMALDEHYDE

Most composite wood products are fairly simple combinations of wood and water-based adhesives, which are composed of either urea-formaldehyde (UF) or phenol-formaldehyde (PF) resin, inorganic components that act as catalysts, and other minor components such as wax. Plywood products may also contain fillers and extenders such as hydrolyzed corn cobs, wheat flour, or nut shell flour. A small number of products are bonded with polymeric methylene diisocyanate, but these products are for specialized purposes. Emissions of VOCs potentially can arise from each of the materials that compose the panels, but attention until recently has been on emissions of formaldehyde from UF resins used to bind the particleboard and MDF. During the 1970s and 1980s concern focused primarily on formaldehyde emissions from particleboard and hardwood plywood bonded with UF resins. These concerns led to regulations[3] and standards[4] in the United States that restricted the amount of formaldehyde that could be emitted from a product. The Department of Housing and Urban Development (HUD) regulations for materials used in mobile homes limit emissions to 0.3 ppm, and the American National Standards Institute (ANSI) standards for particleboard flooring products restrict formaldehyde gas emissions to 0.2 ppm as measured in the American Society for Testing and Materials (ASTM) large chamber test. A11 other materials must emit less than 0.3 ppm to meet the ANSI standard. Regulations in Europe are generally based on the amount of free formaldehyde in a product rather than the actual emmissions from the product, because it is presumed that the free formaldehyde would be emitted later. The German standard is currently the most stringent and sets the allowable level of formaldehyde at 6.5 mg/100g of dry board for partlcleboard and 7.0mg/100g of dry board for MDF, with the goal of achieving no more than 0.1 ppm formaldehyde in a steady state climate chamber test.

The principal method used to decrease formaldehyde emissions from particleboard is a change in resin formulation. The UF resin formulations in 1980 generally had formaldehyde-to-urea ratios (F/U) of 1.4 to 1.6. Today the ratios range from 1.05 to 1.2, which is generally achieved by separate additions of urea during the resin cook. A decrease in F/U ratio in the resin from 1.5 to 1.1 yields approximately a 10-fold decrease in free formaldehyde in the panel.[6] Between 1980 and 1985, U.S. industry saw an average 80-percent drop in initial formaldehyde emission rates from particleboard.[7] However, further decreases in F/U ratio will not likely be attained without unduly sacrificing mechanical performance of the bonded panel product. To further decrease emissions, other changes in resin formulation and application have been developed. In the United States, the principal methods of decreasing emissions include the use of a formaldehyde scavenger, such as urea solution, or the use of a high F/U resin mixed with a low F/U resin shortly before addition to the particleboard furnish. The use of melamine-urea-formaldehyde (MUF) resins to decrease formaldehyde emissions has largely been limited to European manufacturers. Although the addition of melamine increases the cost of producing panels, U.S. manufacturers are beginning to consider the use of MUF resins in order to meet the more stringent European formaldehyde regulations.

Use of other resin systems that do not emit as much or any formaldehyde, such as phenol-formaldehyde (PF) or polymeric methylene diisocyanate (pMDI), is limited for several reasons. Both PF and pMDI resins are considerably more expensive than UF resin; PF is dark colored; phenol supplies are not great enough to match the demand if UF resins were replaced by PF; pMDI has a tendency to adhere to press platens during manufacture; and there are concerns about worker health when using an isocyanate.

A pilot study was recently conducted by the EPA, with funding from the National Particleboard Association, to evaluate the contribution of UF-bonded building products to fomaldehyde concentrations in a newly constructed, single-family, two-story, unoccupied house that contained UF-bonded building materials with known emissions characteristics.[8] The reachers found levels within the house were between 0.02 and 0.06 ppm, well below the World Health Organization (WHO) recommendation of 0.1 ppm. These levels were much lower than the researchers expectations, which were based on commonly used EPA indoor air quality models. One possible reason for the lower than predicted indoor air concentrations in the house is the adsorption of formaldehyde by other materials in the room, most notably the painted gypsum wallboard. Whether EPA will conduct further research on the emissions of formaldehyde in a test home under this program is still unclear.

OTHER CHEMICAL EMISSIONS FROM WOOD PRODUCTS

Recently, interest has turned to other VOCs that may be emitted from wood products. For the wood industry, the "wake up call" came in 1992 when Radian Corporation, under an EPA contract, developed and circulated a draft Wood Products chapter to an *Indoor Air Pollutant Source Catalog.* This draft contained a significant amount of incorrect and misleading information about chemical emissions from wood products. including the assertion that "of the wood products, the natural wood products probably have the lowest emission potential." The authors of the chapter acknowledged that no studies were identified that measured emissions from natural wood, so this assertion was not based upon research data. Information that particularly concerned the wood industry included the listing of benzene, methylene chloride, toluene, and xylenes as either constituents of or emissions from particleboard. These chemicals are not components of either PF or UF adhesives and have not been shown to be constituents of wood itself. The studies from which these data were taken[9,10] were not specifically designed to evaluate chemical emissions from wood. They studied only one or two pieces of particleboard -- not a wide range of products. Thus, it is impossible to say that these data are representative of the entire industry.

The *Indoor Air Pollutant Source Catalog* episode led the wood industry and other wood researchers to the realization that accurate, up-to-date information about wood product emissions was needed. Without such information, wood products could potentially lose market share to other building and furnishing materials whose chemical emissions have already been well documented or are presumed to be very low, as in the case of steel.

Whereas the concerns about formaldehyde focused almost exclusively on the contributions from the adhesive resins, non-formaldehyde VOC emission may arise from any component of the wood composite. A wide variety of VOCs have been found to be emitted from composite wood products, and many of these VOCs are natural components of the wood. Following are brief descriptions of some recent and ongoing studies on emissions from wood products. It should be noted that the types and quantities of VOCs may be significantly impacted by the test method; test conditions, such as ventilation rate, temperature, air velocity, and relative humidity; wood species; adhesive type; and sample handling prior to testing. The wide varability in the data shows how these factors may affect the resulting data and contributes to the still contentious nature of the debate concerning VOC emssions from wood products.

RECENT RESEARCH ON VOCS FROM WOOD PRODUCTS

The first published study [11] that included a variety of wood products, including lumber, was completed by researchers in Sweden. Hardboard, plywood, MDF, lumber, particleboard, sawdust, and coated particleboard were included in this study. The researchers quantified total VOCs, the higher aldehydes, terpenes, and formaldehyde. The sample with the highest total VOC emissions was freshly planed pine lumber, followed by 2-week-old particleboard, then sawdust. For lumber, total VOC emissions were 920 µg/m^3, with 81 percent of the VOC emissions attributed to terpenes, which are naturally occuring components of the wood; only 1 percent of the emissions were higher aldehydes, mainly hexanal. However, for the particleboard and sawdust, the total VOCs were 430 and 190 µg/m^3, respectively, terpenes contributed 22 and 20 percent, and aldehydes made up 32 and 27 percent of the emissions. With the exception of formaldehyde, individual aldehydes were not identified or quantified. The fact that this change in distribution occurred both in the particleboard, containing UF resin, and the sawdust indicates that the wood itself is responsible for the emission of the aldehydes. As these high concentrations of aldehydes have not been shown to be present in raw wood, it is proposed that their occurrence in particleboard and sawdust is the result of thermal degradation of the wood components during drying and pressing.

More recently, the North American particleboard trade associations, the National Particleboard Association (NPA) in the United States and the Canadian Particleboard Association (CPA) in Canada, have made significant commitments of money and time to ensure accurate and complete research on their members' products. To that end, the NPA provided funding to GEOMET Technologies, Georgia Tech Research Institute (GTRI), and the USDA-FS Forest Products Laboratory (FPL) for several studies on VOC emissions from unfinished and finished particleboard and MDF samples produced in the United States. The CPA has cooperated with and provided funding to scientists at Forintek to investigate emissions from particleboard, MDF, and coated wood products produced by Canadian manufacturers.

Moat of the NPA- and CPA-funded studies used small environmental chambers as described in ASTM D5116-90[12] to enclose the samples during testing. Many other parameters such as chamber loading, air flow, and sample handling were similar to allow for comparison of results among studies. A synopsis of the types of emissions found in studies conducted at GEOMET[13] and Forintek[14] is presented in Table 1.

In the GEOMET study, concentrations of total VOCs ranged from 196 to 2599 µg/m^3 for uncoated samples and from 87 to 2520 µg/m^3 for coated samples. The major contributors to the VOC concentrations were acetone, hexanal, and fomaldehyde. On average, the concentrations of VOCs from the coated samples were about 40-percent lower than emissions from the uncoated samples, indicating that coating the samples with high-pressure laminates, melamine-saturated paper, or low-basis-weight paper may provide a means of decreasing VOC emission rates. Samples in this study containing a vinyl overlay were inconsistent, so the VOC mitigating effect of this type of coating cannot be assessed. A significant concern with the data from this study is that among the uncoated samples. α– and β –pinene were identified in the emissions from hardwood samples but not in either the Southern Pine or the western fir. None of the coated particleboard samples exhibited pinenes although all of these samples used Southern Pine as a substrate.

The Forintek study of CPA samples found that total VOC emissions from unfinished particleboard and MDF ranged from 0.23 to 23.45 µg/m^3, while emissions from coated samples ranged from 0 to 2.56 µg/m^3. Surface coatings in this study included low-pressure melamine and vinyl overlays. Emissions from the coated samples averaged less than 15 percent of the emissions from the uncoated samples. It is striking how much lower the concentrations of VOCs in this study were than in the GEOMET study, although both were done using very similar experimental methods. There are several possible explanations for these differences: (1) it is not clear in the studies how old the samples were before they were put into the test chambers, so the difference in emission concentrations could be due to sample age; (2) the species were not identified for the samples in the Forintek study, and it is likely that different species will have significantly different VOC emissions; (3) the Forintek study reports the total VOC expressed as α– pinene, but since mass special response for different compounds can vary greatly,this method may lead to erroneous results; and (4) the Forintek study did not report either formaldehyde or acetone, both of which were present in significant amounts in the GEOMET study. These differences point out the importance of experimental planning and sample handling to obtain results that are reproducible and comparable to the work of others.

Another study that was funded by NPA is worth noting. In 1993, NPA submitted samples of uncoated particleboard and particleboard with oak veneer to GTRI for VOC evaluation. This study did not target specific compounds as the GEOMET and Forintek studies did but rather attempted to identify all compounds that were emitted. In 23 different measurements, including some duplicates, almost 100 different compounds were found. Compounds that were present in high concentrations included acetone, akdehydes (benzaldehyde, hexanal, nonanal, octanal, pentanal), halogenated hydrocarbons, hydrocarbons, and terpenes (pinenes, 3-carene, camphene, thujone, and others). Contamination was a concern in this study because every sample contained chlorofluorocarbons (CFCs); the most notable was trichlorofluoromethane, which was emitted from every sample at an average of 218_µg/m^3. Because blank samples of air from the chambers showed no traces of these hydrocarbons and samples were handled in the same manner as they had been in the GEOMET study, there is no explanation of the source of these chemicals in the wood samples. No studies in the published literature identify CFCs in natural wood, composite wood products, or the components used to manufacture wood products.

The EPA has funded research at Research Triangle Institute (RTI) to find methods of pollution prevention from composite wood products. In the first step, researchers evaluated emissions from several coated wood products. In this round, particleboard with oak veneer overlay and sealer and topcoat emitted the highest concentrations of VOCs. Further testing was conducted on individual components of the panel. The particleboard, before application of veneer, sealer, or topcoat, gave concentrations of nearly 1600 µg/m^3, with about 70 percent of the emissions being either ketones or aldehydes. The veneer itself emitted very little, and only moderate emissions came from the particleboard with veneer applied before the addition of sealer or topcoat. However, the addition of sealer brought emissions up to the level of the unfinished particleboard. Putting the topcoat over the sealer increased the emissions even further. In the sealed and coated samples, the increase in emissions was principally due to an increase in the presence of alcohols, including 1-pentanol, 2-methoxy-1-butanol, 1-butanol, and 2-(2-butoxyethoxy)ethanol. Emissions of aldehydes and ketones from the sealed and topcoated samples were about 65 percent of those found in the unfinished particleboard. The next step in the RTI study is to investigate emissions from panels made with non-traditional substrates and adhesives. Alternative panels that are scheduled to be tested include straw with a pMDI binder, recycled newspaper with no binder, and lumber and plywood residuals with either a phenol-formaldehyde or a pMDI binder.

Research conducted at Trätek, the Swedish Institute for Wood Technology, was aimed at identifying chemical emissions from the wood itself, before any adhesive or binder was added.[13] The researchers obtained samples of pine, spruce, oak, birch, and beech at the time the trees were felled and ensured careful handling of the green wood samples prior to tasting. Planks were cut from the tree samples and the VOCs were measured from the green wood. The wood was then dried in a climate chamber under conditions similar to those used in a commercial dry kiln. Measurements of VOCs were taken after the wood had been dried to 18-percent moisture content (MC) and after further drying to between 8- and 10-percent MC. The pine and spruce samples emitted terpenes almost exclusively, although at 18-percent MC the pine also showed significant emissions of hexanal. Emissions from the beech samples were dominated by aldehydes, including pentanal, hexanal, and heptanal, ethanol, and acetic acid, with almost no terpenes. Emissions of all compounds appeared to peak when the moisture content was near 18 percent, but were lower in both green wood and wood with MC less than 18 percent. The researchers noted that sorbent compounds used to collect emissions for analysis yield nonanal, decanal, and benzaldehyde upon decomposition. therefore, definitive data on the presence or absence of these compounds is not available. The data for oak and birch samples indicate that further research is needed to fully identify types and quantities of chemicals emitted.

ON-GOING STUDIES

Currently, the CPA and NPA have studies that are nearly complete at both Forintek and FPL. In the Forintek study 27 Samples of raw and coated particleboard were investigated. Samples were collected at mills at different times of the year to evaluate the effect of manufacturing conditions on ultimate VOC emmission rates. At FPL, small chamber tests were used to evaluate emissions from the unfinished products of 55 mills that produce particleboard and MDF in the United States. Emissions were sampled over a period of 4 days to estimate the rate of emission decay. The results From this research are being analyzed and will be published shortly.

Two studies of building and furnishing materials, including pressed wood pmducts, are just being started in Canada and are worth noting for completeness and for future reference. In the first, the Canadian Task Force on Material Emissions and the Saskatchewan Research Council are conducting round-robin testing of a variety of building materials utilizing numerous testing laboratories in North America The principal objective of this study is to determine the consistency of data from dynamic chamber testing when the testing occurs in different laboratories. The second study, being conducted at the National Research Council of Canada, hopes to develop standard small and large chamber test methods for building materials and furnishings; develop a database of material emission characteristics and develop models to predict concentrations of VOCs in rooms based on room conditions and the emissions characteristics of materials within the rooms. This work is being supported by a consortium of interested parties including the EPA, the Canadian Wood Council, USG Corporation, the U.S. National institute for Standards and Technology, the Canada Mortgage and Housing Corporation, and others.

CONCLUSIONS

The composite wood industry has been wrestling with the issue of chemical emissions from its products since formaldehyde became a concern in the 1970s. While concerns about formaldehyde emissions have resulted in significant changes in products to reduce the emissions of this chemical, new concerns about other chemicals from wood products have recently surfaced. Although these are no government regulations for non-formaldehyde VOCs, the public, building owners and designers, and regulatory agencies are showing increasing interest in ensuring that building materials, including wood products, do not adversely affect indoor air quality. Current and ongoing research has been aimed at determining the extent to which wood products may affect indoor air, determining ways in which emissions from wood products may be mitigated, and developing databases to allow for prediction of indoor air concentrations of VOCs. The coming years will surely see considerably more research in this important area.

Table 1: Percentage of samples containing the chemical compound in the GEOMET and Forintek studies.[:]

Compound	GEOMET Uncoated	GEOMET Coated	Forintek Uncoated	Forintek Coated
Formaldehyde	100	100	*	*
Acetaldehyde	75	100	--**	--
Acetone	88	100	--	--
Benzaldehyde	100	10	--	--
Benzene	--	--	--	--
Borneol	75	--	--	--
Camphene	12	--	40	10
3-Carene	*	*	33	10
p-Cymene	38	--	33	10
Ethyl acetate	*	*	--	--
Ethylbenzene	--	20	13	--
Heptanal	88	50	--	--
Heptane	ND	30	--	--
1-Heptanol	75	--	--	--
2-Heptanone	50	--	--	--
3-Heptanone	*	*	13	--
Hexanal	100	90	60	--
Limonene	25	--	47	10
Nonanal	88	50	7	--
Octanal	88	30	--	--
t-2-Octanol	88	20	--	--
Pentanal	88	70	--	--
Pentane	--	--	--	--
1-Pentanol	75	30	--	--
a-Pinene	25	--	100	90
b-Pinene	12	--	47	30
Toluene	--	--	60	40
Phenol	--	50	*	*
Xylenes	--	60	60	40

: There were 8 uncoated and 10 coated samples in the GEOMET study, and 15 uncoated and 10 coated in the Forintek study.

* Not one of the target compounds for this study.

** Not detected in this study.

REFERENCES

1 Andersson, B.-I. And Salö, S., 1995. "Timber-frame houses especially for allergic families". The Swedish Institute for Wood Technology Research, Stockholm.

2 National Particleboard Association, 1995. "1994 Annual Shipments and Production: U.S. Particleboard and Medium Density Fiberboard Industry", Gaithersburg, MD.

3 a) Department of Housing and Urban Development. 1985. Manufactured home construction and safety standard. U.S. code of Fed. Regs. 24, Part 3280.406, and Fed. Register 48:37136-38195 (1983). b) Department of Health, Minnesota. 1985. Formaldehyde product standard. Minnesota Statutes. Section 144.495.

4 a) American National Standards Institute. 1993. Particleboard. ANSI A208.1-1003. National Particleboard Association, Gaithersburg, MD. b) American National Standards Institute. 1994. Medium density fiberboard. ANSI A208.2 - 1994. National Particleboard Association. Gaithersburg, MD.

5 American Society for Testing and Materials, 1990. Standard test method for determining formaldehyde levels from wood products under defined test conditions using a large chamber. ASTM-E1333-90. ASTM, Philadelphia, PA.

6 Markessini, A.C. 1993. Formaldehyde emission a novel approach — Standards and limitations in Europe. In Proceedings of the 27th International Particleboard/Composite Materials Symposium, Washington State University, Pullman, WA. pp. 207-219.

7 Graves, G. 1993. Formaldehyde emission control via resin technology — North American practices. In Proceedings of the 27th International Particleboard/Composite Materials Symposium. Washington State University, Pullman, WA. pp. 221-232.

8 Koontz, M.D., H.E. Rector, D.R. Cade, C.R. Wilkes, and L.L. Niang. 1996. Residential indoor air formaldehyde testing program: pilot study. Final Report, IE-2814, prepared at GEOMET Technologies, Germantown, MD, under US EPA control No. 68-D3-0013.

9 Nelms, L.H., M.A. Mason, and B.A. Tichenor. 1986. The effects of ventilation rates and product loading on organic emission rates from particleboard. In Proceedings of IAQ '86, Managing Air for Health and Energy Conservation, Atlanta, GA.

10 Bayer, C.W. 1990. An investigation into the effect of "building bakeout" conditions on building materials and furnishings. In Proceedings of the 5th Determination Conference on Indoor Air Quality and Climate. 3:581-585.

11 Sundin, E.B., M. Risholm-Sundman, and K. Edenholm. 1992. Emission of formaldehyde and other volatile organic compounds (VOC) from sawdust and lumber, different wood-based panels and other building material: a comparative study. In Proceedings of the 26th International Particleboard/Composite Materials Symposium, Washington State University, Pullman, WA. pp. 151-171.

12 American Society for Testing and Materials, 1991, Standard Guide for Small-Scale Environmental Chamber Determination of Organic Emissions from Indoor Materials/Products. ASTM-E51160-90. ASTM, Philadelphia, PA.

13 Koontz, M.D. and M.L. Hoag. 1995. Volatile organic compound emissions from particleboard and medium density fiberboard. In: Measuring and Controlling Volatile Organic Compounds and Particulate Emissions from Wood Processing Operations and Wood-Base Products. Proceedings No. 7301, Forest Products Society, Madison, WI. pp. 76-87.

14 Barry, A.O. 1995. Measurement of VOCs emitted from particleboard and MDF panel products supplied by CPA mills. Final report of Project No. 388N871 prepared for the Canadian Particleboard Association.

15 Englund, F. and J. Kristensson. 1995. Emissions of volatiles from Nordic timber species. In: Indoor Air Quality in Practice, Proceedings of an International Symposium on Indoor Air Quality held in Oslo, Norway, June, 1995. G. Flatheim, D.R. Berg, K.I. Evardsen, eds. pp. 123-134.