

EFFECTIVENESS OF BARRIERS TO MINIMIZE VOC EMISSIONS INCLUDING FORMALDEHYDE

ALPHA BARRY
DIANE CORNEAU

The authors are, respectively, Research Scientist, and Technologist at Forintek Canada Corp., 319, rue Franquet, Ste-Foy, Quebec, G1P 4R4, Canada

ABSTRACT

Since the energy crisis in the early 1970s, there has been a decided trend towards tightly constructed buildings that conserve energy and reduce costs. The downside of these well-intended efforts has been a lowering of air exchange rates, such that many chemical contaminants are trapped indoors where people spend most of their lives. These contaminants may include volatile organic compounds (VOCs), such as formaldehyde, that have been suggested by some to be among the factors responsible for this air quality deterioration. Wood composite panels such as particleboard and medium density fiberboard (MDF) are often targeted for strict emission regulations or prohibited altogether despite the fact that industry has reduced formaldehyde emissions of raw panels by more than 80% over the past twenty years to minimize indoor air contaminants. Moreover, most consumer products made with composite panels are not used in a raw form, but instead have some type of surface finish over the substrate that generally acts as a barrier to off-gassing, thereby reducing emissions. In this 2003 research, ten commonly used finishes were evaluated for their effectiveness as emissions barriers for formaldehyde and total volatile organic compounds (TVOC). Three different MDF and four particleboard unfinished products from different manufacturers were analyzed and compared to their corresponding finished products. Formaldehyde and VOCs measurements were conducted according to ASTM D 6007-96 and ASTM D 5116-97, respectively. For the finishes and coatings, results indicated that the epoxy powder coatings used to finish the MDF sample performed the best, achieving

99+% emission reductions in formaldehyde and up to 94% reduction of TVOC emissions (Noted as (99+%/94%)). This compared to reductions of 89%/85% for the UV paint and 11%/27% for the acrylic paint on MDF, respectively. A multiple (3) topcoat wet process treatment showed a 28% reduction in formaldehyde emissions but an increase in TVOC emissions,. The respective formaldehyde/TVOC emission reductions for the laminates were 99%/88% for phenolic paper laminates; 99%/66% for Vinyl; 93%/85% for the 80-gram melamine paper and 73%/75% for the 60-gram foil on particleboard. This very limited data suggests that several of the treatments are very efficient formaldehyde and TVOC emission barriers when applied to particleboard and MDF, though epoxy powders are typically applied only to MDF. The next phase of this research will extend the data acquisition to confirm that these findings are statistically significant and will test the barrier effectiveness of a broader selection of commercial products.

INTRODUCTION

As regulatory and non-governmental organizations (NGOs) address indoor air quality issues, they tend to focus on volatile organic compounds (VOCs), including formaldehyde, as key factors relating to the discomfort reported by people working or living inside "air tight" buildings. This effect is known as the "Sick Building Syndrome." The World Health Organisation (WHO) has defined VOCs as organic compounds with boiling points between 50 and 260°C. Finished wood composite products are suspected of emitting some of these organic chemicals namely formaldehyde, alpha- and beta-pinene, carene, camphene, limonene, aldehydes, ketones and acetic acid. Although VOC and formaldehyde emissions from unfinished wood composite panels are very well documented, very little data exists on finished products that often are constructed with a surface treatment over the composite panel that inhibits off-gassing from the substrate. Hence, the off-gassing potential of an unfinished substrate may have little to no affect on indoor air quality. The first VOCs emission results from particleboard were reported during the nineteen

eighties (Nelms et al (1986), Tichenor and Mason (1988)). Since that period, several laboratories have investigated indoor sources of these volatile organic chemicals (Tichenor (1989), Tichenor and Mason (1988), Sanchez et al (1987), Colombo et al (1990); Sundin et al (1992)), Barry et al (1999, 2000), and Beaumann et al (1999, 2000)). The most frequently used equipment for carrying out such investigations is a small environmentally controlled chamber.

Primary manufacturers of particleboard and MDF, as well as secondary manufacturers, are concerned with their products' potential impact on indoor air quality. The importance of finishes and laminates as barriers for formaldehyde emissions is widely recognized. However, most regulations focus on emissions from raw panels disregarding finished product emissions. Different types of surface treatments that are applied to panel products can act as barriers to VOCs. There is, however, a lack of empirical data on the effectiveness of these treatments as emission barriers.

The trial phase of this project and subsequent work will address the need for empirical data on the emission barrier effectiveness of today's commonly applied surface treatments. The information will help particleboard, medium density fibreboard (MDF) and hardboard manufacturers, as well as secondary manufacturers, understand the impacts of various coatings and laminates on VOC off-gassing from finished products. In this report different treatment methods have been evaluated for their effectiveness as emission barriers. These include paint, UV topcoat, acrylic topcoat, vinyl resin system (ethyl-vinyl acetate), phenolic saturated film, melamine saturated paper, multiple (3) topcoat wet process, foil resin system (polyvinyl acetate) and powder coating.

MATERIALS AND METHODS

Materials sampling, packaging, transportation and conditioning

The test materials, three samples of 30 cm x 30 cm, were cut from a freshly finished lot of panels near the center of the stack along with the matching raw panel. The test materials were sampled by a CPA field representative and the packaging and shipping were accomplished by the primary or secondary manufacturer within twenty-four hours after the surface treatment was applied. As most VOC emissions decrease over time, sampling freshly finished material would intentionally reflect the highest potential emission levels, or the worst case scenario. CPA field representatives were given training to assure an accurate chain of custody of the samples was documented as well as protection against contamination by such things as colognes or cutting tool lubricants. Latex gloves were worn during the whole sampling and packaging processes in order to avoid any potential contamination of the samples. Before cutting the samples, a towel was used to clean the saw blade and samples were wrapped with aluminium foil and put in the first polythene bag with no writing on the sample and on the bag. This bag containing the sample was then inserted in a second polythene bag wrapped and identified with a permanent marker. The wrapped sample was then inserted in an envelope with data sheet and shipped to CPA. Two of the triplicate specimens for each sample were then sent to Forintek for testing. One specimen was retained at the CPA office as an additional back-up.

Formaldehyde and VOC test samples of 10.5 cm x 10.5 cm were cut in the laboratory in the middle of the 900 cm² specimen received from CPA. Formaldehyde samples were edge-sealed with aluminium tape and conditioned at 23°C ± 0.5°C and 50% ± 5% relative humidity for 10 days before analysis. VOC samples of the same sizes were conditioned for ten days at 23°C±0.5°C and 50% ± 5%. One day prior to analysis, VOC samples were edge-sealed using aluminium tape.

Methods

A constant and adjustable airflow, conditioned for the relative humidity, was fed through small environmental chambers. The VOC sampling procedures excluding formaldehyde analytical

procedures and equipment, were similar to those described in the ASTM guide D 5116-97. The material used in the construction of the chambers was stainless steel. The chambers were equipped with suitable accessories such as inlet and outlet ports for airflow and an inlet port for temperature/humidity measurements. The air sampling was accomplished from the airflow outlet port. The small chambers were placed inside a temperature room. Adding de-ionized water to the air stream for each line controlled the humidity of the air flowing through the chambers. For collection of emissions, sorbent cartridge tubes constructed of Pyrex glass (11.5cmx6mm OD with 4mm ID) were used. The tubes were packed with three layers: Carbotrap C (300mg), Carbotrap B (200mg) and Carbosieve S-III (30mg). Prior to use, thermal tubes were conditioned at 370°C for 45 min. During the tube conditioning an ultra-high-purity helium flow was maintained through the tubes at 45 ml/min.

As in most small chambers designed for emission measurements from construction materials, large sample volumes were required due to the low concentration of emitted chemicals. The collection of VOCs on an appropriate adsorbent medium is required to avoid overloading of the analytical equipment. In order to maintain integrity of the airflow in the small chambers (one air exchange per hour for TVOC and 0.5 for formaldehyde), the sampling flow rate was set at 100 ml/min for a sampling period of 100 minutes for VOC sampling. Formaldehyde sampling rate was set at 250 cc per minute, the analysis was accomplished according to ASTM D 6007-96 using the same small chamber used to collect the VOC emission from the unfinished panel product. All samples for a given set, as illustrated in Tables 1 and 2, were tested with the same chamber in order to minimize the chamber impact on emission results.

QUANTIFICATION OF FORMALDEHYDE

Formaldehyde emissions were quantified according to the modified National Institute of Occupational Safety and Health (NIOSH) Test Method 3500. The method can be summarized as

follows: 4 mL of the scrubber's content and 0.1 mL of 1.0 % chromotropic acid are poured in a 50-mL Pyrex® test tube with a screw top cap. Six mL of concentrated sulphuric acid (96%) are slowly added and agitated for 2 minutes, then heated for 30 minutes at 100°C and cooled and tested in triplicate. Solution absorbencies were read through a UV-visible spectrophotometer set at 580 nM. Distilled water was run as a blank, and with a formaldehyde solution calibration curve, each absorbency reading was converted into µg/mL of formaldehyde. When the condensate samples were too concentrated to yield absorbencies in the linear range of the calibration curve, aliquots of these samples were diluted with distilled water to a level meeting the linear range of the calibration curve. The concentration obtained from this dilution was back-calculated to the original concentration and presented as micrograms of formaldehyde per litre, which is then converted in parts per million (ppm) and in emission factors as (mg/m².h).

QUANTIFICATION OF THE TVOC's

VOC measurements from panel samples were conducted in accordance to the ASTM D 5116-97 guide and described in great detail in a previous paper (Barry et al (1999)). Without going into detail in the description of the method, one can summarize some key points: the small chamber, maintained at 23±0.5°C and 50±5% relative humidity, has a volume of 50 L and its interior surfaces are electro polished to minimize the sink effect; the loading ratio is fixed at 0.41 m²/m³ with one air exchange per hour (1±0.05). A Thermal Desorber/Gas Chromatograph/Mass Spectrometer (TDU/GC/MS) system was utilized to desorb and quantify the total volatile organic compounds (TVOC). A "cryo-trap" device was connected to the GC column in order to "cryofocus" the thermally desorbed chemicals prior to their injection into the GC. The GC oven was programmed for 10 min at 70°C, followed by ramping up the heat to 200°C at 8°C/min, and held for 10 minutes. The mass scan ranged from 29 to 550 atomic mass units (amu). Quantitative evaluation was achieved by comparing the chromatogram peak area of each compound to the corresponding peak area of a standard.

RESULTS AND DISCUSSIONS

EFFECTIVENESS OF BARRIERS TO REDUCE FORMALDEHYDE AND TVOC EMISSIONS

Tables 1 and 2 and Figure 1 summarize formaldehyde and TVOC emission results, respectively.

A total of seventeen samples were tested for their emissions. Emissions are expressed both in parts per million (ppm) and in mg of formaldehyde, or TVOC per square meter of sample per hour (mg/m².hr). Seven matched sample sets are shown in these tables where each set represents one type of unfinished panel product and its corresponding surface treatment. The last column in both tables indicates the reduction efficiency based on the limited data collected for each finishing type.

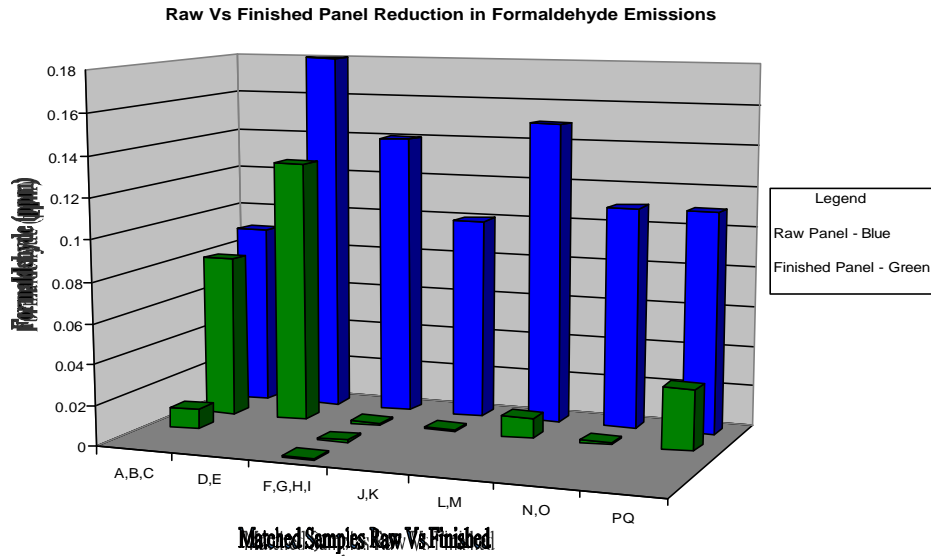
Table 1. Formaldehyde emission results

CPA ID Set	Matched Sample Sets	ASTM D-6007 (ppm) / mg/m ² *hr)	ASTM D-6007 % Reduction
1st Set			
A	7.3 mm MDF unfinished	0.09 / 0.13	
B	painted UV Topcoat	0.01 / 0.02	89
C	Painted Acrylic topcoat	0.08 / 0.12	11
2nd Set			
D	4.76 mm MDF	0.18 / 0.29	
E	multiple (3) topcoat wet process	0.13 / 0.20	28
3rd Set			
F	3/4 inch MDF	0.14 / 0.21	
G	A: epoxy powder coating 3-5 mil	n.d.	> 99
H	B: epoxy powder coating 3-5 mil	n.d.	> 99
I	C: epoxy powder coating 3-6 mil	n.d.	> 99
4th Set			
J	3/4 inch particleboard	0.10 / 0.15	
K	MDO (phenolic 0.002 inch)	n.d.	> 99
5th Set			
L	3/4 inch particleboard	0.15 / 0.25	
M	melamine paper 80 grams	0.01 / 0.02	93
6th Set			
N	1/2 inch particleboard	0.11 / 0.17	
O	Vinyl (3.400 mil)	n.d.	> 99
7th Set			
P	5/8 inch particleboard	0.11 / 0.17	
Q	Foil - 60 gram	0.03 / 0.04	73

Table 2. TVOC emission results

CPA ID Set	Matched Sample Sets	ASTM D-5116 (ug/m ² *hr)	ASTM D-5116 Percent Reduction
1st Set			
A	7.3 mm MDF unfinished	257.3	
B	painted UV Topcoat	39.4	85
C	painted Acrylic topcoat	326.8	{+27}
2nd Set			
D	4.76 mm MDF	53.4	
E	multiple (3) topcoat wet process	84.1	{+57}
3rd Set			
F	3/4 inch MDF	241.6	
G	A: epoxy powder coating 3-5 mil	14.7	94
H	B: epoxy powder coating 3-5 mil	24.9	90
I	C: epoxy powder coating 3-6 mil	17.2	93
4th Set			
J	3/4 inch particleboard	151.6	
K	MDO (phenolic 0.002 inch)	18.4	88
5th Set			
L	3/4 inch particleboard	223.8	
M	melamine paper 80 grams	33.8	85
6th Set			
N	1/2 inch particleboard	147.8	
O	Vinyl (3.400 mil)	50.6	66
7th Set			
P	5/8 inch particleboard	181.7	
Q	Foil - 60 gram	43.7	76

Figure 1.



The first set, which consisted of a 7.3 mm MDF panel, showed a relatively high formaldehyde emission reduction when finished with a UV paint topcoat 89% compared to a 11% reduction when the raw panel is finished with acrylic paint topcoat. Based on these very limited tests, the UV paint appeared to be more efficient as a finishing barrier for formaldehyde emissions. The UV paint also showed much stronger barrier efficiency for VOC emission with its 85 % emissions reduction compared to an increase by 27% for the acrylic paint.

The second set consisted of a 4.76 mm unfinished and multiple (3) topcoat wet process finished MDF samples. The very limited formaldehyde emission reduction observed suggested that this finishing type is not an efficient formaldehyde barrier and the high increase in VOC emission, up to +57%, indicated that it may contain a high amount of solvents. The lack of information on the nature of wet coat chemicals used in this process limits us for further comments. It suggests however the need for more sampling, as is the case for all tested sets of finishes.

The third set is a ¾ inch MDF raw board panel finished with three different epoxy powder coatings (A, B and C). All three finishes showed similar formaldehyde emission reduction

efficiency of 99% and above. These three powder coating materials also showed comparable VOC reduction efficiencies with 94%, 90% and 93%, respectively. This very high formaldehyde and VOC emission reduction, regardless of the limited number of tests, are in agreement with other literature reports (Antony B et al (1999), Bankowsky H.H et al and Jennifer H. (2002)).

The next two sets (4 and 5) consisted of a ¾ inch particleboard with different finishes for each set. The 2 mils of laminated phenolic paper used to finish the fourth set reduced formaldehyde emission by 99% and above while the 80 gram melamine saturated paper used to finish the fifth panel reduced the formaldehyde emissions from 0.15 ppm to 0.01 ppm, which correspond to an emission reduction efficiency of 93%. As a VOC barrier, it showed an emission reduction from 223.8 to 33.8 ug/m²*hr, which correspond to an efficiency of 85% compare to 88% for the phenolic. This compares to the 90% efficiency reported from two papers cited in the literature review (Dombey (1989) and Grot et al (1988)). In a previous study for the Canadian Particleboard Association (Barry et al (1997)), melamine laminated the front and back surfaces of particleboard were investigated for its effectiveness as a formaldehyde emission barrier. Sixteen different samples subdivided into 7 different sets were tested in that study. Results indicated a mean formaldehyde emission reduction of 87% varying from 69 up to 100%. This observation is in agreement with what a CPA technical bulletin reported on VOC emission barrier effects (“The Role of Laminates and Coating as VOC Emission Barriers in Composite Wood Panels”, Technical Bulletin).

The sixth set consisted of an unfinished and a finished ½ inch particleboard with a 3.4 mil vinyl. The formaldehyde emission reduction observed with this barrier indicated an efficiency of 99% and a 66% reduction of VOCs indicating that vinyl is more effective as a formaldehyde barrier than a VOC barrier. Groah (1984) and al reported a formaldehyde emission reduction of about 90% when particleboard is finished with a 2-mil vinyl laminate. The thickness of the laminate can go up to 10 mils suggesting a further reduction potential. However, authors did not evaluate the impact of this finishing on the VOC emission reduction.

The last set consisted of an unfinished and a finished 5/8 inch particleboard panel with a 60 gram foil. As one can see from Tables 1 and 2, this finishing showed a similar efficacy for both formaldehyde and VOCs with 73 % and 76% respectively. The level of effectiveness of this finishing is higher than the 50% range reported in the CPA technical bulletin suggesting again the need for more investigation in this field.

CONCLUSION

This trial study has evaluated ten different wood composite finishing materials used by primary and secondary particleboard and MDF manufacturers in order to determine the most efficient barrier of formaldehyde and/or VOCs. The limited data acquired in this work highlighted some interesting observations. It appeared that the powder coating is a more effective barrier for both formaldehyde and VOCs with more than 90% emission reduction when applied on MDF. A similar efficiency was observed with the phenolic and the vinyl applied on particleboard panels for formaldehyde reduction with, however, a lower VOC emission reduction with 88% and 66%, respectively. These results suggest an evaluation of powder coatings on particleboard, if practical, and vinyl laminated on MDF to more fully evaluate the nature of the substrate impact, if any, to the emission barrier effectiveness of these surface treatments. The multiple (3) topcoat wet process appeared to be the worse with 28% formaldehyde emission reduction and an increase, by 57%, of VOC emissions suggesting the coating may have a high solvents content. A limitation of this trial study was that the formaldehyde and VOC contribution of the surface coating or laminates were not tested by themselves without a substrate. The very limited number of finishes and the number of tests conducted should suggest taking these preliminary results with caution and that more sampling (confirmatory as well as additional coatings/laminates) is necessary to ensure completeness as well as confidence in the data. The next phase of this study will include an inter-laboratory comparison, an intra-laboratory repeatability evaluation, further evaluation of the finishes and the affect of sample aging as it relates to emissions.

LITERATURE CITED

- American National Standards Institute. 1999. American National Standard Particleboard, ANSI A208.1, sponsored by the Composite Panel Association.
- American National Standards Institute. 2000. American National Standard Medium Density Fiberboard (MDF) For Interior Applications, ANSI A208.2, sponsored by the Composite Panel Association.
- ASTM D 5116-97, Standard Guide for Small-Scale Environmental Chamber Determination of Organic Emissions From Indoor Materials/Products
- ASTM D 6007-96. Standard test Method for Determining Formaldehyde Concentration in Air from Wood Products Using a Small-Scale Chamber.
- Anthony, B., S.Larsen. 1999. A Clean Sweep-UV curing of small wood products. RadTech Report.
- Bankowsky, H.H., Beck, E., Reich, W., Enenkel, M., and Lokai, M.2000. Applications., Radcurenent.
- Barry, A.1995. Measurement of VOCs emitted from particleboard and MDF panel Products Supplied by CPA Mills: a report by Forintek Canada Corporation for the Canadian Particleboard Association.
- , D. Corneau, and R.Lovell 2000. Press Volatile Organic compounds Emissions as a Function of Wood Processing Parameters. Forest Products journal 50 (10): 35-42.
- and, D. Corneau. 1999. Volatile organic chemicals emissions from OSB as a function of processing parameters. Holzforschung 53: 441-446.
- Baumann, M., S. Batterman, and G-Z. Zhang. 1999. terpene emissions from particleboard and medium density fiberboard products. Forest products journal 49 (1): 49-56.
- , L. Lorenzo, S. Batterman, and G-Z. Zhang 2000. Aldehyde emission from particleboard and medium density fiberboard products. Forest products journal 50 (9): 75-82.
- Colombo A., M.De Bortoli, E.Pecchio, H.Schauenberg, H.Schlitt, and H.Vissers 1990. Chamber testing of organic emission from building and furnishing materials, The Sci. Of the Total Environ. 91, 237-249.
- Groah, W., G. Gramp, and M. Trant. 1984 Effect of a decorative vinyl laminate on formaldehyde emissions. Forest Products Journal 34 (40): 27-29
- Jennifer H.2001. UV-Powder coating process for MDF.RadTech Report, September/October 2001
- Nelms, L.H., M.A.Mason, and B.A.Tichenor 1986. The effect of ventilation rates and product loading on organic emission rates from particleboard. *In: Proceedings of IAQ 1986, Management Air for Health and Energy Conservation, Atlanta, GA.*

Sanchez D.C., M.Mason and C.Norris 1987. Methods and results of characterization of organic emission from indoor material, *Atmos. Environ.* 21, 337-345.

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: Proceeding of the 26th International Particleboard/Composite Materials Symposium*, Washington State University, Pullman, WA

Supelco: " Use of Thermal Desorption to Monitor C5-C30 Organic Compounds in Polymers," *Sample Handling Bulletin* 866, 1991.

Supelco: "Use Thermal Desorption to Monitor C5-C30 Organic Compounds in Polymers, *Sample Handling Bulletin* 866, 1991.

Supelco: "Carbotrap- An Excellent Adsorbent for Sampling for Many Airborne Contaminants, " *GC Bulletin* 846 C, 1986.

Supelco: *Sample Handling Bulletin* 850 A, 1991.

Tichenor, B, M.A.Mason 1988. Organic emissions from consumer products and building materials in the indoor environment. *JAPCA* 38, 264-268.

------. 1989. Measurement of organic compound emissions using small test chambers, *Env. Int.*, 15, 389-396.

National Institute of Occupational Safety and Health. 1984. NIOSH 3500 CHROMOTROPIC ACID METHOD. *In: NIOSH Manual for analytical methods.* Cincinnati, Ohio.