JAPCA 38: 1403–1411 (1988)   Reprinted from APCA JOURNAL, Vol. 38, No. 11, November 1988

#3435

Validation of Models for Predicting Formaldehyde Concentrations in Residences due to Pressed-Wood Products

Samuel Silberstein and Richard A. Grot
Center for Building Technology
National Institute of Standards and Technology
Gaithersburg, Maryland

Kunimichi Ishiguro
Taisei Corporation
Tokyo, Japan

Joseph L. Mulligan
U.S. Consumer Product Safety Commission
Washington, D.C.

This paper describes a laboratory project to assess the accuracy of emission and indoor air quality models to be used in predicting formaldehyde (HCHO) concentrations in residences due to pressed-wood products made with urea-formaldehyde bonding resins. The products tested were particleboard underlayment, hardwood-plywood paneling and medium-density fiberboard (mdf). The products were initially characterized in chambers by measuring their formaldehyde surface emission rates over a range of formaldehyde concentrations, air exchange rates and two combinations of temperature and relative humidity (23°C and 50% RH; 26°C and 60% RH). They were then installed in a two-room prototype house in three different combinations (underlayment flooring only; underlayment flooring and paneling; and underlayment flooring, paneling, and mdf). The equilibrium formaldehyde concentrations were monitored as a function of air exchange rate. Particleboard underlayment and mdf, but not paneling, behaved as the emission model predicted over a large concentration range, under both sets of temperature and relative humidity. Good agreement was also obtained between measured formaldehyde concentrations and those predicted by a mass-balance indoor air quality model.

Formaldehyde (HCHO) has been implicated as an indoor air pollutant causing both irritation and damage to health.[1,2] A principal formaldehyde source in residences is pressed-wood products made of urea-formaldehyde bonding resins, such as particleboard, plywood and medium-density fiberboard (mdf).

One would like to be able to predict a house's formaldehyde concentration from a characterization of the pressed-wood products inside it. Characterizing pressed-wood products is a complicated task. Formaldehyde surface emission rate depends on temperature, relative humidity (RH), ambient formaldehyde concentration, as well as the history of the product.[3–12] Fick's first law of diffusion, which states that the rate of diffusion of a gas between two points is proportional to the concentration gradient between them, implies that formaldehyde surface emission rate is linear in concentration, with negative slope. This behavior pattern of pressed-wood products was observed by many investigators.[3–12] Oak Ridge National Laboratory (ORNL) derived an empirical formaldehyde emission-rate model that generalized Fick's Law model, predicting surface emission rates of pressed-wood products for various combinations of ambient temperature, RH and formaldehyde concentration from knowledge of the surface emission rate under standard conditions of 23°C, 50% RH, and ambient formaldehyde concentration of 100 ppb.[5,12]

The Consumer Product Safety Commission (CPSC) requested that the National Bureau of Standards (NBS, now the Institute of Standards and Technology) validate the emission model based on Fick's diffusion law, the ORNL generalization of this model, and test a simple mass-balance indoor air quality model which could be used to predict formaldehyde concentrations in residences due to pressed-wood products. ORNL derived the parameters of the emission models using "small-size" chambers having a volume of 7 ft^3 (0.2 m^3) that required that the pressed-wood products, which are usually installed in buildings as intact 4 × 8-ft (1.2 × 2.4-m) boards, be cut into much smaller pieces. Tests by ORNL in an unoccupied research house, agreed with the predictions of the laboratory models fairly well.[13] In order to completely characterize full-size products, "medium-size" chambers were designed and constructed. Medium-size dynamic measuring chambers with a volume of 64 ft^3 (1.8 m^3), which is large enough to accommodate one intact board each, were installed in a very large temperature- and RH-controlled environmental chamber at NBS. A two-room prototype house was also built in the environmental chamber to validate the models' ability to predict formaldehyde concentrations in residences.

Experimental Procedures

Medium-Size Dynamic Measuring Chambers

The medium-size dynamic measuring chambers used for determining formaldehyde surface emission rates of individual pressed-wood products are shown schematically in Figure 1. The interior dimensions are 4 × 8 × 2 ft (1.2 × 2.4 × 0.6 m), for a volume of 64 ft^3 (1.8 m^3). All inner exposed surfaces

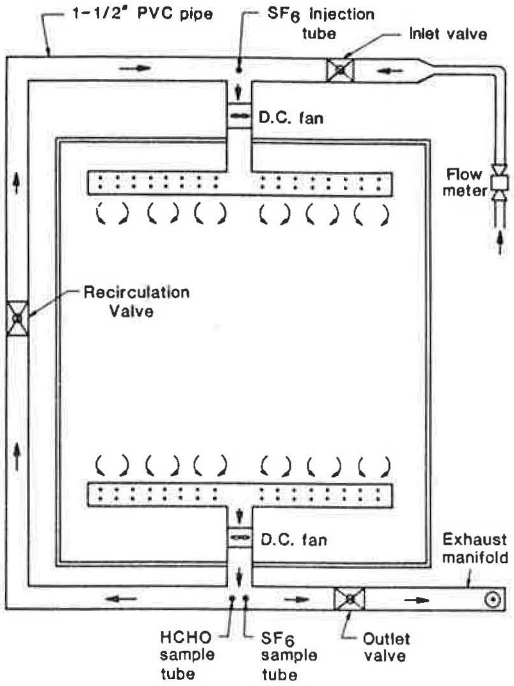

Figure 1. Schematic of medium-size chamber for measuring HCHO emission rates.

were lined with teflon sheets to minimize formaldehyde sorption. Two small DC fans with a rated capacity of 15 ft^3/min (7 L/s) were installed at both ends of the chambers to supply and exhaust the air. Three valves in the system controlled the amount of air brought in, exhausted, and recirculated. The fans were run at constant speed and the air exchange rate was controlled by the three valves in order to try to maintain a constant air velocity over the sample as the air exchange rate was varied. (The velocity was not measured.) The outlet valve was usually adjusted to slightly pressurize the chamber, thus assuring that air entered only through the inlet. Further details of the dynamic measuring chambers are given in Reference 10.

Air exchange rates were measured using a tracer-gas decay method. Sulfur hexafluoride (SF_6) tracer gas was injected into the inlet of the chamber and sampled at the outlet. The formaldehyde concentration was also sampled at the outlet. Mixing in the chamber was maintained by passive means. The inlet and outlet manifolds were designed to cause circulating turbulent flow in the chamber. Good air mixing within the chambers was demonstrated by replacing one side of a chamber with plexiglass to permit smoke visualization of the air-flow pattern. The smoke density quickly became uniform in the chamber and there appeared to be no dead spots.

Two-Room Prototype House

The two-room prototype house installed in the environmental chamber is shown schematically in Figure 2. The interior dimensions were 10 × 20 × 8 ft (3 × 6 × 2.4 m), for a volume of 1600 ft^3 (45 m^3). The two equal-sized rooms were connected by a doorway which was left open during testing. The floor, ceiling, and sidewalls were lined with a polyethylene vapor barrier, which was covered by gypsum board. The prototype house had two supply registers and two return registers, one near the ceiling and one near the floor of each room. Two duct-booster fans were used to supply and exhaust air. A recirculation loop was included in the air-handling system and the system was balanced by three dampers, one in the inlet, one in the outlet, and one in the recirculating loop. Thermistors and teflon air-sampling tubes were installed in the center of each room at heights of 2 ft (0.6 m), 4 ft (1.2 m), and 6 ft (1.8 m), and in the inlet and exhaust air. In general, formaldehyde was sampled by a computer-based instrumentation system at the inlet, outlet and one height in each room at a time. The air exchange rate was determined using the tracer decay method. Sulfur hexafluoride was injected into the inlet air and sampled at the outlet. Further details of the prototype house are given in Reference 10.

Instrumentation System

An automated measurement system was constructed by linking an airborne formaldehyde concentration monitor (a TGM-555 air monitor fitted with a formaldehyde analytical module), which measures formaldehyde concentration by a modified pararosaniline procedure,[2,10,14-16] to a computer-based NBS automated tracer-gas decay system used to measure air exchange rate.[17] One formaldehyde surface emission-rate measurement system was used for the prototype house and one for three or four medium-size dynamic measuring chambers. Details and protocols of the design, calibration, and operation of the automated system, and algorithms and equations used to calculate the air exchange rate, formaldehyde concentration, and formaldehyde surface emission rate are described in Reference 10.

Experimental Plan

The pressed-wood products used in the study were supplied by various manufacturers and trade associations as 4 × 8-ft (1.2 × 2.4-m) boards, area 32 ft^2 (3.0 m^2). The particleboard underlayment came from one manufacturing plant, the mdf from another. The hardwood-plywood overlays of the paneling came from a single plant, but each paneling board was fabricated from blanks from one of two different plants. The mdf was cut into four 2 × 4-ft (0.6 × 1.2-m) pieces at NBS, and made into "table tops" by covering all edges and one side of each with formica.

The pressed-wood products were conditioned at 23°C and 50% RH in a well-ventilated area for about one month. Their formaldehyde surface emission rates were then measured in the medium-size dynamic measuring chambers as a function of formaldehyde concentration, which was varied by adjusting the inlet and exhaust valves to vary the air exchange rate, as described above.

After their surface emission rates at standard conditions were determined, the pressed-wood products were installed in the prototype house and the formaldehyde concentrations were measured at four air exchange rates. Measurements were made for three different combinations of formaldehyde emitters: (1) particleboard underlayment, (2) underlayment and hardwood-plywood paneling, and (3) underlayment, paneling and mdf table tops. The paneling was installed in one room of the prototype house on two opposite walls and the mdf table tops in the other room. This was intended to simulate a living room-kitchen arrangement in a house. Two samples of paneling from manufacturer #1 were installed on one wall and one sample from manufacturer #2 was installed on the opposite wall. Six particleboard underlayment boards were used to cover the floor in both rooms (two of the boards had to be cut). The surface emission rates of the cut boards were determined both before and after cutting, prior to being installed in the prototype house. The air exchange rate was varied over a range encountered in normal houses (about 0.1 to 1 h^{-1}), and formaldehyde concentrations were compared with those predicted, using a mass-balance indoor air quality model. After the prototype-house studies, pressed-wood products were again measured in the medium-size dynamic measuring chambers.

The temperature and RH were then shifted to 26°C and 60% RH, respectively. The products were conditioned under these environmental conditions, and medium-size chamber tests were repeated.

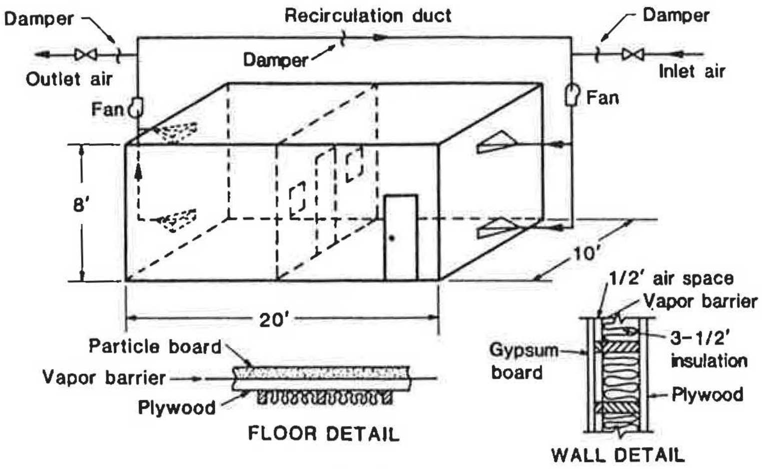

Figure 2. Schematic of two-room prototype house.

Characterization of Boards by Medium-Size Chamber Tests

This section describes how each board was measured in medium-size chambers. A sufficient number of measurement cycles was run at each air exchange rate to ensure that formaldehyde concentrations were stable. Once formaldehyde concentrations stabilized, they were averaged together. Air exchange rates were also averaged together after stabilization. It was found that SF_6 was rarely detected in the environmental chamber, and formaldehyde concentration rarely exceeded 10 ppb, so background concentrations of either gas could be ignored. Formaldehyde surface emission rates were then calculated according to the following equations:

$$SER = g \cdot C/(l \cdot AI) \qquad (1)$$

where: SER = HCHO surface emission rate, mg/m^2·h.
g = formaldehyde concentration conversion factor from ppb to mg/m^3 = 1.228×10^{-3} mg/m^3 · ppb at 25°C.
C = HCHO concentration, ppb.
AI = air exchange rate, h^{-1}.
V = volume of enclosure, m^3.
$AREA$ = area of board, m^2.
l = loading = $AREA/V$, m^2/m^3.

For each board, formaldehyde surface emission rate was found to depend linearly on concentration, in accordance with Fick's diffusion law:

$$SER = a_i' - b_i' \cdot C \text{ if } C < a_i/b_i \qquad (2)$$
$$= 0 \text{ otherwise}$$

where: SER = formaldehyde surface emission rate, mg/m^2 · h.
C = formaldehyde concentration, ppb.
a' (mg/m^2 · h) and b' (mg/m^2 · h · ppb) are material coefficients.

The parameters a_i' and b_i' were determined statistically for the measured data. These parameters were used to calculate SER_{100}, and a cutoff concentration above which no formaldehyde emission occurs. The cutoff concentration was determined from Equation 2 by setting $SER = 0$ mg/m^2 · h and solving for C. SER_{100} was calculated by setting $C = 100$ ppb and solving for SER.

The ORNL Surface Emission Models

ORNL developed models for predicting the surface emission rate of formaldehyde at any temperature, RH, and ambient formaldehyde concentration, from the results of a test to determine the surface emission rate at 23°C, 50% RH,

Table I. Characterization of particleboard underlayment from medium-size chamber HCHO emission rate data.[a]

	SER_{100} mg/m^2 · h	a' mg/m^2 · h	b' mg/ppb · m^2 · h	Cutoff conc ppb	Std error mg/m^2 · h	r^2
	Four uncut boards at 23°C and 50% RH					
Before and during house study	0.10	0.18	0.75×10^{-3}	240	0.042	0.47
After house study	0.13	0.21	0.81×10^{-3}	260	0.025	0.86
Combined	0.11	0.19	0.73×10^{-3}	260	0.037	0.63
	Four uncut boards at 26°C and 60% RH					
Before house study	—	0.43	1.17×10^{-3}	370	0.048	0.89
After house study	—	0.52	1.33×10^{-3}	390	0.047	0.91
Combined	—	0.44	1.50×10^{-3}	380	0.064	0.81
	Two cut boards at 23°C and 50% RH					
Prior to cutting	0.09	0.14	0.46×10^{-3}	300	0.016	0.55
Before house study	0.18	0.29	1.17×10^{-3}	250	0.037	0.90
After house study	0.13	0.21	0.79×10^{-3}	270	0.020	0.88
Combined after cutting	0.15	0.25	0.97×10^{-3}	250	0.031	0.84
	Two cut boards at 26°C and 60% RH					
Before house study	—	0.48	1.22×10^{-3}	390	0.021	0.98
After house study	—	0.45	1.08×10^{-3}	420	0.013	0.99
Combined	—	0.44	1.03×10^{-3}	430	0.049	0.89

[a] a' and b' are coefficients for the linear regression equation: $SER = a' - b' \cdot C$.

Table II. Characterization of hardwood-plywood paneling from medium-size chamber HCHO emission rate data.[a]

	SER_{100} mg/m² · h	a' mg/m² · h	b' mg/ppb · m² · h	Cutoff conc ppb	Std error mg/m² · h	r^2
			Two boards from manufacturer #1 at 23°C and 50% RH			
Before house study	0.033	0.048	0.15×10^{-3}	310	0.006	0.85
After house study	0.005	0.040	0.40×10^{-3}	110	0.018	0.48
Combined	0.026	0.039	0.13×10^{-3}	300	0.014	0.35
			Two boards from manufacturer #1 at 26°C and 60% RH			
Before house study	—	0.06	0.38×10^{-3}	160	0.015	0.58
After house study	—	0.06	0.35×10^{-3}	180	0.016	0.77
Combined	—	0.06	0.38×10^{-3}	160	0.015	0.59
			One board from manufacturer #2 at 23°C and 50% RH			
Before house study	0.05	0.06	0.05×10^{-3}	1,250	0.046	0.02
After house study	0.11	0.18	0.65×10^{-3}	270	0.035	0.74
Combined	0.10	0.14	0.42×10^{-3}	340	0.050	0.44
			One board from manufacturer #2 at 26°C and 60% RH			
Before house study	—	0.14	0.21×10^{-3}	670	0.012	0.83
After house study	—	0.17	0.25×10^{-3}	700	0.040	0.83
Combined	—	0.15	0.21×10^{-3}	710	0.019	0.78

[a] a' and b' are coefficients for the linear regression equation: $SER = a' - b' \cdot C$.

and an ambient concentration of 100 ppb. According to the models, for each class the ratio of SER to SER_{100} is independent of the individual product specimen, and determined from the equation:

$$SER/SER_{100} = a_i - b_i \cdot C \text{ if } C < a_i/b_i \qquad (3)$$
$$= 0 \text{ otherwise}$$

where: SER_{100} = formaldehyde surface emission rate at 23°C, 50% RH, and 100 ppb concentration.

ORNL empirically determined the coefficients a_i and b_i to be as follows:

$$b_i = [1 + B_i \cdot (T - 296.15)] \cdot [1 + E_i \cdot (RH - 50)]/(C_{B_{i,std}} - 100) \qquad (4)$$

$$a_i = b_i \cdot \exp[-c_i \cdot (T^{-1} - 296.15^{-1})] \cdot (RH/50)^{A_i} \cdot C_{B_{i,std}} \qquad (5)$$

where: A_i, B_i, c_i, E_i, and $C_{B_{i,std}}$ are given in Table IV for each type of pressed-wood product.[12]
T = absolute temperature, K.
RH = relative humidity, %.

For standard temperature and RH, $b_i = (C_{b_{i,std}} - 100)^{-1}$ and $a_i = b_i \cdot C_{B_{i,std}}$, so Equation 3 becomes:

$$SER/SER_{100} = (C_{B_{i,std}} - C)/(C_{B_{i,std}} - 100) \qquad (6)$$

Substituting appropriate values of $C_{B_{i,std}}$ from Table IV into Equation 6, one obtains the following equations under standard conditions, with concentrations in ppb:

$$SER/SER_{100} = 1.38 - 0.0038 \cdot C \text{ (particleboard)} \qquad (7)$$
$$SER/SER_{100} = 1.32 - 0.0032 \cdot C \text{ (plywood paneling)} \qquad (8)$$
$$SER/SER_{100} = 1.12 - 0.00125 \cdot C \text{ (mdf)} \qquad (9)$$

Since the paneling from manufacturer #1 never produced formaldehyde concentrations much above 100 ppb, Equation 8 could not be used for these specimens.

The equations for normalized surface emission rate, SER/SER_{100}, at 26°C and 60% RH derived from the ORNL model (Equations 4 and 5) are given by:

$$SER/SER_{100} = 2.54 - 0.0048 \cdot C \text{ (particleboard)} \qquad (10)$$
$$SER/SER_{100} = 2.78 - 0.0048 \cdot C \text{ (plywood paneling)} \qquad (11)$$
$$SER/SER_{100} = 2.39 - 0.0016 \cdot C \text{ (mdf)} \qquad (12)$$

The SER for each specimen of particleboard underlayment, hardwood-plywood paneling from manufacturer #2 and mdf table tops was normalized by division by the most recent value of SER_{100} determined for that specimen. The SER/SER_{100} values were plotted against formaldehyde concentration for all boards of a given type for each combination of temperature and RH.

Medium-Size Chamber Test Results

Results for groupings of boards are shown in Tables I–III for particleboard underlayment, hardwood-plywood paneling, and mdf table tops, respectively.

Table III. Characterization of medium-density fiberboard table tops from medium-size chamber formaldehyde emission rate data.[a]

	SER_{100} mg/m² · h	a' mg/m² · h	b' mg/ppb · m² · h	Cutoff conc ppb	Std error mg/m² · h	r^2
			Two table tops at 23°C and 50% RH			
Before and during house study	1.21	1.51	3.11×10^{-3}	490	0.76	0.13
After house study	1.39	1.63	2.45×10^{-3}	660	0.20	0.58
Combined	1.30	1.57	2.75×10^{-3}	570	0.55	0.17
			Two table tops at 26°C and 60% RH			
Before house study	—	2.72	1.09×10^{-3}	2,500	0.34	0.73
After house study	—	2.15	1.60×10^{-3}	1,340	0.28	0.86

[a] a' and b' are coefficients for the linear regression equation: $SER = a' - b' \cdot C$.

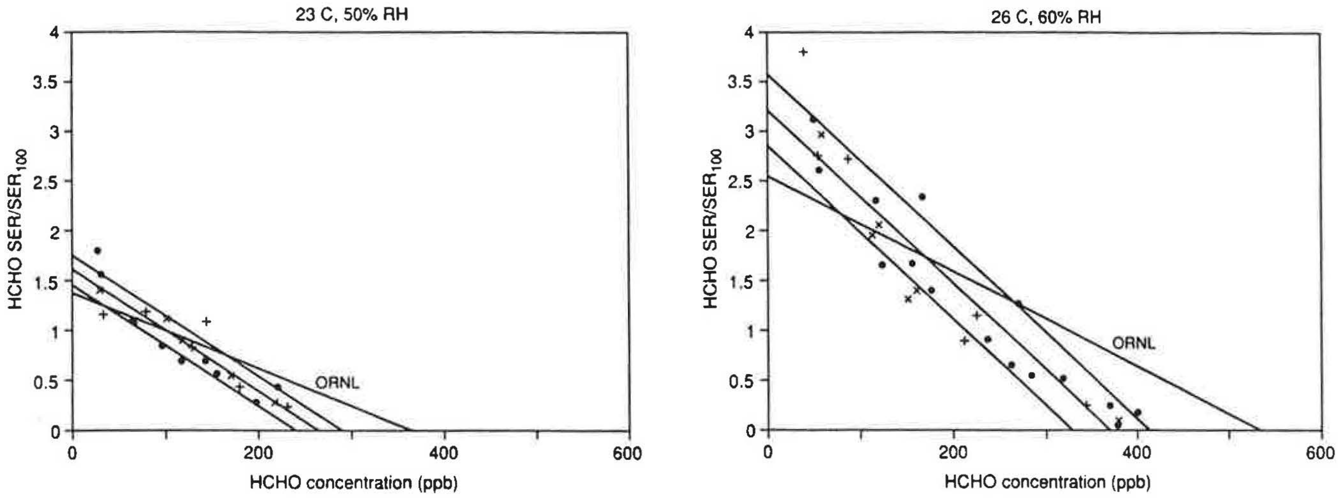

Figure 3. Comparison of normalized formaldehyde emission rates for uncut underlayment to those predicted by ORNL emission model. The upper graph shows the latest data at 23°C and 50% RH. The lower graph shows the earliest data at 26°C and 60% RH. The lines labeled ORNL are predicted by Equations 7 (upper graph) and 10 (lower graph). The middle of the three parallel lines is the best-fit linear regression line of formaldehyde concentration vs. normalized surface emission rate. The regression line is surrounded by lines representing 1 standard error unit. Each symbol represents a different board. (*SER* = formaldehyde surface emission rate; SER_{100} = surface emission rate at 23°C, 50% RH, and 100 ppb concentration.)

Some features common to all types of boards are as follows. Formaldehyde surface emission rates decreased as formaldehyde concentration rose for all specimens tested. There was more scatter in the earlier tests (those before and during prototype house) than in the later tests (those after prototype house) at 23°C and 50% RH, especially for hardwood-plywood paneling and mdf table tops. Other than the scatter, the earlier and later results were similar to each other for mdf and uncut particleboard at 23°C and 50% RH. During the latest tests performed at 23°C and 50% RH, the data were fit well by straight lines for each board, and there was little variation in the behavior of boards comprising each class of board (particleboard underlayment whether cut or uncut, paneling from each manufacturer, and mdf table tops). This continued to be true for each test series at 26°C and 60% RH. For all types of boards except paneling from both manufacturers, surface emission rates increased markedly when conditions were changed from 23°C and 50% RH to 26°C and 60% RH.

Underlayment. Table I shows that at 23°C and 50% RH, there was little change in SER_{100} and cutoff concentration, which were both close to the combined average of 0.11 mg/m^2 · h and 260 ppb, respectively, between the time uncut particleboard underlayment was placed into and removed from the prototype house. Emission rates of the particleboard tested at NBS were at the low end of the range of those of particleboard used in the United States.[18] They were also lower than for the products tested by ORNL.[12] SER_{100} was about 0.4–0.5 mg/m^2 · h for particleboard tested by ORNL.

While SER_{100} doubled immediately after two particleboard underlayment boards were cut, it then declined to approximately the same value as for uncut particleboard by the time of the post-prototype house tests at 23°C and 50% RH, that is within 4 months, showing that any effects of cutting are transitory. After that, cut and uncut underlayment continued to behave indistinguishably.

Paneling. Table II shows that paneling boards from manufacturer #1 were much weaker formaldehyde emitters than the board from manufacturer #2. Because the cutoff concentrations for paneling from manufacturer #1 were close to 100 ppb, SER_{100}, and therefore normalized concentrations, could either not be calculated at all or could not be calculated meaningfully. At 23°C and 50% RH, the cutoff concentration for paneling from manufacturer #2 was about 270 ppb and SER_{100} was about 0.11 mg/m^2 · h after being removed from the prototype house, or nearly the same

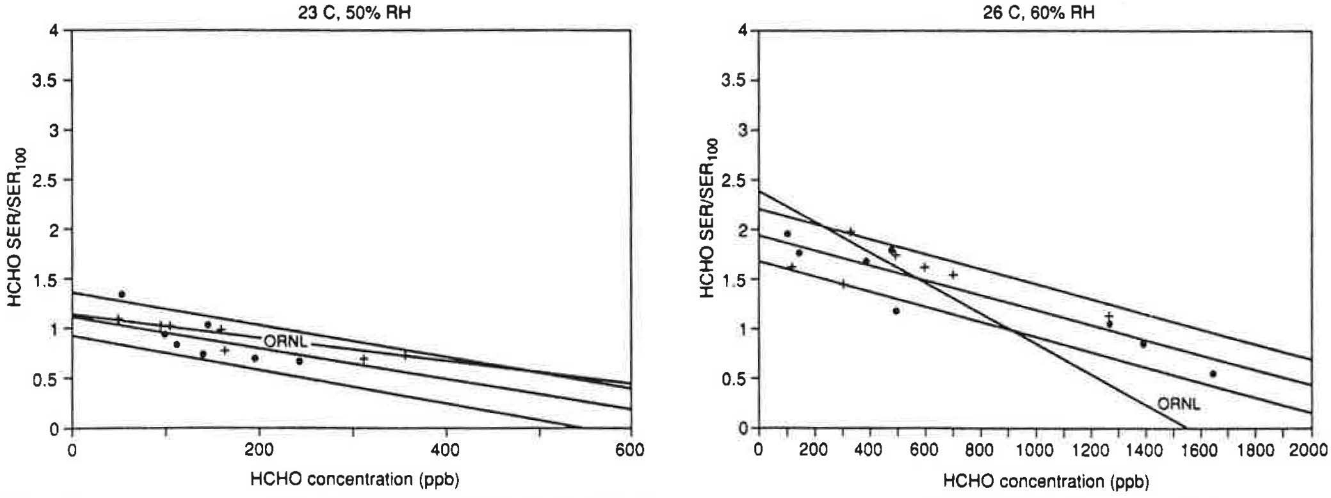

Figure 4. Comparison of normalized formaldehyde emission rates for Mdf table tops to those predicted by ORNL emission model. The upper graph shows the latest data at 23°C and 50% RH. The lower graph shows the earliest data at 26°C and 60% RH. The lines labeled ORNL are predicted by Equations 9 (first graph) and 12 (second graph). The middle of the three parallel lines is the best-fit linear regression line of formaldehyde concentration vs. normalized surface emission rate. The regression line is surrounded by lines representing 1 standard error unit. Each symbol represents a different board.

Table IV. Coefficients for the ORNL models.

Pressed-wood product	c K	A	$C_{b_{std}}$ ppb	B K^{-1}	E $\%^{-1}$
Particleboard underlayment	9,400	0.37	360	0.025	0.016
Hardwood-plywood paneling	6,500	0.66	410	0.053	0.029
Medium-density fiberboard	5,000	1.90	900	0.090	0.000

as for particleboard underlayment. As in the case of particleboard, the emission rates of the plywood tested at NBS were at the low end of the range of plywood used in the United States.[18] They were also at the low end of products tested by ORNL.[12]

Mdf. Table III shows that by the time the mdf table tops were removed from the prototype house at 23°C and 50% RH, SER_{100} was 1.4 $mg/m^2 \cdot h$ and the cutoff concentration was 660 ppb. These results confirm other reports in showing that mdf is a far stronger emitter than either particleboard underlayment or hardwood-plywood paneling.[4,12,19] The SER_{100} of mdf tested at NBS, was well within the range of mdf used in the United States[18]; ORNL tested mdf with both higher and lower values than NBS.[12]

In contrast to underlayment and paneling, and to their own behavior at 23°C and 50% RH, mdf emission rates declined during the five months between surface emission rate measurements. This can be seen from the fact that the best-fit regression line for the earlier data had an intercept of 2.72 $mg/m^2 \cdot h$ compared to 2.15 $mg/m^2 \cdot h$ for the line fitting the later data, which was about 2 standard error units apart. In addition, the difference between the two lines increases with increasing concentration because the magnitude of the slope of the line fitting the earlier data is smaller than that for line fitting the later data. To test whether the rapid decline in emission rates is in accordance with the ORNL model, one would have to determine SER_{100} for the post-prototype house experiment. This would be difficult, if not impossible, to obtain because it is not possible to quickly return to standard conditions, obtain SER_{100}, and then return to 26°C and 60% RH. As for obtaining SER_{100} after the experiment at 26°C and 60% RH, it is shown elsewhere[8] that after pressed-wood products were returned to 23°C and 50% RH and conditioned for about 2 months, their emission rates increased over their previous values at 23°C and 50% RH, so using this value of SER_{100} would not be comparable to using one obtained before raising the temperature and RH.

Table V. Results of tests of prototype-house containing underlayment.

Air exchange rate[a] h^{-1}	HCHO concentration[a] (ppb) Outlet	 Room 1	 Room 2	 Inlet
1.28	50	—	—	6
(0.1)	(2)			(2)
0.47	110	—	—	5
(0.01)	(10)			
0.14	140	150	150	1
(0.02)	(13)	(18)	(19)	(5)
0.78	60	70	70	2
(0.07)	(6)	(5)	(6)	(4)

[a] Quantities in parentheses are standard deviations.

Comparisons of Results to ORNL Model Predictions

Comparisons of best-fit regression lines to the lines predicted by the ORNL models are shown in Figures 3 and 4. The SER_{100} values shown in Tables I–III were not the ones used for normalization of the SER values. Instead, surface emission rates of each board for both late 23°C and 50% RH tests and early 26°C and 60% RH tests were normalized by SER_{100} determined specifically for that board during late 23°C and 50% RH tests. Because boards of a given class behaved similarly to each other in the latest tests at 23°C and 50% RH, these values of SER_{100} were very close to the values shown in Tables I–III. Similarly, the cutoff concen-

Table VI. Results of tests of prototype-house containing underlayment and paneling.

Air exchange rate[a] h^{-1}	HCHO concentration[a] (ppb) Outlet	 Room 1	 Room 2	 Inlet
0.86	70	70	80	2
(0.04)	(4)	(6)	(5)	(3)
0.59	80	80	90	3
(0.02)	(6)	(7)	(7)	(5)
0.26	110	120	120	0
(0.02)	(4)	(5)	(6)	(3)
0.75	70	70	80	1
(0.04)	(4)	(3)	(4)	(3)

[a] Quantities in parentheses are standard deviations.

Table VII. Results of tests of prototype-house containing underlayment, paneling, and mdf.

Air exchange rate[a]	HCHO concentration[a] (ppb)			
h^{-1}	Outlet	Room 1	Room 2	Inlet
0.80	120	130	140	0
(0.02)	(15)	(22)	(19)	(9)
0.58	120	120	120	2
(0.07)	(6)	(5)	(3)	(2)
0.27	200	220	210	0
(0.02)	(5)	(8)	(7)	(2)
0.75	120	130	130	1
(0.01)	(2)	(7)	(8)	(1)

[a] Quantities in parentheses are standard deviations.

trations shown in Tables I–III are similar to those shown in Figures 3 and 4, which were obtained using normalized *SER* values.

Figure 3 shows comparisons between the ORNL model (Equation 7) and the best-fit linear regression line of formaldehyde concentration vs. surface emission rate at standard temperature and RH for uncut particleboard underlayment. The line predicted by the ORNL model fits the data well, even though it was derived for a different collection of boards. It is within 1 standard error unit of the best-fit regression line between 10 and 190 ppb. It is within two standard error units over its entire range.

Figure 3 shows that the ORNL model continues to fit the data about as well at 26°C and 60% RH as at 23°C and 50% RH. At 26°C and 60% RH, the ORNL line is within one standard error unit of the best-fit line between about 100 and 310 ppb for uncut underlayment. It is within two standard error units between 50 and 410 ppb. However, the slope of the surface emission-rate line and the cutoff concentration are not accurately determined by the ORNL model.

Figure 4 shows that at 23°C and 50% RH, the ORNL line relating formaldehyde surface emission rate to concentration fit the medium-size chamber results well for mdf. The ORNL line was within one standard error unit over the concentration range 0–520 ppb; and within two standard error units over the range 0–980 ppb. The ORNL line was within one standard error unit of the best-fit line between 230 and 920 ppb, and within 2 standard error units between about 0 and 1270 ppb at 26°C and 60% RH. The ORNL model adequately predicts the slope and cutoff concentration at 23°C and 50% RH. However, it does not accurately predict the temperature- and RH-dependence of the slope and cutoff concentration.

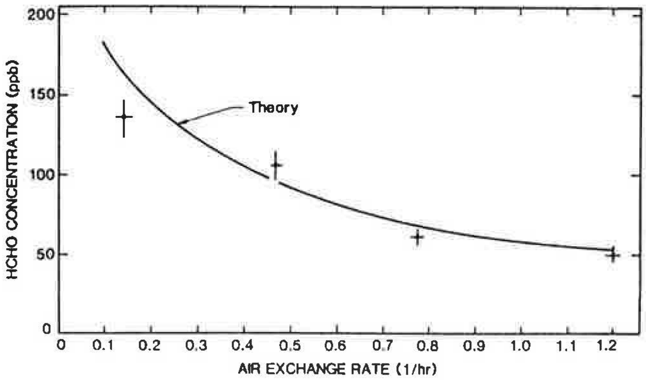

Figure 5. Comparison of outlet formaldehyde concentration measurements (points) and predictions of Equation 14 (curve) for prototype-house containing underlayment.

The Mass Balance Model for Predicting Formaldehyde Concentrations in the Prototype House

Formaldehyde concentrations in the two rooms of the prototype house were usually found to be so close together (see Tables V–VII and Figures 5–7) that it was unnecessary to use a two-room model to predict formaldehyde concentration from the surface emission rates of the pressed-wood products it contained. Instead a model relating formaldehyde concentration to n formaldehyde emitters was derived from a mass-balance equation, assuming a single well-mixed chamber:

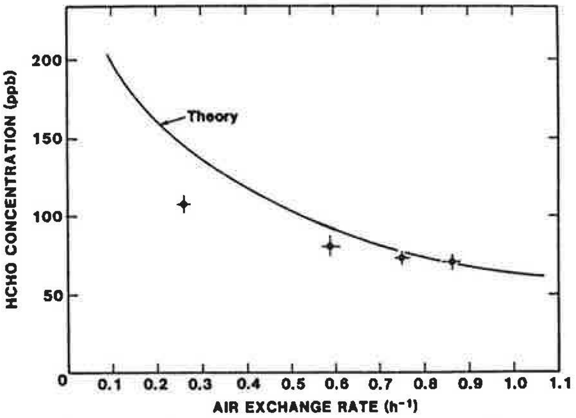

Figure 6. Comparison of outlet formaldehyde concentration measurements (points) and predictions of Equation 14 (curve) for prototype-house containing underlayment and paneling.

$$g \cdot dC/dt = -g \cdot AI \cdot (C - C_{ext}) + \sum_{i=1}^{n} l_i \cdot SER_i \qquad (13)$$

where: g = formaldehyde concentration conversion factor from ppb to mg/m^3 = 1.228×10^{-3} mg/m^3 · ppb at 25°C.
C_{ext} = chamber-background HCHO concentration, ppb.
l_i = loading of the ith emitter, m^2/m^3.
SER_i = HCHO surface emission rate of the ith emitter, mg/m^2 · h.
n = number of distinct pressed-wood products.

Substituting the expression for SER_i given by Equation 2, assuming steady-state conditions (dC/dt = 0 ppb/h) and that C_{ext} = 0 ppb, and rearranging terms, Equation 13 becomes:

$$C = (\Sigma\, l_i \cdot a_i')/(g \cdot AI + \Sigma\, l_i \cdot b_i') \qquad (14)$$

Equation 14, for $n = 1$, is similar to the Hoetjer-Berge-Fujii equation,[9,20,21] which relates steady-state formaldehyde concentration to air exchange rate and product loading. It was reported that it was difficult to apply this equation reliably to dwellings, and to mix together equations for different products.[11] The methodology presented here allows prediction of the coefficients for the Hoetjer-Berge-Fujii equation from chamber tests, and shows how to combine test results for pressed-wood product combinations in dwellings.

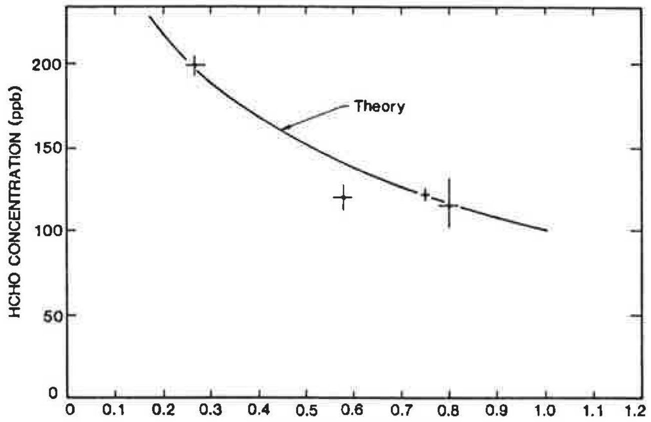

Figure 7. Comparison of outlet formaldehyde concentration measurements (points) and predictions of Equation 14 (curve) for prototype-house containing underlayment, paneling and mdf table tops.

Prototype House Results at 23°C, 50% RH

The results of the two-room prototype house tests for the three combinations of pressed-wood products installed in the prototype house are given in Tables V–VII and Figures 5–7. The two-room prototype house was measured at four air exchange rates between about 0.1 and 1 h^{-1} for each combination of pressed-wood products. After changing the air exchange rate, a period of at least four days was required before the formaldehyde concentration in the prototype house stabilized. The lag in response to change in air exchange rate is believed to be caused by absorption of formaldehyde by the bare gypsum wall and ceiling boards in the prototype house.[8,19]

Table V shows that formaldehyde concentrations due to the presence of particleboard underlayment varied from 50 ppb at 1.28 h^{-1} to 140 ppb at 0.14 h^{-1}. Figure 5 shows the comparison of the measured formaldehyde concentrations in the prototype house and the concentrations predicted by Equation 14 for particleboard underlayment. The mass-balance model seems to predict the measured values well. The maximum deviation occurred at the lowest air exchange rate, where the formaldehyde concentration was less than 20 percent below that predicted.

The data for the combination of particleboard underlayment and hardwood-plywood paneling are given in Table VI. Five days after installing the paneling, the combination produced a concentration of 70 ppb of formaldehyde in the prototype house with an air exchange rate of 0.86 h^{-1}. This increased to 80 ppb at 0.54 h^{-1} and to 180 ppb at 0.26 h^{-1}. When the air exchange rate was increased to 0.75 h^{-1}, the formaldehyde concentration decreased to 70 ppb. A comparison of the predicted and measured values for this combination of pressed-wood products is shown in Figure 6. The agreement is good except at the lowest air exchange rate, where the addition of the paneling results in a formaldehyde concentration about 25 percent lower than predicted by the theory.

The results for the combination of particleboard underlayment, paneling and two mdf table tops are given in Table VII. The addition of the two mdf table tops produced formaldehyde concentrations of 120 ppb, 120 ppb, 200 ppb and 120 ppb at air exchange rates of 0.80, 0.58, 0.27 and 0.75 h^{-1}, respectively. The comparison of these measured concentrations with the concentrations predicted by theory is shown in Figure 7. The agreement is good at all air exchange rates. The greatest deviation between predicted and actual formaldehyde concentrations was about 15 percent at 0.58 h^{-1}.

The comparatively large errors that occurred for particleboard, and for particleboard in combination with paneling at low air exchange rates were probably due to the large relative error in low air exchange rate measurements.[8] The error was estimated to be 0.1–0.15 h^{-1};[8] assume that it is 0.1 h^{-1}. Then the denominator of Equation 14 is changed by a smaller percentage as more pressed-wood products are included in the calculation, or as the air exchange is increased. The concentrations resulting from the assumed air exchange rate error for the lowest air exchange rates used in this study can change by up to about 35 percent for particleboard, 20 percent for particleboard and paneling, and 15 percent for particleboard, paneling and mdf from their "true" values. This explains why the measured concentrations for particleboard, paneling and mdf fit the experimental curve better than in the other two experiments at low air exchange rates.

It should be noted that the formaldehyde concentration usually increased from the outlet to room 1 to room 2, but that the difference between concentrations at the lowest and highest sites was always less than 30 ppb, and the differences between rooms 1 and 2 was always less than 12 ppb. As mentioned earlier, this made the use of a two-chamber model unnecessary.

Conclusions

A major goal of this study was to test a formaldehyde emission model developed by ORNL. First, measurements were made of the formaldehyde surface emission rates of particleboard underlayment, hardwood-plywood paneling and mdf table tops in medium-size dynamic measuring chambers. These measurements, at two sets of temperature and RH, confirmed the previously reported linear relationship between surface emission rate, and concentration with negative slope in accordance with Fick's first diffusion law. The data derived from these measurements were then compared with predictions of ORNL models.

It was already noted that the models were tested on products having formaldehyde emission rates in the low range of those commonly found in the United States. However, the trend is towards lower emission rates in new production.[4] Emission rates also tended to be lower or in the low range of those of products used by ORNL to derive the models. Nevertheless, the ORNL models predicted surface emission rates quite well at standard conditions. The model was also successful at higher temperature and relative humidity for particleboard and mdf, but not for paneling. It would be desirable to expand this study to confirm the ORNL model at combinations of temperature and RH further from standard conditions.

In developing its models, ORNL assumed that there is relatively free formaldehyde diffusion within the "bulk phase" of pressed-wood products.[12] Formaldehyde emission results from the difference in concentration between this "bulk phase" and the atmosphere, in accordance with Fick's first diffusion law. This assumption is apparently fairly descriptive of particleboard and mdf, but not of hardwood-plywood paneling. It is hypothesized that internal diffusion is important in formaldehyde emission by pressed-wood products, and layering of solid thin sheets of plywood obstructs diffusion to a greater extent than do chips and pieces in the other pressed-wood products. In other words, formaldehyde emission may not be as diffusion-limited in plywood as it is in other pressed-wood products. This would explain why formaldehyde emission by plywood appeared relatively insensitive to temperature and RH used in the present study. Higher temperature and RH increase resin degradation to formaldehyde and increase the formaldehyde diffusion rate.[22] Apparently, the small changes of temperature and RH used in the present study did not increase the "bulk-phase" formaldehyde concentration or the diffusion rate sufficiently to overcome the obstructing layers of the relatively low-emitting plywood used in this study.

ORNL had another difficulty in applying Fick's Law to hardwood-plywood paneling, the choice of 100 ppb for normalization. ORNL excluded data from paneling with low emission rates in model development.[5] The inapplicability of the model to low-emitting plywood was illustrated above for plywood from manufacturer #1.

It should be noted, however, that the apparent lack of correlation of the hardwood-plywood model does not preclude or invalidate its use in prediction and control of formaldehyde in homes. To use the model for these purposes, it suffices that the predicted emission rates be higher than the scattered measured emission rates. This applies also to using the model for predicting emissions by mdf. At elevated temperature and RH, emission rates are at first as predicted by the model, but then decline rapidly.

Another goal of this study was to test how well a mass-balance equation for a well-mixed chamber predicts formaldehyde concentrations resulting from pressed-wood products in buildings under realistic conditions, using the results of the measuring chamber characterizations. The model was tested in a two-room prototype house at air exchange rates ranging from about 0.1 to 1 h^{-1}, and the predictions of the model were close to the actual results. The greatest deviations from predictions occurred at low air exchange rates (0.1 to 0.3 h^{-1}). It would be desirable to repeat the experiment using a measurement technique that is accurate at low air exchange rates.

Acknowledgment

This project was made possible by support from the U. S. Consumer Product Safety Commission.

References

1. J. A. Swenberg, W. D. Kerns, R. I. Mitchell, E. J. Gralla, K. L. Pavkov, "Induction of squamous cell carcinomas of the rat nasal cavity by inhalation exposure to formaldehyde vapor," *Cancer Res.* **40:** 3398 (1980).
2. *Formaldehyde and Other Aldehydes*, National Research Council, National Academy Press, Washington, DC, 1981.
3. G. E. Myers, M. Nagaoka, "Formaldehyde emission: methods of measurement and effects of several particleboard variables," *Wood Sci.* **13:** 140 (1981).
4. "Formaldehyde Exposure in Residential Settings: Sources, Levels, and Effectiveness of Control Options," Versar, Inc., prepared for U.S. Environmental Protection Agency, Springfield, VA, 1986.
5. T. G. Matthews, "Environmental Dependence of Formaldehyde Emissions From Pressed-Wood Products: Experimental Studies and Modeling," proceedings, 18th International Washington State University Particleboard/Compressed Materials Symposium, Pullman, WA, 1984.
6. A. A. R. Kazakevics, "Studies on the Reduction of Formaldehyde Emission from Particleboard by Polymers," Ph.D. thesis, University of Auckland, New Zealand, 1984.
7. B. Meyer, K. Hermanns, "Formaldehyde Release from Pressed Wood Products," in V. Turoski, ed., *Formaldehyde Analytical Chemistry and Toxicology*, American Chemical Society, Washington, 1985, pp. 101–116.
8. S. Silberstein, R. A. Grot, K. Ishiguro, W. S. Dols, "Validation of Models for Predicting Formaldehyde Concentrations in Residences due to Pressed-Wood Products, Final Report," in preparation.
9. A. Berge, B. Milligaard, P. Haneto, E. B. Ormstad, *Holz als Roh und Werkstaff* **38:** 251 (1980).
10. R. A. Grot, S. Silberstein, K. Ishiguro, "Validation of Models for Predicting Formaldehyde Concentrations in Residences Due to Pressed-Wood Products, Phase I," National Bureau of Standards, Interagency Report 85-3255, Gaithersburg, MD, 1985.
11. G. E. Myers, "Effect of ventilation rate and board loading on formaldehyde concentration: a critical review of the literature," *Forest Prod. J.* **34:** 59 (1984).
12. T. G. Matthews, T. J. Reed, B. J. Tromberg, K. W. Fung, C. V. Thompson, J. O. Simpson, A. R. Hawthorne, "Modeling and Testing of Formaldehyde Emission Characteristics of Pressed-Wood Products: Report XVIII to the U. S. Consumer Product Safety Commission 1985," Oak Ridge National Laboratory, Report No. TM-9867, Oak Ridge, TN, 1985.
13. T. G. Matthews, K. W. Fung, B. J. Tromberg, A. R. Hawthorne, "Impact of indoor environmental parameters on formaldehyde concentrations in unoccupied research houses," *JAPCA* **36:** 1244 (1986).
14. "Low-Level Formaldehyde in Air (Mercury-Free Procedures)," CEA Instruments, Inc., Emerson, NJ, 1984.
15. R. R. Miksch, *et al.*, "Modified pararosaniline method for the determination of formaldehyde in air," *Anal. Chem.* **53:** 2118 (1981).
16. G. R. Lyles, F. B. Dowling, V. J. Blanchard, "Quantitative determination of formaldehyde in parts per hundred million concentration level," *JAPCA* **15:** 106 (1965).
17. R. A. Grot, D. M. Burch, S. Silberstein, L. Galowin, "Measurement Methods for Evaluation of Thermal Integrity of Building Envelopes," National Bureau of Standards, Interagency Report 82-2605, Gaithersburg, MD, 1982.
18. T. G. Matthews, T. J. Reed, B. J. Tromberg, C. R. Daffron, A. R. Hawthorne, "Formaldehyde Emission from Combustion Sources and Solid Formaldehyde-Resin-Containing Products," in V. Turoski, ed., *Formaldehyde Analytical Chemistry and Toxicology*, American Chemical Society, Washington, 1985, pp. 131–150.
19. T. G. Matthews, A. R. Hawthorne, C. V. Thompson, "Formaldehyde sorption and desorption characteristics of gypsum wallboard," *Environ. Sci. Technol.* **21:** 629 (1987).
20. S. Fujii, T. Suzecki, S. Koyagaehiro, "Study on liberated formaldehyde as renewal for JIS particleboard," *Kenjai Shiken Joho* **9:** 10 (1973).
21. J. J. Hoetjer, "Introduction to a Theoretical Model for the Splitting of Formaldehyde from Composition Board," Methanol Chemie Nederland, June 1978.
22. G. E. Myers, "Hydrolytic stability of cured urea-formaldehyde resins," *Wood Sci.* **15:** 127 (1982).

Samuel Silberstein and Richard A. Grot are with the Center for Building Technology, National Institute of Standards and Technology, Gaithersburg, MD 20899. Kunimichi Ishiguro is with Taisei Corporation, Tokyo, Japan. Joseph L. Mulligan is with the U.S. Product Safety Commission, Washington, DC 20207. This paper was submitted for peer review March 13, 1987; the revised manuscript was received June 17, 1988.