Formaldehyde emission from particleboard and plywood paneling: measurement, mechanism, and product standards

George E. Myers

Abstract

A number of commercial panel products, primarily particleboard and hardwood plywood, were tested for their formaldehyde emission behavior using desiccator, perforator, and dynamic chamber methods. The results were analyzed in terms of the source of formaldehyde observed in the tests (free vs. hydrolytically produced) and the potential utility of the testa as product standards for boards in mobile homes. A greater than tenfold range of formaldehyde emissions was observed, well above and below levels that would be acceptable for proposed mobile home air levels. It was demonstrated that observed maxima in dynamic concentration-time curves were due to depletion of initial board free formaldehyde (as measured by perforator) and emission of hydrolytically produced formaldehyde at a lower rate. The 2-hour desiccator test measures less than 0.5 percent of the boards' initial free formaldehyde content and therefore does not necessarily reflect resin hydrolytic stability. Approximate linear correlations were observed between desiccator or perforator values and dynamic chamber concentrations. However, large deviations occurred from the linear regressions. It was concluded that without large safety factors and/or much more testing to clarify those deviations neither the desiccator nor perforator test could provide reliable product standards for board emission.

Indoor air-pollution by formaldehyde that is emitted from adhesively bonded wood products has been a major concern in the forest products industry in recent years. A very important facet of the overall problem has been the development and evaluation of methods to characterize the formaldehyde off-gassing tendency of materials such as particleboard, hardwood plywood paneling, and medium-density fiberboard (MDF).

There were two primary goals in the methods development effort. First, a simple, reproducible test was desired that could be reliably performed in board manufacturers' laboratories – i.e., a quality control test. For this purpose it was essential that a one-to-one correlation exist between such quality control test values for boards and the consequent air contamination levels that would be produced in a dwelling made with those same boards. Second, as a consequence of meeting the first goal it was expected that valid product standards could be established for boards – i.e., maximum quality control test values that would prevent specific air-contamination levels from being exceeded.

Efforts at the Forest Products Laboratory (FPL) during the past several years have been directed toward these goals. We have examined several potential quality control tests, with emphasis upon the desiccator and perforator methods (7). The desiccator test was emphasized because it appeared likely to be adopted as the industry quality control method in the United States (2, 8). The perforator test was studied because it is widely used in Europe as a quality control test and because it is believed to measure a very important board emission characteristic, the board's free' formaldehyde content (9).

We have also investigated in some detail (4-7) the use of dynamic chamber testing because that method models the actual home air-contamination process and, therefore, constitutes a primary characterization of board emission. Finally, we have considered whether meaningful product standards can be defined on the basis of desiccator or perforator measurements – i.e., in effect whether such test values can be expected to possess a one-to-one correlation with dynamic chamber air concentrations of formaldehyde.

An earlier report (7) provided some preliminary answers regarding the possibilities of meeting the goals

[1]Throughout this paper the phrase "free formaldehyde" connotes the formaldehyde that is determined by the perforator test. The physical and chemical state of such formaldehyde is ill-defined, but the material presumably exists in a weakly bonded state.

The author is a Chemist USDA Forest, Prod, Lab., P.O. Box 5130, Madison, WI 53705. The Lab. is mantained in cooperation with the Univ. of Wisconsin. Board samples were supplied by the National Particleboard Assoc., Hardwood Plywood manufacturers Assoc. Clayton Environmental Consultntants, Inc. and Envirotech, Inc. Measurements were made by M. Nagaoka, R. Grundman, and R. Schaeffer. This paper was received for publication in July 1982.

Forest Prod. J. 33(5):27-37.

TABLE 1. – *Board sources and preconditioning.*

Group	Source	Preconditioning
1	Clayton Environmental Consultants, Inc. From board lots used to manufacture mobile homes in 1980-81.	Received as panels 0.6 by 1.2 m (2 by 4 ft.) individually wrapped in plastic. Stored wrapped at 2°C. Cut into specimens and conditioned 14 days at. 23°C/44% RH prior to testing.
2	Clayton Environmental Consultants, Inc Board lots used by Commodore Home Systems, Inc., in August 1981 to construct model homes. Cooperative effort by HUD/Clayton/industry (10).	Received as desiccator specimens, each type wrapped as a group in plastic. Stored wrapped at 2°C. Particleboard conditioned at ~22°C/50% RH for 7 days prior to testing. Plywood similarly conditioned for 24 hours. Perforator specimens cut from desiccator specimens after conditioning.
3	HPMA/NPA Round Robin.[a] Commercial boards. 1979	Received as desiccator specimens, each type wrapped as a group in plastic. Stored at ambient. Unwrapped just prior to testing.
4	Miscellaneous commercial boards available 1978-1980.	Received as panels of varying sizes. Cut into specimens and tested as received.

[a]HPMA = Hardwood Plywood Manufacturers Association. NPA = National Particleboard Association.

outlined above. At that time our data covered rather sparsely a wide range of formaldehyde emission rates from boards. More recently we have concentrated on a narrower, currently more realistic, range of board emissivities and also on the dynamic chamber behavior of a variety of boards. This paper summarizes both the earlier (7) and the recent data, and it analyzes the data in terms of the indicated goals. The recent data are emphasized in the analysis because they include the dynamic chamber characterization of board emission behavior.

Materials and methods

Boards and conditioning

Approximately 50 different commercial boards were examined (Table 1). The majority were urea-formaldehyde (UF)-bonded particleboard and hardwood plywood. Also included were several UF-bonded medium-density fiberboards (MDF), one phenol-formaldehyde (PF)-bonded waferboard, and several PF-bonded particleboards. They are divided into four groups on the basis of their source and their conditioning prior to testing (Col. 3, Table 1). Ceiling tile was commercial cellulosic material, 12 mm thick and painted on one side; it was used only for mixed product desiccator tests in combination with particleboard.

Except where variability was being investigated, the specimens for all tests were selected randomly from the total number available for each board type. Pretest conditioning (Table 1) was conducted such that all specimen surfaces were exposed.

Some Group 1 boards (Table 1) were tested before and after aging for 30 days at 75°C and 50 percent relative humidity (RH). Specimens were aged in the vapor space within sealed cans that contained a beaker of saturated NaCl to control humidity. The cans were placed in temperature-controlled air ovens. After aging, the specimens were again conditioned by the Group 1 procedure (Table 1) prior to testing.

Testing

In the desiccator test (2, 8), board specimens (70 by 127 mm) were placed in a glass desiccator around the outside of a container of distilled water. After a specified time the concentration of formaldehyde in the distilled water was determined. That concentration, in μg/mL, is termed the desiccator value of the particular board. In the earlier desiccator tests reported upon here, the time allotted was 24 hours and 300 mL of water was contained in a 400-mL beaker (2). In later experiments, a 2-hour test with 25 mL of water in a 100-mm Petri dish (8) was performed and was immediately succeeded by a 24-hour test with 300 mL of water. Eight specimens were used except where board thickness was $\geqslant$ 16 mm, in which case the number of specimens was reduced to seven (8). Mixed product desiccator tests used four specimens each of two board types.

Most of the reported desiccator values resulted from one experiment each. However, the reproducibility of the 24-hour desiccator test was examined briefly in two test series. In each series the effect of within-panel variation was minimized by selecting each of the eight specimens for a test from different regions of a panel. In the first series, nine replicate specimen sets were obtained from each of three panels (one plywood and two particleboard). In the second series, duplicate specimen sets were obtained from three panels from each of four board lots (two plywood and two particleboards).

The perforator test (9) involves a 2-hour reflux in boiling toluene with approximately 100 g of 25- by 25-mm specimens. Before the refluxing toluene returns to the boiling pot it is bubbled through distilled water which extracts any dissolved formaldehyde. Final analysis of the water for formaldehyde leads to the perforator value, expressed as milligrams of free formaldehyde per 100 g of dry board. Most of the values reported here resulted from single experiments. However, test reproducibility was investigated in one series in which duplicate runs were made upon one panel each of five different board types.

Dynamic chamber tests were conducted in four 3-liter glass desiccators containing a magnetically activated stirring vane. The desiccators were placed in ovens maintained at 35°C and 60 percent RH. Each desiccator held two board specimens (50 by 100 mm each) with paraffin-sealed edges. Conditioned oven air was pulled through the desiccators at different rates. The resultant ratios of N/L (where N is air changes per hour, in $hr.^{-1}$, and L is exposed board area, in m^2, per chamber volume, in m^3) were 0.24, 0.49, 0.74, and 0.99 m/hr. At intervals varying from 2 hours to a usual maximum of 14 days after test initiation, the formaldehyde concentration (*C* in ppm) in the chamber air was determined by absorbing the formaldehyde in water and analyzing the resultant solution for formaldehyde (5).

The formaldehyde concentration in water was determined by acetylacetone fluorometric analysis (5) for all three types of test. In one series of desiccator tests the solutions were also analyzed by a chromotropic acid spectrophotometric procedure (2, 8).

Board moisture contents were determined in conjunction with desiccator and perforator tests by weighing specimens before and after drying overnight at 105°C.

Results

Comparison of acetylacetone (AC) and chromotropic acid (CA) analyses

Parallel analyses of formaldehyde content in a total of 28 solutions from 2- and 24-hour desiccator tests gave a mean ratio (CA/ACA) of 1.28 with a standard deviation of 0.09. The consistently higher CA values could not be the result of a standardization bias since both procedures had been standardized in parallel using the same stock formaldehyde solution (methanol-stabilized). One possible explanation was that the desiccator solutions contained some formaldehyde in a polymeric form that could not be determined by ACA, but could by CA due to the high temperature and strongly acidic conditions used with the latter reagent. Mock desiccator experiments, in which trioxane (formaldehyde cyclic trimer) was scattered in the desiccator in place of boards, demonstrated (Table 2) that this material readily transferred through the vapor phase into water and that the resultant solution could be analyzed as formaldehyde by CA but not by ACA.

These results indicate that the analytical discrepancy noted with the board desiccator experiments might have been the consequence of trioxane in the boards. Whether the ACA or CA analysis is the more desirable from an air-pollution point of view – i.e., whether the vaporized trioxane should be included as an air contaminant – is not clear, however, since earlier reports (11) indicate that exposure to trioxane may be less hazardous than exposure to formaldehyde.

Desiccator and perforator values

Ranges and errors. – Perforator and 24-hour desiccator values were obtained upon almost all of the boards examined at the FPL during 1978 to 1981 (Table 3, Col. 9 & 4). The 2-hour desiccator test was performed upon only those boards available to us in 1980 and 1981 (Groups 1 & 2). The 2-hour values (Col. 3) ranged from 0.03 to 2.8 µg/mL for plywood and from 0.09 to 2.5 µg/mL for Particleboard. In comparison, the product standards tentatively proposed for the United States in 1981 were 2-hour desiccator values of 1.0 µg/mL for plywood and 1.8 µg/mL for particleboard. The European standard for lowest emission particleboard is a perforator value of 10 mg/100 g (9), whereas the observed range (Col. 9) was 1.1 to 51. Some of the tested boards were, therefore, well above or below the proposed standards.

TABLE 2. – ***Sublimation of trioxane into water during "desiccator" test.***[a]

Weight of trioxane initially in desiccator (mg)[b]	$10^2 \times$ wt. formaldehyde in solution / Weight initial trioxane		
	2 hr.	24 hr.	Total
100	88.9	0.7	89.6
500	36.6	51.0	87.6

[a]Solution concentrations measured by chromotropic acid. No formaldehyde detected by acetylacetone.
[b]Crystals spread on aluminum foil. No crystals remaining after 2 hours in first (100 mg) test and after 24 hours in second test.

Most of the desiccator and perforator values resulted from single determinations. Limited investigations into test reproducibility indicated that within-panel coefficients of variation (CV) were about 4 percent for perforator and from about 10 to 20 percent for 24-hour desiccator tests. It appeared, however, that panel-to-panel variability was significantly greater, CV being perhaps 30 to 40 percent.

Two-hour versus 24-hour desiccator.[2]– Values from the two testing times are approximately linearly correlated (Fig. 1, and regressions 1 and 2, Table 4). Although the particleboard data are rather scanty, it appears that a given 2-hour value results in a higher 24-hour value for plywood than for particleboard. That difference is shown more clearly by the mean ratios of 24-hour to 2-hour values - 2.6 for plywood and 1.5 for particleboard; the two ratios differ at the 99 percent confidence level.

The greater increase in 24-hour formaldehyde emission for plywood was paralleled by plywood's greater moisture uptake during the 24-hour test (Table 3, Col. 5). The 24-hour increase in moisture content (relative to initial content) for the plywood boards averaged 34.0 ± 8.9 percent, but was only 9.1 ± 1.6 for the particleboards. It will be shown later, however, that the desiccator test measures only a small fraction of a board's initial free formaldehyde content. Therefore, it is unlikely that the greater moisture uptake by plywood causes greater formaldehyde emission due to resin hydrolysis. Instead, the greater water content apparently enhances the rate of free formaldehyde liberation from the board.

Desiccator versus perforator. – Perforator values correlated approximately with 2-hour desiccator (Fig. 2) and with 24-hour desiccator values (regressions 3 to 5, Table 4). Although large deviations occurred about the regression line of perforator versus 2-hour desiccator

[2]Unless stated otherwise, all quantitative data comparisons and regressions exclude test values that were above the range of anticipated practical interest. Thus, the approximate upper limits were: 2-hour desiccator - 3.0 µg/mL; 24-hour desiccator – 6.0 µg/mL; perforator – 35 mg/100 g, dynamic chamber concentration – 1.2 ppm at 25°C.

TABLE 3. – *Board characterization results.*

		Desiccator test[a]						Perforator tests		Dynamic parameters[c]			
		Unaged			Aged[b]								
	Thick-ness	Values (µg/mL)		Moisture content[d]	Values (µg/mL)		Moisture content[d]	Value	Moisture content[e]	C'_{eq}	K'	r^2	Standard error[f]
Board[a] (1)	(mm) (2)	2 hr. (3)	24 hr. (4)	(%) (5)	2 hr. (6)	24 hr. (7)	(%) (8)	(mg/100 g) (9)	(%) (10)	(ppm) (11)	(m/hr.) (12)	(13)	(%) (14)
1-PL-1	5	—	1.20	9.9/—/11.9	0.136	0.32	6.5/6.7/8.8	4.8	8.1	2.0	0.65	0.77	12
1-PL-2	5	—	.34	7.8/—/9.6	.092	.187	6.7/6.8/8.9	4.0	7.4	.85	.41	.82	10
1-PL-3	5	0.32	.91	8.6/8.6/10.4	—	—	—	—	—	—	—	—	—
1-PL-4	4	.49	1.51	8.5/8.7/11.3	—	.080	7.5/—/9.1	10.7	8.7	1.17	.87	.58	18
1-PL-5	4	2.8	5.4	9.1/9.5/12.3	.170	.55	6.6/6.8/9.5	34	8.7	6.8	.57	.97	5
1-PL-6	4	.36	.99	8.5/8.8/11.2	—	—	—	6.7	7.6	—	—	—	—
1-PL-7	4	2.0	3.6	8.6/8.9/11.0	.27	.48	6.5/6.8/9.0	13.6	8.8	9.6	.16	.99	4
1-PL-8	4	.87	2.2	8.5/8.8/11.4	.13	.31	6.1/—/9.1	12.6	7.5	—	—	—	—
1-PL-9	4	.63	1.40	9.4/9.6/12.1	—	—	—	11	8.5	—	—	—	—
1-PL-10	4	.030	.101	6.5/—/9.1	—	—	—	—	—	-.070	-.22	.84	21
1-PL-11	4	.083	.26	7.2/—/10.1	—	—	—	4.6	6.6	.32	.38	.99	3
1-PL-12	4	1.63	3.9	8.5/—/11.6	—	—	—	27	7.7	6.0	.18	.96	6
1-PB-1	19	—	.30[h]	6.8/—/7.2	—	—	—	3.4	6.6	.87	.15	.82	16
1-PB-2	16	—	.59	8.1/—/8.9	—	—	—	8.5	8.2	—	—	—	—
1-PB-3	16	.64	.88	7.6/7.6/8.1	—	.29	6.9/—/7.0	12.5	7.9	.74	1.0	.94	5
1-PB-4	19	2.5[h]	2.6[h]	7.6/7.7/8.2	.56[h]	.64[h]	6.5/6.5/7.1	25	7.3	5.8	.28	.98	4
1-PB-5[g]	16	.092	.125	6.3/—/6.9	—	—	—	1.09	6.6	1.1	.082	.76	20
1-PB-6	16	.32	.46	6.3/—/6.9	—	—	—	5.3	5.8	1.0	.58	.98	4
1-PB-7	16	.73	1.10	7.2/—/7.9	—	—	—	11.7	6.8	2.9	.74	.99	1
1-MDF-1	20	6.4[h]	6.9[h]	6.2/6.2/6.7	—	—	—	64	5.0	—	—	—	—
1-MDF-2	13	5.9	8.7	6.7/6.7/7.4	1.1	2.1	6.0/6.1/6.7	60	6.5	100	.020	.89	14
1-MDF-3	13	7.3	10.7	5.6/5.7/6.4	2.6	4.1	5.3/—/6.0	84	5.5	28	.44	.99	3
2-PL-1	4	.038	.144	7.1/7.5/10.7				—	—				
2-PL-2	6	.63	2.0	6.6/6.9/9.2				3.3	6.1				
2-PB-1	19	1.57[h]	3.7[h]	7.0/—/7.7				23	7.1				
2-PB-2	19	.81[h]	1.52[h]	6.2/—/6.9				10.4	6.3				
3-PL-1	4	--	.37	7.5/—/10.0				1.38	7.3				
3-PL-2	4		.39	7.6/—/10.1				1.42	7.6				
3-PL-3	4		.16	8.2/—/10.5				.82	8.3				
3-PL-4	4		7.8	8.7/—/10.7				8.2	8.5				
3-PL-5	4		7.3	9.3/—/11.3				16.9	9.2				
3-PL-6	4		7.5	8.6/—/10.5				19.4	7.5				
3-PB-1[g]	16		.12	5.7/—/6.2				1.16	5.6				
3-PB-2[g]	16		.17	5.8/—/6.5				1.20	5.5				
3-PB-3[g]	16		.26	5.6/—/6.2				1.37	5.1				
3-PB-4	16		10.8	7.9/—/8.5				50	8.0				
3-PB-5	16		10.4	8.1/—/8.7				51	8.2				
3-PB-6	16		9.9	7.9/—/8.6				48	7.9				
4-PL-1	4		.22	5.4/—/9.6				.75	5.5				
4-PL-2	4		.73	5.6/—/10.0				3.5	6.0				
4-PL-3	4		1.83	5.5/—/9.0				10.4	6.2				
4-PL-4	5		1.53	5.7/—/8.8				8.6	6.6				
4-PL-5	5		1.62	5.7/—/8.3				7.8	6.5				
4-PL-6	4		4.2	5.3/—/8.5				30	6.7				
4-PL-7	4		1.71	8.4/—/11.9				8.9	8.4				
4-PL-8	4		.75	9.3/—/13.2				1.70	9.6				
4-PL-9	4		.38	8.3/—/12.1				4.0	8.9				
4-PL-10	4		.71	8.6/—/13.1				6.2	8.4				
4-WB-1	12		.042	1.0/—/2.3				.16	1.8				
4-PB-1	16		1.29	6.3/—/7.5				13.9	6.6				
4-PB-2	9		2.1	6.1/—/7.5				25.1	6.4				

[a]Group — Type — Board No. PL = plywood; PB = particleboard; MDF = medium-density fiberboard; WB = waferboard.

[b]30 days at 75°C/50% RH. Conditioned 2 weeks at 23°C/44% RH prior to remeasurement.

[c]From regression analysis of 14-day concentrations at four N/L.

$$\frac{1}{C'} = \frac{1}{C'_{eq}}\left[1 + \frac{1}{K}\frac{N}{L}\right]$$. N = ventilation rate (hr.$^{-1}$); L = loading (m^2/m^3).

[d]Pretest/post 2 hr./post 24 hr.

[e]Pretest.

[f]100 × one standard error in calculated C' ÷ calculated C' at N/L = 1.0 m/hr.

[g]Phenol-formaldehyde bonded. All others urea-formaldehyde.

[h]Number of specimens in desiccator test reduced to seven (9).

(Fig. 2), there seemed to be no tendency for different correlations for plywood and particleboard. Consistent with the higher 24-hour desiccator values for plywood, however, at a given perforator value the plywood 24-hour desiccator values were greater (~70%) than those for particleboard (cf., a_1 values for regressions 4 and 5, Table 4).

Aging. – The decrease in desiccator values after aging at 75°C/50 percent RH for 30 days vaned greatly from board to board (Table 3, Col. 3 and 4 vs. 6 and 7).

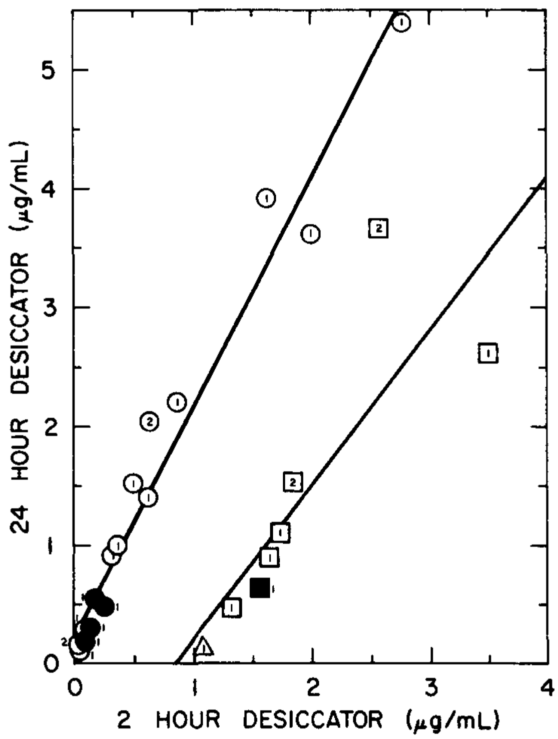

Figure 1. – Relation between 24- and 2-hour desiccator values. (O = plywood; U = particleboard; T = waferboard; numbers in or beside symbols indicate Group 1 or 2 boards; filled=aged; U and T x axis shifted 1.00 unit.)

The ratio of aged over unaged (Col. 6/3 and 7/4) vaned from 0.05 and 0.55, the mean ratio 2 one standard deviation being 0.22 ± 0.13. The existence of such differences is not surprising, however, since the change upon aging would depend upon board history, physical structure, free formaldehyde content, and resin stability.

Mixed desiccator tests. – In actual mobile home usage a given plywood will be present with a particleboard and with other materials, e.g., ceiling tile. Limited desiccator tests upon 50/50 mixtures (Fig. 3) indicated that for low emitting pairs the observed desiccator value may fall well below the value expected from simple additivity. Presumably, the lower emitting board of a pair – ceiling tile being a notable example – will act as a formaldehyde sink rather than a source. That sink plus the water sink in the desiccator test may then exceed the emitting capacity of the other board, leading to a desiccator value that is less than proportional to board loading.

Dynamic testing

It has been predicted (3, 6) that after insertion of formaldehyde-emitting boards into a ventilated

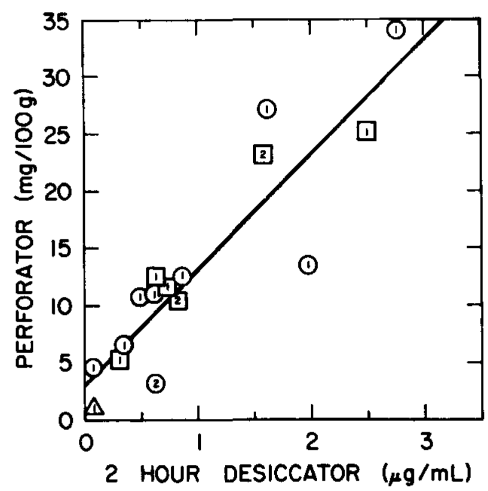

Figure 2. – Correlation between perforator and 2-hour desiccator. (O = plywood; U = particleboard; T = waferboard; numbers in symbols indicate Group 1 or 2 boards.)

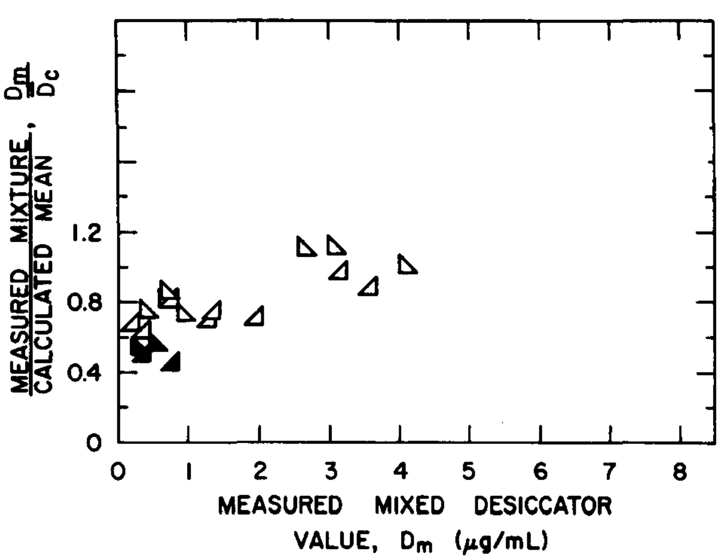

Figure 3. - Mixed (50/50) desiccator effects. (h=2-hourvalues;e= 24-hour values; unfilled symbols–plywood/particleboard; filled symbols – particleboard/ceiling tile.)

TABLE 4. – *Linear regression parameters.*[a]

Regression No.	Variables: Y	Variables: X	Regression parameters: a_0	a_1	r^2	$CV_{y \cdot x}$(%)[b]
1	24-hr. desiccator (plywood)	2-hr. desiccator (plywood)	0.21	1.94	0.96	24
2	24-hr. desiccator (particleboard)	2-hr. desiccator (particleboard)	.21	1.29	.70	51
3	Perforator	2-hr. desiccator	3.20	9.99	.81	32
4	Perforator (plywood)	24-hr. desiccator (plywood)	–.12	6.13	.92	29
5	Perforator (particleboard)	24-hr. desiccator (particleboard)	.28	10.6	.97	19
6	2-hr. desiccator	Concentration at 14 days and N/L = 0.5, corrected to 25°C, 50% RH	.013	2.69	.87	38
7	2-hr. desiccator	Concentration at 14 days and N/L = 1.0, corrected to 25°C, 50% RH	.115	3.86	.81	46
8	24-hr. desiccator	Concentration at 14 days and N/L = 0.5, corrected to 25 °C, 50% RH	.040	4.71	.84	41
9	24-hr. desiccator	Concentration at 14 days and N/L = 1.0, corrected to 25°C, 50% RH	.23	6.70	.77	50
10	Perforator	Concentration at 14 days and N/L = 0.5, corrected to 25°C, 50% RH	3.8	26.1	.72	41
11	Perforator	Concentration at 14 days and N/L = 1.0, corrected to 25°C, 50% RH	4.8	37.8	.69	44
12	2-hr. desiccator	Concentration at 1 day and N/L = 0.5, corrected to 25°C, 50% RH	.020	3.17	.88	36
13	Perforator	Concentration at 1 day and N/L = 1.0, corrected to 25°C, 50% RH	–.02	4.75	.92	29

[a] $Y = a_0 + a_1X$.
[b] Standard error of regression × 100/mean X.

chamber, the concentration of formaldehyde in the air will rise exponentially to a steady-state concentration C_s (ppm) given by

$$C_s = \frac{C_{eq}}{1 + \frac{1}{K} \cdot \frac{N}{L}} \quad [1]$$

where: N = ventilation rate (hr.$^{-1}$)
L = board loading (m^2 board area per m^3 chamber free volume)
K = material transport parameter (m/hr.)
C_{eq} = equilibrium concentration (ppm) when N/L is zero

Some boards do indeed follow the exponential time pattern (1, 3) and/or the steady-state dependence upon N/L that is described by Equation [1] (1, 3, 6).

In the present work, dynamic testing was performed upon 16 Group 1 boards (plywood, particleboard, MDF) at 35°C/60 percent RH, subsequent to a 2-week conditioning in a laboratory at 23°C/44 percent RH. In almost all cases the formaldehyde concentration rose initially, passed through a maximum within 1 to 5 days, and decreased thereafter at differing rates. The percent decrease per day from maximum concentration to the value at 14 days varied from zero to 5 percent. Steady-state concentrations were generally not seen within the usual 14 days of testing.

The left portion of Figure 4 typifies the observed behavior for the first 14 days – in this case for a UF-bonded plywood (1-PL-12) at four ratios of *N/L*. The initial 14-day test was followed here by a 50-day laboratory air exposure at 23°C/44 percent RH and further testing, as shown in the right portion of Figure 4. Only during the second test period did the system appear to be approaching a steady-state condition, with concentrations much below those at the original maxima. Note, however, that after a few hours the concentrations at any fixed time were in the order required by Equation [1], i.e., decreasing with increasing *N/L*.

Although Equation [1] was derived for steady-state behavior, we have examined the dynamic chamber data for all 16 boards to determine whether the equation

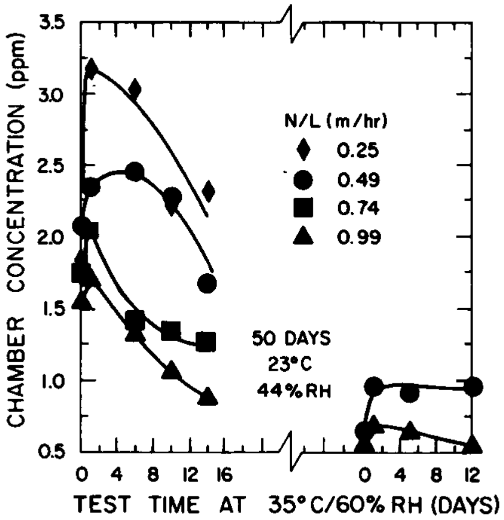

Figure 4. - Dynamic chamber testing of 1-PL-12 at 35°C/60%RH. (Intermediate exposure period of 50 days at 23°C, 44% RH.)

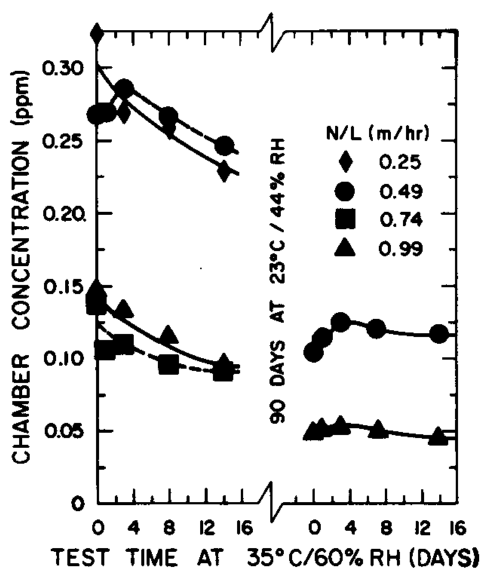

Figure 5. – Dynamic chamber testing of 1-PB-5 at 35°C/60% RH. (Intermediate exposure period of 90 days at 23°C, 44% RH.)

might be employed simply as an empirical description of N/L effects under nonsteady-state conditions. For each board, smooth curves were drawn visually through the concentration-time data at each N/L, as illustrated by the curves in Figures 4 and 5. From those smooth curves, concentrations were read at various fixed times – e.g., one value of concentration for each of the four N/L's at times of 1, 7, and 14 days. Linear regressions were then performed upon each data set (four concentrations and four N/L values at each fixed time), using thereciprocal form of Equation [1],

$$\frac{1}{C'} = \frac{1}{C'_{eq.}}\left[1 + \frac{1}{K'}\frac{N}{L}\right] \qquad [2]$$

where the primes signify nonsteady-state conditions.

The resultant values of C'_{eq} and K' are given in Table 3 along with correlation coefficients and standard errors (Col. 11 to 14). The standard error in calculated C' values at N/L=1.0 m/hr. varied from 1 to 21 percent; corresponding errors at N/L=0.5 were from 2 to 59 percent. Since the concentration data at each N/L were obtained with only two specimens (50 by 100 mm), the primary source of the regression errors was very likely nonuniformity among the specimens used at the four N/L values. Data obtained for a PF-bonded particleboard (Fig. 5), for example, illustrate the inconsistent effect of N/L observed with some boards.

Equation [1], therefore, acts to smooth out the effects of board nonuniformity and appears to provide a reasonable empirical description of ventilation rate and loading effects upon air contamination. Large chamber testing of full-size panels would, of course, minimize nonuniformity problems. Testing at lower temperatures would reduce the emission rate and, thereby, the strong time dependence observed here at 35°C; the dynamic behavior should then conform more closely to the theory (1, 3, 6) underlying Equation [1].

The range of calculated C'_{eq} values (Table 3, Col. 11) was very large, from 0.32 to 100 ppm. (Negative values were due to the influence of data scatter upon the regression intercept of Equation [2].) The temperature and humidity dependence of C_s is believed (1, 3) to reside primarily in C_{eq}. Using the factor 0.204 (1) for the change from 35°C/60 percent RH to the more normal indoor ambient condition 25°C/50 percent RH, the observed range of 0.32 to 100 ppm in C'_{eq} was reduced to 0.07 to 20 ppm. The range in K's (Table 3, Col. 12) was somewhat less, 0.02 to 1.0 m/hr. For a K' of 0.02, for example, a change in N/L from 0.5 to 1.0 m/hr. reduces C' by one half; for a K' of 1.0 the same change in N/L reduces C' by only one-quarter.

Discussion

There are two questions of concern:

1) Can we identify the source of emission (free or hydrolytically produced formaldehyde) during dynamic chamber testing and thereby explain the general absence of a steady state?

2) Does the emission source during a desiccator test differ from that in a dynamic chamber test? If so, does that imply that a one-to-one correlation between desiccator values and chamber concentrations is inherently unlikely, and therefore, that the desiccator test is inherently unsuitable as a board emission product standard?

Emission source

As an aid to answering thesequestions the amounts of formaldehyde lost from the boards during desiccator and dynamic chamber tests were compared (Table 5) with board free formaldehyde content, as measured by perforator values. The total formaldehyde lost by the board specimens in a chamber test up to a testing time t (hr.) was calculated from

$$w(t)_{Dyn}(mg/m^2) = 0.178\,[C(t) + N\alpha(t)] \qquad [3]$$

TABLE 5. – *Board formaldehyde losses versus free formaldehyde.*[a]

Board (1)	Free formaldehyde[b] w_F (2)	10^2 × free ÷ total[c] (3)	10^2 × dynamic loss after 14 days[d] ÷ free[b] N/L = 0.5 (4)	N/L = 1.0 (5)	10^2 × desiccator loss[e] ÷ free[b] 2 hr. (6)	24 hr. (7)	10^2 × dynamic loss after 14 days[d] ÷ desiccator loss[e] N/L = 0.5 2 hr. (8)	24 hr. (9)	N/L = 1.0 2 hr. (10)	24 hr. (11)	Time for dynamic loss[c] to equal free[b] N/L = 0.5 (12)	N/L = 1.0 (13)
	(mg/m²)	(%)									(days)	
1-PL-1	66	~0.09	380	540	—	3.9	—	410	—	620	4	3
1-PL-2	56	~.07	150	200	—	1.3	—	490	—	680	~8	~10
1-PL-4	113	~.15	170	270	0.076	2.8	~700	410	~1,200	660	7	5
1-PL-5	301	~.4	70[f]	100[f]	.16	3.8	~600	540	~900	850	>3	~3
1-PL-7	156	~.2	430	510	.23	4.9	~500	700	~500	850	~3	~2
1-PL-10	—	—					~1,000	590	~900	550		
1-PL-11	41	~.05	110	120	.036	1.2	~800	560	~1,300	820	~13	~11
1-PL-12	239	~.3	230	250	.12	3.5	~500	430	~500	610	~6	~5
1-PB-1	243	~.12	30	30	—	.30	—	380	—	480	>14	>14
1-PB-3	790	~.5	20	30	.014	.24	~300	440	~500	700	>14	>14
1-PB-4	1,770	~.9	30	40	.028	.36	~300	540	~100	740	>14	>14
1-PB-5	63	~.07	100	90	.026	.42	~1,000	1,600	~1,000	1,700	14	~14
1-PB-6	290	~.2	40	70	.019	.33	~400	770	~600	1,200	>14	>14
1-PB-7	674	~.4	10[f]	10[f]	.019	.35	~900	820	~900	1,200	—	—
1-MDF-2	2,670	~4.0	40	30	.039	.69	~200	320	~300	290	>14	>14
1-MDF-3	3,900	~5.0	90	120	.033	.58	~1,000	1,000	~1,600	1,500	~16	~12

[a]Comparison on basis of mg formaldehyde per m² board area (≡w), where area includes both sides of board.
[b]w_F = 10^{-2} × perforator value × g dry board per m².
[c]Total formaldehyde estimated from representative spread rates, resin formaldehyde contents, etc.
[d]Dynamic loss, w_{Dyn}, from Equation [3]. At 35°C, 50% RH.
[e]Desiccator loss, w_{Des}, = 0.176 × des. value for 2-hour test and 2.11 × des. value for 24 hours.
[f]After 3 days.

where the quantity 0.178 includes chamber volume, board area, and conversion factor from ppm at 35°C to mg/m³. The area under the time versus concentration, $C(t)$, curve from zero to t is given by a(t), and N is ventilation rate (hr.$^{-1}$). Corresponding formaldehyde losses in mg/m² were calculated from perforator and desiccator values, the latter by assuming that all the formaldehyde emitted from the board specimens was absorbed by the 25 or 300 mL of water.

Comparison of the various quantities in Table 5 leads to several conclusions regarding the source of formaldehyde in these tests:

1) Except for the two MDFs, whose emissions are well beyond the region of primary interest, the free formaldehyde contents, as estimated from perforator values, constituted less than 1 percent of the boards' total resin formaldehyde (Table 5, Col. 3). Once the original free formaldehyde content is lost from a board, therefore, there still exists in the board an ample source of formaldehyde that might be emitted via hydrolytic processes.

2) Formaldehyde loss from the particleboards after 14 days of dynamic testing at 35°C (perhaps 60 days at 25°C) was less than or comparable to the original free formaldehyde (Table 5, Col. 4 & 5). The mean percentage of dynamic loss to free formaldehyde for five particleboards at *N/L*=0.5 was 40 ± 30. For plywood, however, the dynamic loss was generally greater than the original free formaldehyde (mean percentage for six boards at *N/L*=0.5 was 240 ± 130). Similarly, the time required at 35°C for plywood dynamic loss to equal the free formaldehyde content was generally less than for particleboard (Col. 12 & 13).

In most, if not all, of the cases examined, therefore, hydrolytically produced formaldehyde must have contributed significantly to emission rather early in the board's dynamic exposure life. Thus the occurrence of a maximum in the dynamic concentration time curve (Figs. 4 & 5) must have resulted from a depletion of the board's free formaldehyde content and an effective rate of hydrolytic formaldehyde production that was lower than the board's initial emission rate of free formaldehyde.

3) Board loss of formaldehyde during a 2-hour desiccator test was less than 0.5 percent of original free formaldehyde content (Col. 6) and less than 5 percent of original free formaldehyde during a 24-hour desiccator test (Col. 7). The mean percentages of 2-hour desiccator loss to free formaldehyde for all boards tested were 0.15 for plywoods and 0.03 for particleboards. For 24-hour desiccator loss the percentages were 3.1 for plywood and 0.32 for particleboard. In general, therefore, the desiccator test is a measure of initial free formaldehyde emission rate and does not necessarily reflect formaldehyde produced by resin hydrolysis during the test.

4) Dynamic loss after 2 or 24 hours at 35°C was several times that during corresponding desiccator tests (Table 5, Col. 8 to 11). At 25°C, however, the 2- and 24-hour dynamic losses would be more comparable to those during desiccator testing.

In sum, therefore, these various tests may measure different quantities at different rates. The perforator is generally believed to measure free formaldehyde; this may be composed of residual material from board manufacturing and/or material produced by resin hydrolysis. The 2-hour desiccator test measures the most

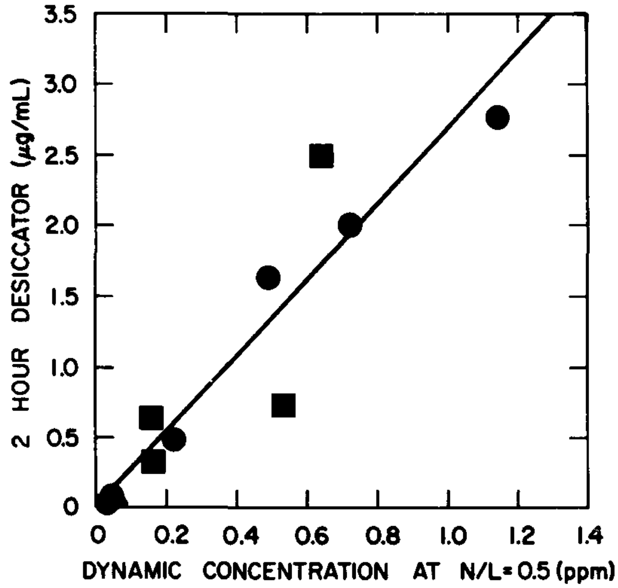

Figure 6. – Relation between 2-hour desiccator values and dynamic concentration at 25°C/50% RH and *N/L* =0.5. (Group 1 boards; O = plywood; C = particleboard; T = PF particleboard.)

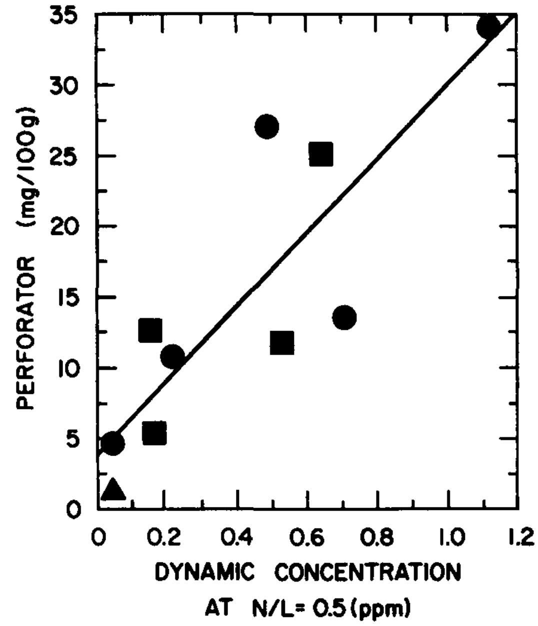

Figure 7. – Relation between perforator and dynamic concentration at N/L= 0.50, 25°C/50% RH. (Group 1 boards; O= plywood; C = particleboard; f= PF particleboard.)

easily liberated portion of the free formaldehyde. The 24-hour desiccator test measures a somewhat larger, though still small, portion of the free formaldehyde and is influenced by board moisture uptake. The dynamic test measures varying combinations of initial free and subsequent hydrolytically produced formaldehyde, depending upon exposure time and conditions. In either dynamic or desiccator tests, plywood appears to lose a greater fraction of its free formaldehyde than does particleboard.

Product standards

For a board emission test to qualify as a product standard ita test values must bear a monotonic relation to air contamination levels. To verify this criterion for the desiccator and perforator data reported here, the dynamic parameters (C'_{eq} and K', Table 3) were used tu calculate concentrations at N/L = 0.5 and 1.0 m/hr. Such N/L values approximate those for plywood and particleboard, respectively, in single-wide mobile homes when ventilation rates, *N*, are 0.5 $hr.^{-1}$. The resultant concentrations would, of course, be those existing after 14 days at 35°C (95°F) and 60 percent RH. They have been approximately corrected to the more realistic dwelling condition of 25°C (77°F) and 50 percent RH by multiplication by 0.204 (1). This condition of 25°C and 50 percent RH is specified in the proposed Wisconsin mobile home standard (12). This conversion to milder conditions implies that the 14-day experimental period would be extended to a more acceptable time, possibly up to 60 days.

These calculated dynamic concentrations have been found to be approximately linearly correlated with values from perforator and 2- and 24-hour desiccator tests. Figures 6 and 7 illustrate the correlations for 2-hour desiccator and perforator test values with concentrations at N/L = 0.5. Linear regression parameters are summarized in Table 4 (regressions 6 to 13).

Considerable data scatter was observed, however. Individual points deviated from the regression line by as much as a factor of 2, and coefficients of variation for calculated test parameters were of the order of 40 percent (Table 4, last column for regressions 6 to 13). There were several possible contributors to the scatter of points about the regression lines, including testing error, sample nonuniformity, and differences in emission mechanism from board to board. That the last-mentioned contributor is a distinct possibility was demonstrated in the preceding section.

However, the data here are not extensive enough to permit definitive conclusions about the relative magnitudes of these error sources. If mechanistic effects were paramount, for example, comparison of dynamic concentrations existing at times equivalent to the desiccator test (2 or 24 hr.) should yield greatly improved correlations. Unfortunately, the shortest time permitted for comparison with the present data is 1 day at 35°C, and the resultant correlations are not significantly improved (compare regressions 12 & 13 with 6 & 7, Table 4).

If we assume that correlations such as those in Figures 6 and 7 have a general, albeit approximate, validity, what conclusions can be drawn about the magnitudes of desiccator or perforator product standards? The regression equations in Table 4 were used to calculate values for comparison with European per-

TABLE 6. – *Comparison of proposed and calculated product standards.*

Test	Product standard at dwelling concentration (ppm)		
	0.1[a]	0.4[b]	1.0[c]
Perforator value, particleboard (mg/100 g)			
Proposed	≤10[a]		≤30[c]
Calculated	9±13[d]		43±18[d]
2-hr. desiccator value, plywood (µg/mL)			
Proposed		1.0[e]	
Calculated		1.1±0.7[f]	
2-hr. desiccator value, particleboard (µg/mL)			
Proposed		1.8[g]	
Calculated		1.7±0.9[h]	

[a]At *N/L*=1.0 m/hr. German El standard, 1980.
[b]Proposed Wisconsin mobile home standard (12).
[c]At *N/L*=1.0 m/hr. German E2 standard, 1980.
[d]Regression 11, Table 4. Ninety percent confidence interval.
[e]Hardwood Plywood Manufacturers Association, 1981.
[f]At *N/L*=0.5 m/hr. Regression 6, Table 4. Ninety percent confidence interval.
[g]National Particleboard Association. 1981.
[h]At *N/L*=1.0 m/hr. Regression 7, Table 4. Ninety percent confidence interval.

forator standards and with the proposed U.S. desiccator standards.

The results (Table 6) show surprisingly close agreement, particularly considering the data scatter and the uncertainty in temperature correction of the dynamic data from 35°C to 25°C (1). Note, however, that within a confidence level of 67 percent, the calculated desiccator standard for plywood could lie between 0.4 and 1.8 and that for particleboard between 0.8 and 2.6. Without additional data, certainly, these product standard values could not be employed without a large safety factor.

Another factor which must also be considered in setting product standards is the fact that boards are not used in isolation. Mixed product desiccator (Fig. 3) and chamber tests (10) indicated that contributions from plywood and particleboard are less than additive. However, a more conservative approach would assume additivity. The total formaldehyde concentration in a mobile home with a ventilation rate of 0.5 hr^{-1} would then, for example, be the sum of the concentration from plywood at its loading (L~1.0 m^2/m^3) and from particleboard at its loading (L~0.5 $m^2/m3$):

$$C_{Total} = \underset{Plywood}{C\ (N/L = 0.5)} + \underset{Particleboard}{C\ (N/L = 1.0)} \qquad [4]$$

Using the appropriate regression parameters (regressions 6 & 7, Table 4), and imposing the proposed Wisconsin mobile home air standard of 0.4 ppm (12), leads to the following description of allowable pairs of 2-hour desiccator values for the two board types:

$$1.44\ desiccator\ (plywood) = 1.68 - desiccator\ (particleboard) \qquad [5]$$

This boundary line is illustrated in Figure 8. Also included is the boundary line for an assumed air standard of 0.2 ppm total. Instead of the isolated particleboard and plywood standards (Table 6) of 1.7 and 1.1 µg/mL, the conservative Equation [5] would require a particleboard with a 2-hour desiccator value of 1.0 µg/mL, for example, to be paired with a plywood whose desiccator value was ⩽0.8 µg/mL.

In a cooperative program during the fall of 1981, Commodore Homes constructed two duplicate sets of mobile homes using two pairs of carefully characterized particleboard and plywood paneling (10). Monitoring of formaldehyde levels in those homes led to measured values after 9 weeks at 25°C of approximately 0.55 and 0.25 ppm (10). The paired 2-hour desiccator values measured at the FPL for the same boards used in making the homes are designated in Figure 8 by filled octagons. The data are in reasonable concordance with the conservative boundaries in Figure 8.

Summary

Perforator and 24-hour desiccator tests were conducted on approximately 50 commercial boards. About one-fourth of those boards, available in 1980 and 1981, were also subjected to 2-hour desiccator and dynamic chamber (35°C/60% RH) testing, after conditioning for 2 weeks at 23°C/44 percent RH. Major findings were:

1) Sublimation of trioxane may account for higher test values determined with chromotropic acid than with less severe reagents such as acetylacetone.

2) These commercially available boards exhibited greater than a tenfold range in formaldehyde emission behavior.

3) At 35°C/60 percent RH most of the boards tested in dynamic chambers produced concentrations which passed through a maximum in a few days. Rates of decrease after the maximum concentration probably would be approximately 1 percent per day or less at 25°C/50 percent RH. Dependence of concentration upon N/L (ventilation rate over loading) at fixed time was

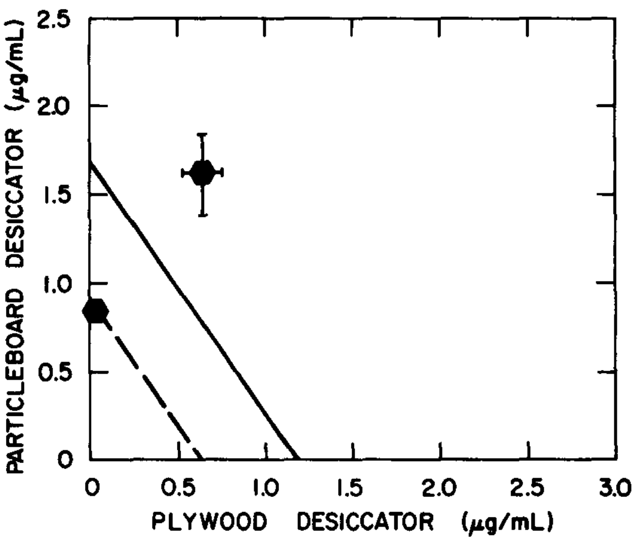

Figure 8. - Allowable mixed desiccator pairs for additivity of plywood (*N/L* = 0.5 m/hr.) and particleboard (*N/L* = 1.0 m/hr.) air concentrations. (—boundary for C≤0.4 ppm; -- boundary for C≤0.2 ppm; ⬣-values for Commodore model home boards (10).)

described approximately by a 2-parameter equation developed for steady-state conditions.

4) Calculations of formaldehyde lost by the boards during dynamic testing demonstrated that the maxima in concentration-time curves were due to depletion of initial free formaldehyde. Hydrolytically produced formaldehyde, therefore, contributed significantly to air contamination early in the experiments. This effect began sooner for plywood than for particleboard.

5) In contrast to the mixed sources (free and hydrolytic) of formaldehyde in dynamic air contamination, desiccator test values reflect only a small fraction of the boards' initial free (perforator) formaldehyde content (<0.5% in 2-hr. and <5% in 24-hr. test).

6) Approximate linear correlations were observed among all test methods, e.g., 2-hour versus 24-hour desiccator, desiccator versus perforator, desiccator versus dynamic concentration. However, test values for some boards deviated greatly from the linear regression lines. To what extent the deviant data points resulted from experimental error, from sample heterogeneity, or from differences in emission mechanism (free vs. hydrolysis formaldehyde) cannot be determined from these limited data.

Conclusions

1) A monotonic relation between dynamic air concentrations and desiccator or perforator values is essential for the latter tests to be useful as product standard methods. Because of the uncertainties noted above, however, the data presented here indicate that neither the desiccator nor perforator should be so employed as yet without large (factor of 2?) safety factors.

2) At the present time, product standards should be based upon dynamic chamber behavior. To minimize problems arising from board heterogeneity, from transient behavior, and from uncertainties in temperature correction, chamber and panel sizes and test conditions should approach real life as closely as is feasible.

3) The development and application of board product standards for mobile home usage must consider that boards are not used in isolation but in combination with others. A conservative approach would assume that contributions are additive.

4) Board exposure history may strongly influence both the level of formaldehyde emission and ita source (free vs. hydrolytically produced formaldehyde). Board history must be an essential part of a product standard test method. Moreover, efforts to reduce board emission must consider that both sources are potential contributors rather early in board history.

5) More study is needed to clarify a number of points, including: a) source of deviation from test method correlations and their removal, if possible, in order to define the utility of the desiccator test as a product standard method; b) temperature effect upon emission tests, as influenced by board type, board history, and formaldehyde emission source; and c) board mixture effects.

Literature cited

1. BERGE, A., B. MELLEGARD, P. HANETHO, and E. B. ORMSTAD. 1980. Formaldehyde release from particleboard — evaluation of a mathematical model. Holz als Roh- und Werkstoff 38:251-255.
2. FORMALDEHYDE INSTITUTE TECHNICAL COMMITTEE. 1980. Tentative test method for emission of formaldehyde from wood products. Desiccator method: June 24.
3. HOETJER, J. J. 1978. Introduction to a theoretical model for the splitting of formaldehyde from composition board. Report. Methanol Chemie Nederland, Delfzijil. Translation available from George E. Myers, Forest Prod. Lab., Madison, Wis.
4. MYERS, G. E. 1982. Formaldehyde dynamic air contamination by hardwood plywood: effects of several variables and board treatments. Forest Prod. J. 32(4):20-25.
5. ________ and M. NAGAOKA. 1981. Formaldehyde emission: methods of measurement and effects of some particleboard variables. Wood Sci. 13(3):140-150.
6. ________ and ________. 1981. Emission of formaldehyde by particleboard: effect of ventilation rate and loading on air-contamination levels. Forest Prod. J. 31(7):39-44.
7. ________ and ________. 1980. Formaldehyde from UF-bonded panels — its measurement and its relation to air contamination. Symp. on Wood Adhesives — Research, Application, and Needs. Forest Prod. Lab., Madison, Wis., Sept. 23-25.
8. NATIONAL PARTICLEBOARD ASSOC. 1981. Tentative test method for emission of formaldehyde from wood products: desiccator method. National Particleboard Assoc., Silver Spring, Md.
9. ROFFAEL, E., and L. MEHLHORN. 1980. Influence of marginal conditions on the determination of extractable formaldehyde by the Perforator method. Holz als Roh- und Werkstoff 38:85-88.
10. SINGH, J., R. WALCOTT, C. ST. PIERRE, T. FERREL, S. GARRISON, G. GRAMP, and W. GROAH. 1982. Evaluation of the relationship between formaldehyde emissions from particleboard mobile home decking and hardwood plywood wall paneling as determined by product test methods and formaldehyde levels in experimental mobile homes. Final rept. for HUD contract HC-5222. Clayton Environmental Consultants, Inc., Southfield, Mich.
11. WALKER, J. F. 1975. Formaldehyde. Krieger Publishing Co., Huntington, N.Y.
12. WISCONSIN DEPARTMENT OF INDUSTRY, LABOR, AND HUMAN RELATIONS. 1980. Formaldehyde report and standards. Wisconsin Dept. of Industry, Labor, and Human Relations, Madison, Wis.