Environ. Sci. Technol. **1999**, *33,* 81−88

Emission Rates of Formaldehyde from Materials and Consumer Products Found in California Homes

THOMAS J. KELLY,*
DEBORAH L. SMITH, AND JAN SATOLA
Battelle, 505 King Avenue, Columbus, Ohio 43201-2693

Formaldehyde (HCHO) is a toxic air contaminant released indoors from pressed-wood materials and numerous consumer products. Formaldehyde emission data are needed for modeling of indoor personal exposures, health risks, and risk reduction measures. This study determined HCHO emission rates from 55 diverse materials and consumer products under two realistic chamber test conditions, using both time-integrated and continuous real-time measurements. Among dry products, relatively high emissions were found from bare pressed-wood materials made with urea-formaldehyde (UF) resins, and from new (unwashed) permanent press fabrics. UF materials with paper, vinyl, laminate, and other coatings showed HCHO emissions lower by about a factor of 10 than those from bare UF materials. Among wet products, an acid-cured floor finish showed the highest HCHO emissions, greatly exceeding those of any dry product even 24 h after application. Fingernail polish and hardener showed relatively high emission rates, and latex paint and wallpaper relatively low emission rates, but these products emit similar amounts of HCHO because of widely different surface areas of application. Acid-cured finishes, and personal activity patterns and exposures during application of wet products, are key areas for further study.

Introduction

Formaldehyde (HCHO) is a suspected human carcinogen that is known to be released from pressed-wood products used in home construction, including products made with urea-formaldehyde (UF) resins (e.g., particleboard, hardwood plywood, medium-density fiberboard (MDF), and panelling) and those made with phenol-formaldehyde (PF) resins (e.g., softwood plywood, oriented strandboard) (*1, 2*). As a result, concern exists about personal exposures to HCHO indoors. For example, on the basis of a 1 in 100 000 cancer risk over a 70-year lifetime, the state of California has set an allowable daily HCHO exposure of 40 μg (*3*). With a typical adult daily respired volume of 20 m^3, this exposure equates to a HCHO concentration of 2 $\mu g/m^3$ (1.6 ppbv).

Because of concern over HCHO emissions, procedures for chamber testing of pressed-wood products are now well established (*4, 5*), voluntary emission standards for particleboard and MDF now rely on such tests (*6, 7*), and chamber testing of particleboard and hardwood panelling used in mobile homes is required by the U.S. Department of Housing and Urban Development. However, HCHO may also be emitted from many other consumer products, such as permanent press fabrics, cosmetics, fiberglass insulation, paints, and coatings (*1, 2, 8−10*), and these products have not been tested as extensively as have pressed-wood products. For example, over a decade ago Pickrell et al. (*8*) assessed HCHO emission from a greater variety of products than in any other study but only at 100% relative humidity (RH) and a constant (and not necessarily realistic) product loading. A subsequent study (*9*) employed a wider range of test conditions but for only a few products. As a result, few current, realistic data exist with which to conduct modeling of indoor HCHO concentrations, personal exposures, health risks, and risk reduction measures for the variety of consumer products found in homes.

This paper presents results from a study that fills that gap by determining the emission rates of formaldehyde from a wide variety of materials and consumer products found in California homes (*11*). This study also determined the emission rates of acetaldehyde, propionaldehyde, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK) because, like HCHO, they are designated as Toxic Air Contaminants by the California Air Resources Board and as Hazardous Air Pollutants in the 1990 Clean Air Act Amendments. However, no emission of MEK or MIBK was detected from any product tested, and the emission rates of acetaldehyde and propionaldehyde were generally much lower than those of HCHO from the same products (*11*). Consequently, this paper focuses on the results for HCHO.

Experimental Methods

The aim of this study was to test in a consistent way a broad variety of HCHO-emitting products found in California homes. The products tested included both “dry” products (i.e., those that emit HCHO at a steady rate) and “wet” products (i.e., those that produce a peak in emission after application followed by decreasing emissions as the product cures or dries). Examples of the former are pressed-wood products, decorative laminates, and permanent press fabrics; of the latter, paint, wallpaper, fingernail hardener, and floor finish. Because of the nature of national markets, the products tested were undoubtedly similar to those available throughout the U.S. However, the diversity and realism of the selected products was the focus of this study. Thus, while the products tested represent diverse product categories, they should not be taken as a statistical sampling of those categories.

Product Selection. Sample selection was based on four criteria: (1) market share or quantity of production of the material, (2) extent of use in a home, (3) likely or demonstrated product emission rate, and (4) the potential intensity of user exposure that might result from any emissions (*11*). The last criterion relates to the manner of use of the product: proximity of the user during application of a product could enhance any resulting exposure. The products selected were not intended to be a statistically representative sampling of all materials and products sold in California but rather a diverse set of samples characteristic of what a California resident would purchase, use, or be exposed to in the home.

Product Acquisition. The required samples were purchased in California, cut to sizes appropriate for testing, sealed in plastic film, and shipped to Battelle’s (Columbus, OH) laboratories. Information recorded for each sample included a description of the product, identification of the vendor and manufacturer, product characteristics, sample size, indication of single or duplicate sample, and the dates of purchase, shipping, receipt, and testing. For two wood products, sufficient quantities were obtained to allow testing of the products in a large chamber for comparison to the small chamber results. Wood and laminate sample pieces

---

* Corresponding author phone: (614)424-3495.

10.1021/es980592+ CCC: $18.00

were sandwiched between extra sheets of the identical product before wrapping in film for shipping.

Samples were obtained at intervals between May 1995 and February 1996, primarily in the Los Angeles basin, the Sacramento area, and the San Francisco Bay area. These areas were chosen as densely populated areas of the state in which consumer products and building materials were moving actively through the marketplace. Most samples were purchased directly from common retail outlets, in common sizes, and in the usual packaging. For some materials, such as industrial particleboard and other wood products, it was necessary to contact wholesalers to obtain samples. For some product types more than one sample was obtained, from different vendors in different parts of the state. A few products were obtained directly from manufacturers, including industrial particleboard with and without paper and vinyl laminates; particleboard mobile home decking, with and without a waterproofing coating needed in kitchen and bath areas; cabinet doors of MDF, with and without a manufacturer-applied acid-cured finish; and a two-coat acid-cured finish for wood floors.

Product Documentation and Storage. After receipt in the laboratory, all samples were stored in a continuously ventilated vacant office, maintained at 70(±3) °F and 50 (±5)% relative humidity (RH). Samples that ordinarily would be enclosed until use were kept in their original packaging until just before placement in the test chamber. All other products were unwrapped, separated from extra protective sample sheets, and allowed to equilibrate in the storage room for 2−7 days before testing. The edges of all wood product samples were sealed with sodium silicate solution and allowed to dry for 24 h before chamber testing.

Testing Procedures. All products were tested under two sets of conditions, designated typical and elevated, and chosen to represent a reasonable range of indoor conditions. “Typical” conditions were 70 °F, 50% RH, and 1.0 air changes per hour; “elevated” conditions were 80 °F, 50% RH, and 0.3 air changes per hour. Each product was tested simultaneously under these two sets of conditions, using twin steel and glass chambers of 1.43 m^3 volume. All tests were of 24 h duration. Wet products were applied to substrate materials outside the test chambers, and the substrates were then immediately placed into the chambers. Substrate materials were gypsum wallboard for paints and wallpaper; oak flooring for floor finish; artificial fingernails for fingernail polish; and aluminum foil over a wooden support for fingernail hardener. Temperature and RH data from both chambers, and the output of the real-time HCHO monitor, were recorded continuously during each test.

For eight dry and two wet products, chamber tests were run twice on separate samples, to assess the degree of repeatability of the entire test procedure. The duplicate tests were conducted on successive days, so that sample storage was as nearly identical as possible for the duplicate samples. The comparability of the present results to those obtained in large chambers was also assessed by testing samples of 5/8 in. particleboard underlayment and 3/4 in. stock hardwood plywood in the 1.43 m^3 chambers and simultaneously in a 17.3 m^3 chamber. The large chamber test used the same product loading as in the 1.43 m^3 chambers and the same air exchange rate as in the typical conditions. However, the large chamber temperature could not be maintained at 70 °F, as for the typical conditions. Instead, both the typical and large chamber results were adjusted to conditions of 77 °F and 50% RH using the correction factors in the ASTM large chamber procedure (*5*).

Chemical Measurement Methods. Both a continuous monitor (*12*) and EPA Method TO-5, based on derivatization with 2,4-dinitrophenylhydrazine (DNPH) (*13*), were used for determination of HCHO. The continuous HCHO monitor is highly specific for HCHO and has a detection limit of 0.1 ppbv, a lag time of 90 s, and a response time to step changes of about 60 s. At 1 ppmv of HCHO, the departure from linearity was 3%; HCHO results above 1 ppmv were corrected for nonlinearity.

The continuous HCHO monitor sampled alternately from the two chambers in all tests by means of an automatic valve. For dry products the monitor sampled for alternate 30-min periods from each chamber. For wet products the cycling time was shortened to 5 min on each chamber. In all tests, the HCHO monitor sampled the chamber background air before introduction of samples. In testing of dry samples, the continuous HCHO data were used to document stabilization of chamber HCHO levels and as a check on the DNPH method. For wet products, the continuous HCHO data were the primary measurement and were used to model the time behavior of emissions. The HCHO monitor was calibrated using 1×10^{-6}−4×10^{-4} M solutions of HCHO, prepared by serial dilution from a 37% (13.3 M) formalin primary standard (*12*). A standard of 1.33×10^{-5} M was run on every day of testing and is equivalent to about 100 ppbv gaseous HCHO. The sample air and scrubber solution flows that determine the exact equivalence were measured independently on every test day.

The DNPH results were the primary means of quantitation for HCHO in testing of dry products. Sampling was conducted by drawing air at 1.65 L/min through midget glass impingers containing 20 mL of the reagent solution. All background sampling and some product emission sampling was of 60-min duration. The sampling period was shortened to 30 min for those products which produced relatively high HCHO levels in the chambers, as indicated by the real-time monitor. Calibration of the HPLC determination of HCHO used standard solutions containing 2 or 20 μg/mL of the DNPH derivative of HCHO. The detection limit of the DNPH method was 0.16 ppbv (0.20 μg/m^3) for HCHO. In all tests the convention was adopted that an increase above chamber background of at least 1 ppbv of HCHO was required to initiate calculation of emission rates.

Calculation Procedures—Steady-State Sources. For products that produced steady-state concentrations in the test chambers, the following equation was used (*5*)

$$E = \frac{CN}{L} \tag{1}$$

where E = emission rate of target compound, in μg/m^2/h, C = concentration of the target compound under steady-state conditions, in μg/m^3, corrected for background concentration at the start of the test, N = air exchange rate, in h^{-1}, and L = product loading rate in the chamber, in m^2/m^3.

The steady-state concentration (C) was determined by DNPH sampling near the end of the test. In the few cases where problems with DNPH sampling or analysis invalidated the DNPH result, the HCHO concentration determined by the real-time monitor was used.

Calculation Procedures—Wet Sources. A four-parameter empirical model was used (*14*−*16*), having the form

$$C = a(1 - e^{-bt}) - c(1 - e^{-dt}) \tag{2}$$

where C is the concentration of HCHO (in μg/m^3) at time t (in hours). The coefficients a and c also have units of μg/m^3, whereas the exponential coefficients b and d have units of h^{-1}. From the values of the coefficients, the emission rates can be calculated. For example, the initial emission rate per m^2 of product surface may be calculated as

$$R_o = \frac{(ab - cd)}{L} \tag{3}$$

TABLE 1. Formaldehyde Emission Rates from Bare and Coated UF Wood Products (μg/m^2/h)[a]

no.	product group and identity		product loading[b] (m^2/m^3)	formaldehyde emission	
				typical	elevated
	Bare Urea-Formaldehyde (UF) Wood Products				
1	1/4" UF particleboard		0.46	1580	1170
2	5/8" particleboard underlayment		0.46	508	393
3	bare MDF cabinet doors		*c*	364	535
4	3/4" medium-density fiberboard (MDF)		0.26	258	254
5	5/8" industrial particleboard (I.P.)		0.46	237	311
6	5/8" MDF	dup 1[d]	0.26	210	318
		dup 2	0.26	335	385
7	1/4" prefinished hardwood plywood wall panelling		0.46	181	140
8	5/8" mobile home decking		0.46	174	241
9	1/2" hardwood veneer plywood		0.46	170	154
10	3/4" industrial particleboard	dup 1	0.46	170	181
		dup 2	0.46	120	130
11	5/8" industrial particleboard	dup 1	0.46	158	164
		dup 2	0.46	130	172
12	3/4" industrial particleboard		0.46	147	153
13	5/8" particleboard underlayment		0.46	119	134
14	3/4" industrial particleboard		0.46	117	177
15	5/8" industrial particleboard		0.46	104	110
16	1/2" stock hardwood plywood		0.46	103	147
17	1/4" stock hardwood plywood		0.46	101	71
18	3/4" stock hardwood plywood	dup 1	0.46	77	66
		dup 2	0.46	65	69
19	3/4" stock hardwood plywood		0.46	8.6	6.8
	Coated UF Wood Products				
20	MDF cabinet doors w. white acid-cured finish		*c*	460	1300
21	5/8" I.P. w. textured nonrecoatable paper laminate		0.46	55	120
22	5/8" I.P. w. recoated paper, waterborne topcoat		0.46	48	83
23	5/8" mobile home decking w. waterproof coating		0.46	35	52
24	3/4" I.P. w. melamine laminate (imported)	dup 1	0.46	29	44
		dup 2	0.46	16	86
25	5/8" I.P. w. paper laminate		0.46	26	29
26	3/4" I.P. w. melamine laminate (imported)		0.46	21	18
27	5/8" I.P. w. rigid vinyl laminate		0.46	16	31
28	5/8" I.P. vinyl coated		0.46	8.6	2.9
29	interior door w. particleboard core		0.46	7.0	15
30	5/8" I.P. vinyl coated	dup 1	0.46	6.7	1.7
		dup 2	0.46	<2.7	1.3
31	3/4" I.P. w. melamine laminate (domestic)	dup 1	0.46	5.7	2.2
		dup 2	0.46	3.4	3.2
32	5/8" I.P. w. electron-beam-cured acrylic coating		0.46	<2.7	5.7
33	3/4" I.P. w. melamine laminate (domestic)		0.46	<2.7	4.6

[a] All test results are steady-state emission rates after 20−24 h in the test chamber. [b] Product loading: Exposed surface area of product divided by 1.43 cubic meter chamber volume. [c] In testing of products 3 and 20, loading rates were 0.58 m^2/m^3 in typical conditions, and 0.52 m^2/m^3 in elevated conditions, due to sizes of cabinet doors received. [d] dup 1,2: Results indicate emission rates determined in duplicate chamber tests.

where R_o has units of μg/m^2/h. In applying this model, the recommendations of Colombo et al. (*14*) were followed. The initial value of a was set equal to the observed maximum concentration in the data set. The initial value of c was set equal to the difference between that maximum value and the final asymptotic level of the decay curve. The initial value of d was set equal to the air exchange rate (N) in the chamber, and the initial value of b was set to 3, based on experience in trial runs. Convergence of the model generally occurred within five iterations. The total emission of HCHO during a test was determined by integration of the concentration−time curve, multiplication of that result by the air flow rate through the chamber, and addition of the “residual” HCHO present in the chamber at the end of the test (*15*). Close fitting of the initial concentration increase, the timing and magnitude of the peak, and the decay of HCHO concentrations were achieved in all tests (*11*). The determination of R_o was sensitive to the timing of the initial increase in HCHO, but the determination of total integrated HCHO emissions was relatively insensitive to the fitting of the initial peak. In most wet product tests, HCHO concentrations achieved or approached a steady state by the end of the 24-h test. For such cases eq 1 was used to calculate the final HCHO emission rate at the end of the test.

Data Quality

Test Protocols. All testing was subject to the requirements of a Quality Assurance Project Plan (QAPP), which included Data Quality Objectives (DQOs). Testing was based on written test protocols, and the data quality was assessed relative to the DQOs (*11*).

Chamber Characterization. Automated gas chromatographic measurements of SF_6 over several hours indicated leak rates of 1.38% per hour for the typical chamber, and 0.65% per hour for the elevated chamber, in good agreement with data from past studies. To check the stability of gaseous HCHO at test conditions, levels of 50−300 ppbv were prepared in the chambers by vaporizing small quantities of 0.01 M HCHO solution. HCHO concentrations then were determined over several hours using the real-time monitor. The loss rates of HCHO to the chamber surfaces were found to be 5−6% per hour.

Of the 131 DNPH determinations of chamber background HCHO, 118 were below 10 ppbv, and all but five were below

TABLE 2. Formaldehyde Emission Rates from Various Dry Products (μg/m^2/h)[a]

no.	product group and identity		product loading[b] (m^2/m^3)	formaldehyde emission	
				typical	elevated
	Permanent Press Fabrics				
34	permanent press draperies		3.25	215	173
35	permanent press shirts (unwashed)		7.05	107	77
	permanent press shirts (washed once)		7.05	42	33
36	permanent press shirts		7.05	45	55
37	permanent press sheets		3.24	42	53
	Decorative Laminates				
38	20 mil cabinet liner decorative laminate		1.83	51	59
39	50 mil rigid general purpose laminate		1.83	14	15
40	50 mil general purpose laminate	dup 1[c]	1.83	4.0	6.0
		dup 2	1.83	4.2	6.1
	Fiberglass Products				
41	fiberglass R-19 roll insulation		0.87	32	31
42	fiberglass ceiling tiles		1.04	23	18
43	fiberglass ceiling tiles		1.02	16	11
	Bare Phenol-Formaldehyde (PF) Wood Products				
44	1/4" perforated PF hardboard		0.46	9.2	9.5
45	3/4" softwood plywood		0.46	8.0	6.9
46	3/4" oriented strandboard		0.46	6.8	16
47	3/4" softwood plywood		0.46	4.1	13
	Paper Products				
48	paper grocery bags		2.73	<0.5	0.7
49	paper towels		2.08	<0.6	<0.2

[a] All test results are steady-state emission rates after 20−24 h in the test chamber. [b] Product loading: Exposed surface area of product divided by 1.43 cubic meter chamber volume. [c] dup 1,2: Results indicate emission rates determined in duplicate chamber tests.

14 ppbv. Of the 140 chamber background measurements with the real-time monitor, 128 were below 10 ppbv, and all but five were below 14 ppbv. Chamber background HCHO levels above 10 ppbv were tolerated only when emissions from the product to be tested were expected to greatly exceed the background level.

Calibration Standard Checks. The 2 μg/mL DNPH HCHO standard was compared to a new HCHO standard from Radian Corporation, with agreement within 2%. The peak areas from 48 analyses of that standard had a relative standard deviation (RSD) of 5.9% over the five months of testing. The 1.33×10^{-5} M HCHO standard was also analyzed by the DNPH method, showing agreement within 1.6%. Based on the 1.33×10^{-5} M HCHO standard run on every test day (73 total analyses), the full scale of the real-time HCHO monitor on the most frequently used sensitivity range averaged 140.6 ppbv (±12.8 ppbv), for a percent RSD of 9.1%.

DNPH Duplicates. In all tests, two simultaneous DNPH samples were taken from each chamber for determination of product emissions. A linear regression of these duplicate pairs (134 data points, ranging from 2.2 to over 1800 ppbv HCHO) has the form DUP 2 = 1.013 (DUP 1) − 0.64 ppbv, with an r^2 value of 0.999.

DNPH/Real-Time Comparison. Averaging of the real-time HCHO data over the periods of collection of DNPH samples allows a direct comparison between the HCHO results from the two methods. For 385 data points, including both chamber background and product test samples, ranging from 0.3 to over 1800 ppbv, the linear regression has the form real time HCHO = 0.992 (DNPH HCHO) + 0.14 ppbv, with $r^2 = 0.973$.

External Analysis. Aliquots of DNPH samples, blanks, and standards were submitted to a commercial laboratory for analysis. Excluding a single outlier in which the commercial lab (CL) found no HCHO, the linear regression of HCHO data has the form CL = 0.959 (Battelle) + 0.09 μg/5 mL sample, for 51 data points, with $r^2 = 0.999$.

Uncertainty Analysis. An estimate was made of the overall uncertainty in the measurement of HCHO emission rates, using precision and accuracy data compiled for comparison to DQOs set forth in the QAPP (*11*). Combining uncertainties in chamber test conditions and chemical measurements, an overall uncertainty of 12.3% results for the determination of the HCHO emission rate of a dry product in this study. The uncertainties in determining the emissions from wet products are more difficult to quantify but are estimated at 25%, 15−20%, and 10%, for the initial rate, final rate, and total emitted HCHO, respectively (*11*).

Results and Discussion

Emissions from Dry Products. Tables 1 and 2 show the measured emission rates of HCHO from dry products, grouped into product categories, and within categories listed in approximate decreasing order of HCHO emission rate. Table 1 shows results for bare and coated UF wood products, Table 2 for several other product categories. Shown in Tables 1 and 2 are the product identification, the product loading in the chambers (m^2/m^3), the emission rates in both typical and elevated conditions (μg/m^2/h), and an indication of duplicate results for eight products. Calculated upper limits to the emission rates are shown for products with no detectable emissions. For product 35, permanent press shirts, results are also shown both before and after washing (Table 2).

The HCHO emission data for dry products are summarized in Figure 1, which shows a box plot of the HCHO emission rates under typical conditions by product category. The upper and lower ends of the box show the 75th and 25th percentile, respectively, of the emission data for the indicated category. The line within the box indicates the median, and the vertical bars indicate the 90th and 10th percentiles of the data. For those categories with enough data points, individual data points outside the 10−90th percentile range are also shown. Figure 1 shows that uncoated UF wood products exhibited a wide range of HCHO emission rates and the highest overall emission rates of any dry product category. Coated UF products showed a HCHO emission range about 1 order of

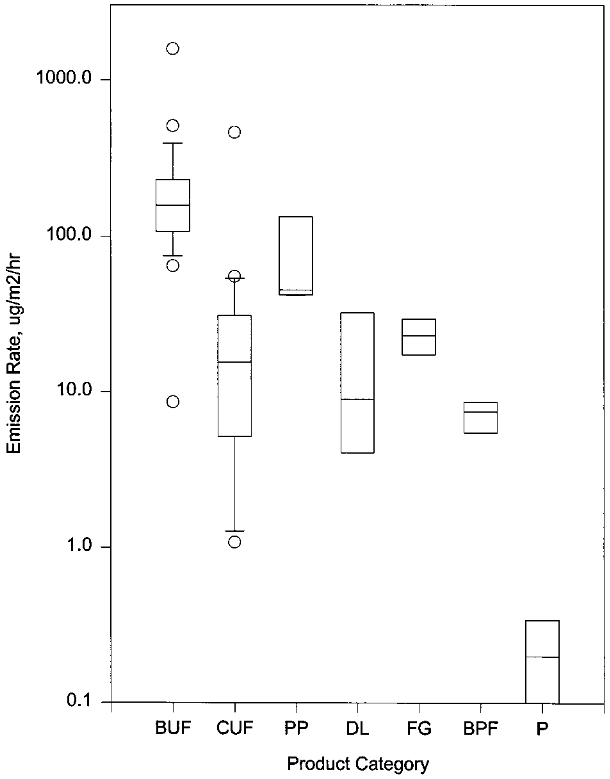

FIGURE 1. Box plot of HCHO emission data from dry products. BUF = bare UF products; CUF = coated UF products; PP = permanent press fabrics; DL = decorative laminates; FG = fiberglass products; BPF = bare PF products; P = paper goods.

magnitude lower than the uncoated UF products. This result is consistent with other observations that HCHO emission from vinyl-, paper-, or decorative-laminate-coated UF wood products is much lower than from bare UF products (e.g., *17, 18*). The lone exception among the coated UF products was the commercially applied acid-cured finish on cabinet doors, which emitted HCHO at a rate comparable to the highest of the bare UF products. New permanent press fabrics emitted at rates intermediate between the bare and coated UF products. Decorative laminates, fiberglass products, and bare PF wood products all showed emission rates roughly 1 order of magnitude lower than the bare UF products and comparable to those of the coated UF products. Paper goods exhibited negligible HCHO emissions, nearly 2 orders of magnitude lower than those of any other product category.

The estimated overall measurement uncertainty of 12.3% implies that values in Tables 1 and 2 that differ by less than about 40% from one another (i.e., less than about 3 times the uncertainty estimate) may not be significantly different. By this criterion, many of the products within each category are quite similar to one another in emission rate, while the highest- and lowest-emitting products within a category may exhibit very different rates. However, the differences between products in different categories are often much larger than the 40% uncertainty criterion.

A comparison with previous data shows that the results in Tables 1 and 2 are generally in the lower end of the range of previously reported HCHO emission rates for similar products. This finding probably results from changes in manufacturing and processing that have reduced or eliminated HCHO emissions in many products. For example, processing changes and voluntary production standards have reduced HCHO emissions from MDF and particleboard products. The voluntary standard for MDF production (*7*) corresponds to an emission rate of about 700 $\mu g/m^2/h$, at $N = 0.5\ h^{-1}$ and $L = 0.26\ m^2/m^3$. All of the bare MDF products tested in this study showed rates below that value (Table 1). The voluntary standard for particleboard production (*6*) corresponds to emission rates of about 440 $\mu g/m^2/h$ for most types and 290 $\mu g/m^2/h$ for flooring products, both at $N = 0.5\ h^{-1}$ and $L = 0.43\ m^2/m^3$. Nearly all particleboard samples in this study showed emissions below those values. One notable exception was the 1/4 in. UF particleboard (product 1), which was the highest-emitting dry product. However, that product was manufactured without the extremes of heat and pressure used in the manufacture of industrial grade particleboard and as such was never intended to meet the particleboard voluntary standard. Although these results indicate that particleboard and MDF sold in California largely meet the applicable voluntary standards, it must be stressed that the appearance or common name of a product is no indication of its emission rate. The 1/4 in. UF particleboard (product 1) was sold as a “hardboard”, a name which is sometimes associated with a highly cured, low-emitting product. The presence of a stamp on the wood product that indicates compliance with the applicable voluntary standards (*6, 7*) is the best indication of relatively low HCHO emissions.

Emissions from Wet Products. Table 3 presents the HCHO emission results from wet products. Shown in Table 3 for each product are the substrate loading in the chamber, the product loading on the substrate surface, the maximum HCHO concentration measured in the test (C_{max}), the initial emission rate of the product after application, the final steady-state emission rate, and the total mass of HCHO released during the test. For each product, results are listed for both the typical and elevated conditions. Duplicate test results are also shown in Table 3 for two products. No correction has been made for the small differences in product loadings (mg/cm^2) in the two chambers or in duplicate tests, i.e., the emission results in Table 3 are for the test conditions as listed.

The commercially applied floor finish exhibited by far the highest HCHO emissions, in terms of both initial and final rate and integrated HCHO emission. Emissions from the base coat were substantially greater than emissions from the top coat, for similar product loadings. For both coats it was necessary to use an unrealistically small surface loading ($0.0047\ m^2/m^3$), to keep chamber HCHO levels within measurable limits. Nevertheless, the floor finish products caused the highest C_{max} values of any wet product and released between about 6 and 9 milligrams of HCHO into the test chambers. The nail hardener exhibited the second highest R_o values, with a similar application surface area, but released only about one tenth as much HCHO as the floor finish products. Nail polish produced a still lower R_o value and much lower total HCHO emissions. Although paints and wallpaper exhibited relatively low emission rates, the total amount of HCHO released was substantial because of the realistically high surface area of these products. For all products in Table 3, the final HCHO emission rates were less than 1.7% of the initial rates.

It must be noted that the floor finish products in Table 3 are not used by the general public but are to be applied only by qualified contractors. Thus residential HCHO exposure is likely to be reduced by the time lag between commercial application and exposure of the resident. However, even the final steady-state emission rates from the floor finish (Table 3) were several times higher than those from the highest-emitting dry products (Table 1).

The few previous HCHO emission data for wet products are consistent with the results shown in Table 3. Very high HCHO emissions were reported from a Swedish floor finish (*19*), which may be similar to the product tested here. In another study (*20*), acid-cured floor and cabinet finishes were shown to emit large amounts of HCHO, though emission rates were not calculated. HCHO emission rates of 195−550

TABLE 3. Formaldehyde Emission Results from Wet Products

product	test condition[a]	substrate loading[b] (m^2/m^3)	product loading[c] (mg/cm^2)	C_{max} ($\mu g/m^3$)	initial HCHO emission R_o ($\mu g/m^2/h$)	final HCHO emission ($\mu g/m^2/h$)	integrated HCHO emission[d] (μg)
Paints							
lower quality	T	1.04	9.75	75	518	8.1	649
latex paint	E	1.04	7.88	105	441	7.5	521
(duplicate)	T	1.04	9.80	80	663	9.9	746
	E	1.04	9.07	108	854	10.1	597
higher quality	T	1.04	9.6	79	326	9.8	901
latex paint	E	1.04	10.5	163	494	5.3	611
Wallpaper							
paper-based	T	1.04	NA[e]	165	691	27	1,690
wallpaper	E	1.04	NA	192	[f]	[f]	[f]
Cosmetics							
fingernail	T	0.0049	15.6	180	178 000	124	837
hardener	E	0.0049	15.7	255	293 000	610	721
(duplicate)	T	0.0049	16.4	195	253 000	471	873
	E	0.0049	17.9	295	354 000	260	716
nail polish	T	0.0084	10.3	14.5	20 700		53.7
	E	0.0084	11.4	24.5	62 600		52.8
Commercially Applied Floor Finish							
base coat	T	0.0047	20 mils[g]	950	1 050 000	10 800	7780
	E	0.0047	20 mils[g]	1,950	1 247 000	17 100	9100
top coat	T	0.0047	25 mils[g]	900	421 000	4660	5950
	E	0.0047	25 mils[g]	1,800	799 000	13 600	7500

[a] T = typical conditions, E = elevated conditions. [b] Surface area of substrate divided by 1.43 m^3 chamber volume. [c] Mass of product applied per cm^2 of substrate surface. [d] Duration of continuous HCHO measurement in all tests was 22 h, except: lower quality latex paint = 18 h; paper-based wallpaper = 15.5 h; nail polish = 10.5 h. [e] NA = not applicable. [f] Emissions in this test could not be properly modeled due to loss of control of chamber humidity. [g] Product applied to thickness recommended by manufacturer, mass loading not obtained (1 mil = 0.001 in.). Estimated product loadings are about 60 mg/cm^2.

$\mu g/m^2/h$ reported for three paper-based wallpaper samples (*21*) are similar to the R_o value determined in this study.

Direct Product Comparisons. For a few products, the samples obtained allow direct comparisons of emission rates. The results in Table 1 show that for UF particleboard (product 5), paper coatings on that same particleboard reduced HCHO emissions by 60−90% (products 21, 22, and 25), and a vinyl coating on that particleboard reduced HCHO emission by 90−93% (product 27). A similar effect was seen for mobile home decking (product 8), for which the waterproof coating reduced HCHO emissions by about 80% (product 23). The data for MDF cabinet doors in Table 1 show that HCHO emissions were increased by the presence of the acid-cured finish (product 20), even though the bare MDF doors (product 3) were already a strong HCHO emitter. The increase in HCHO emission was modest (about 27%) at typical conditions but much larger (about a factor of 2.4) at elevated conditions. It must be noted that the acid-cured finish was recently applied by the manufacturer who provided the test samples; the impact of a well-aged finish on HCHO emissions might be different. Table 2 also shows that a single washing reduced HCHO emissions from new permanent press shirts by about 60% (product 35).

Duplicate Chamber Tests. Figure 2 summarizes the duplicate test results for eight dry products. The data are scattered along the 1:1 line, covering a range from 1 to nearly 400 $\mu g/m^2/h$. A linear regression to the data has the form DUP 2 = 1.14 (DUP 1) − 6.7 $\mu g/m^2/h$, with $r^2 = 0.880$. The degree of duplication is also indicated by the percent RSD values of the duplicate data pairs in Figure 2, which range from 3.1 to 46.3%, averaging 23.1%, with a median of 24.0%. The duplicate tests included a variety of products of widely differing emission rates and aimed for realism rather than lengthy equilibration in sample storage and conditioning. In light of these factors, the degree of duplication shown in Figure 2 is good. Given the estimated uncertainty in HCHO determination noted above, it seems likely that sample-to-sample variation in emission rates is an important cause of variability in the duplicate test results. The importance of sample-to-sample variability has also been observed in previous studies (*22*−*24*), even when only a single product was tested and when lengthy sample conditioning was performed to minimize such variability (*22, 23*).

To facilitate comparison, the duplicate results for two wet products in Table 3 were normalized to equal product loadings. With that normalization, the R_o results show RSD values for duplicate pairs of 3.6−36%, with the poorest duplication for the paint in the elevated chamber. Duplication of C_{max} values, final HCHO emission rates, and total HCHO emissions was generally better than for R_o values. RSD values for C_{max} duplicates ranged from 0.6 to 7.8% for the two products. For the latex paint, the final emission rates were 1.2−1.7% of the initial emission rates, and the typical and elevated duplicates showed percent RSD values of 14% and 11%, respectively. Duplication of the final rates was only within a factor of 2−4 for the nail hardener; however, the final rates represent only 0.2% or less of the initial rates, and the poor duplication in final rates may simply be due to near depletion of HCHO emission from the small sample surface areas. Good duplication was found for the integrated HCHO emission results for both products, i.e., percent RSD values of 0.3−10.2%.

Large/Small Chamber Comparisons. For the 5/8 in. particleboard underlayment, the small chamber results (182 $\mu g/m^2/h$) were within 15% of the large chamber results (213 $\mu g/m^2/h$). The 3/4 in. hardwood plywood exhibited a surprisingly low emission rate, but the rate determined in the small chamber (13.0 $\mu g/m^2/h$) was within 25% of that in the large chamber (10.4 $\mu g/m^2/h$). These results are consistent with the agreement found in duplicate tests and indicate that the emission rates obtained in the twin 1.43 m^3 chambers are representative of those that would be obtained in large chambers under the same conditions.

Comparison of Emission Rates under Typical and Elevated Conditions. Figure 3 shows a comparison of the HCHO emission rates in elevated conditions versus those

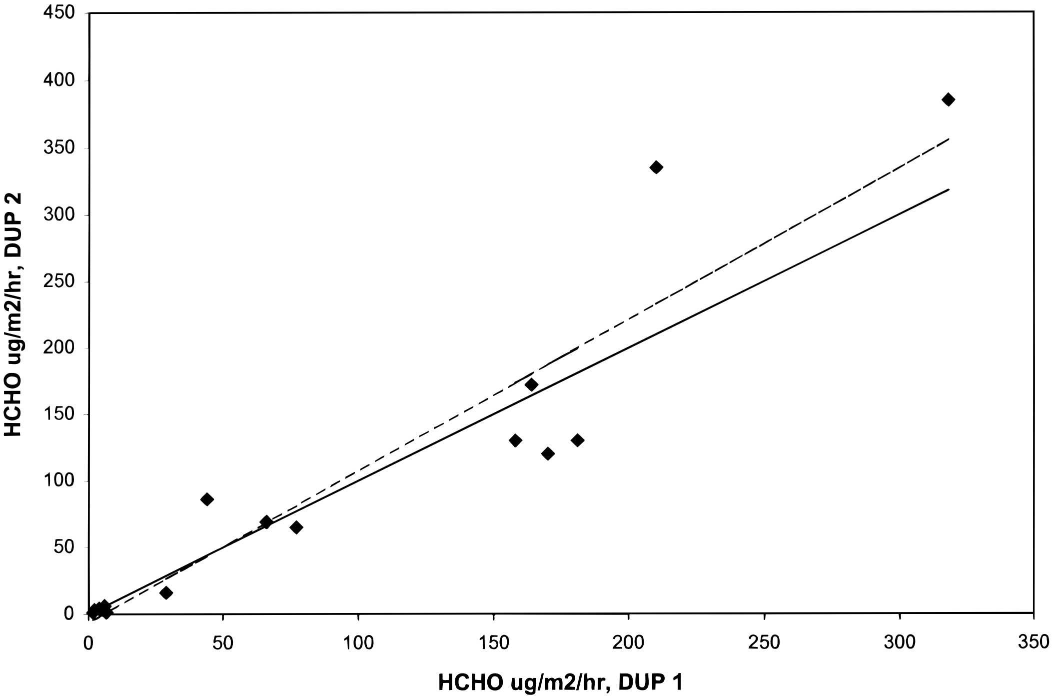

FIGURE 2. Comparison of HCHO emission rates determined in duplicate tests on eight dry products: (—) 1:1 line; (- - -) linear regression.

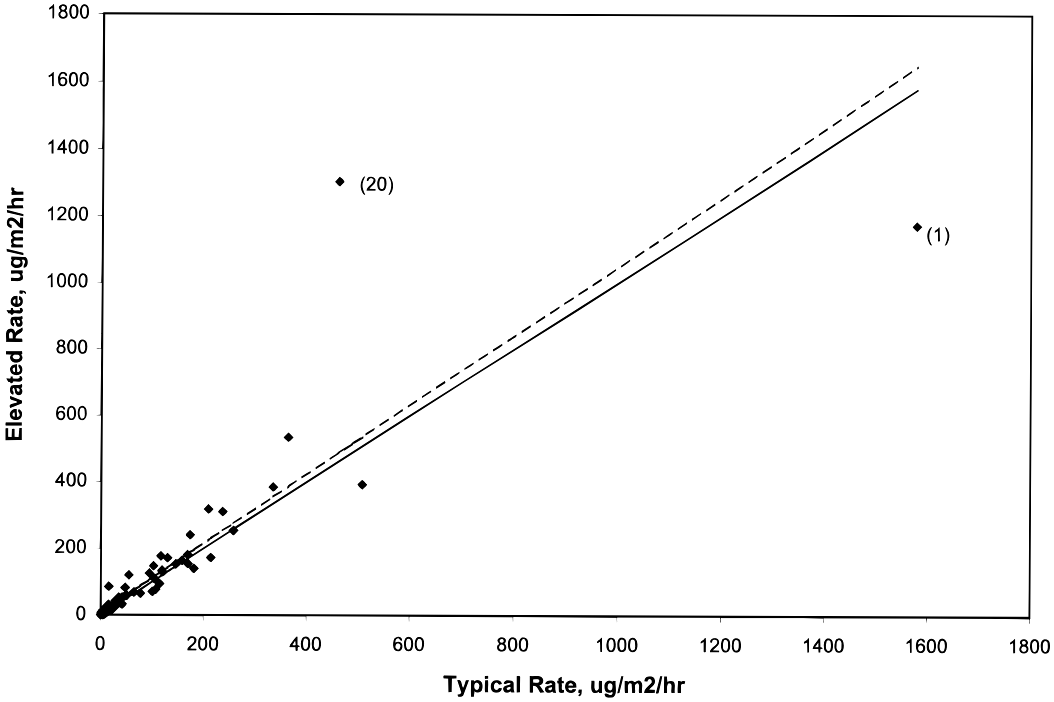

FIGURE 3. Comparison of HCHO emission rates from dry products in typical and elevated conditions: (—) 1:1 line; (- - -) linear regression, excluding the two data points flagged as products 1 and 20 (see text).

determined simultaneously in typical conditions for the dry products (Tables 1 and 2). Most of the data in Figure 3 are scattered along the 1:1 line, and the linear regression has the form elevated rate = 1.04 (typical rate) + 7.6 $\mu g/m^2/h$, with $r^2 = 0.94$. This regression excludes the two highest data points in Figure 3: results for the MDF cabinet doors with acid-cured finish (product 20) are excluded as an outlier, and results for 1/4 in. UF particleboard (product 1) are excluded because they greatly exceed the other data and would unduly influence the regression.

Two main opposing factors control the relative emission rates of HCHO in the elevated and typical conditions. The higher temperature in the elevated conditions favors higher emission rates. However, the lower air exchange rate in the elevated conditions results in higher HCHO concentrations, which can restrict the rate of diffusion of HCHO from the product. The results in Figure 3 show that these two factors are roughly in balance for most of the products tested. This finding is consistent with the few previous quantitative evaluations of the effects of test conditions on HCHO emission rates (*9, 25, 26*). Coated UF wood products and PF wood products showed greater variability than other product categories in terms of relative emission rates in elevated and typical conditions. In the case of the coated UF products, the nature of the coating itself may affect the sensitivity of the emission rate to changes in test conditions. For example, the MDF cabinet doors with acid-cured finish (product 20) showed an elevated/typical ratio of over 2.8, considerably higher than the corresponding ratio of less than a factor of 1.5, found for the bare MDF cabinet doors (product 3). Thus HCHO emission from the acid-cured finish was more sensitive to changes in test conditions than was emission from the MDF itself.

Table 3 shows that in general the wet products exhibited higher R_o values in the elevated conditions. However, the total mass of HCHO emitted was often higher in the typical conditions than in the elevated conditions. This may indicate that more rapid curing or drying of the applied products restricted later emissions of HCHO. This behavior was not universal, however, as both the base and top coats of the commercially applied floor finish showed higher R_o values and higher total HCHO emissions in elevated conditions than in typical conditions.

Recommendations. This study highlights the pronounced effect that surface coatings can have in reducing HCHO emissions from bare wood products and argues for increased emphasis on the characteristics of surface coatings in determining HCHO emission rates. This study also shows high emissions from acid-cured cabinet and floor finishes. The role of such finishes as indoor sources of HCHO merits further study. Determination of long-term emission rates is also needed for some products, such as acid-cured finishes. Finally, further study is needed of human exposures resulting from products such as clothing, cosmetics, paints, and wallpaper. Exposure from such products is likely to be greatly affected by the human activity patterns and microenvironmental characteristics during use or application of the products.

Acknowledgments

We thank Jeffrey Myers, Michael Holdren, Paul Webb, and Sydney Gordon of Battelle and Kevin O'Connor and Tom Scott of KKO Labs, Fremont, CA, for their participation in this study. We are also grateful for the assistance of Elizabeth Ota and Peggy Jenkins of CARB. This work was supported by the California Air Resources Board, Contract Number 93-315. The statements and conclusions herein are those of the authors and not necessarily those of the Air Resources Board. The mention of commercial products, their source, or their use in this work is not to be construed as either actual or implied endorsement of such products.

Literature Cited

(1) Otson, R.; Fellin, P. In *Gaseous Pollutants: Characterization and Cycling*; Nriagu, J. O., Ed.; John Wiley and Sons: New York, 1992; pp 335−421.
(2) Godish, T. *Comments Toxicology* **1988**, *2*(3), 115.
(3) *No Significant Risk Levels for Carcinogens and Acceptable Intake Levels for Reproductive Toxicants*; Safe Drinking Water and Toxic Enforcement Act of 1986, California Office of Environmental Health Hazard Assessment, January 1994.
(4) Tichenor, B. A. *Indoor Air Sources: Using Small Environmental Test Chambers to Characterize Organic Emissions from Indoor Materials and Products*; U.S. Environmental Protection Agency: Research Triangle Park, NC, 1989; EPA-600/8-89-074.
(5) *Standard Test Method for Determining Formaldehyde Levels from Wood Products under Defined Test Conditions Using a Large Chamber*; E-1333-90, American Society for Testing and Materials: Philadelphia, PA, 1990.
(6) *American National Standard: Particleboard*; ANSI A208.1-1993; National Particleboard Association: Gaithersburg, MD, 1993.
(7) *American National Standard: Medium-Density Fiberboard (MDF)*; ANSI A208.2-1994; National Particleboard Association: Gaithersburg, MD, 1994.
(8) Pickrell, J. A.; Mokler, B. V.; Griffis, L. C.; Hobbs, C. H.; Bathija, A. *Environ. Sci. Technol.* **1983**, *17*, 753.
(9) Pickrell, J. A.; Griffis, L. C.; Mokler, B. V.; Kanapilly, G. M.; Hobbs, C. H. *Environ. Sci. Technol.* **1984**, *18*, 682.
(10) Tichenor, B. A.; Mason, M. A. *J. Air Poll. Control Assoc.* **1988**, *38*, 264.
(11) Kelly, T. J. *Determination of Formaldehyde and Toluene Diisocyanate Emissions from Indoor Residential Sources*; Final Report to the California Air Resources Board, Contract No. 93-315, Battelle, Columbus, OH, 1996. (Available NTIS, PB97-148761).
(12) Kelly, T. J.; Fortune, C. R. *Internat. J. Environ. Anal. Chem.* **1994**, *54*, 249.
(13) Winberry, W. T., Jr.; Murphy, N. T.; Riggin, R. A. *Method TO-5*, in *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*; U.S. Environmental Protection Agency: Research Triangle Park, NC, 1988; EPA-600/4-89-017.
(14) Colombo, A.; De Bortoli, M.; Pecchio, E.; Schauenberg, H.; Schlitt, H.; Vissers, H.; *Science Total Environ.* **1990**, *91*, 2370.
(15) Colombo, A.; De Bortoli, M. *Indoor Air* **1992**, *2*, 49.
(16) De Bortoli, M.; Colombo, A. *Determination of VOCs Emitted from Indoor Materials and Products: Interlaboratory Comparison of Small Chamber Measurements*; European Collaborative Action, Indoor Air Quality and Its Impact on Man, Report No. 13, EUR 15054 EN, published by Commission of the European Communities: Directorate-General XIII, L-2920, Luxembourg, 1993.
(17) Groah, W. J.; Gramp, G. D.; Trant, M. *Forest Products J.* **1984**, *34*, 27.
(18) Koontz, M. C.; Hoag, M. L. In *Measuring and Controlling Volatile Organic Compound and Particulate Emissions from Wood Processing Operations and Wood-Based Products*; Proceedings No. 7301, published by The Forest Products Society: Madison, WI, 1995; pp 76−87.
(19) Van Netten, C.; Shirtliffe, C.; Svec, J. *Bull. Environ. Contam. Toxicol* **1988**, *40*, 672.
(20) Godish, T.; Guindon, C. In *Proceedings of the Fifth International Conference on Indoor Air Quality and Climate*; Toronto, Canada, July 29−August 3, 1990; Vol. 3, pp 689−694.
(21) De Bortoli, M.; Pecchio, E.; Schauenburg, H.; Schlitt, H.; Vissers, H. In *Proceedings of the Sixth International Conference on Indoor Air Quality and Climate*; Indoor Air 93: Helsinki, Finland, 1993; Vol. 2, pp 413−418.
(22) Matthews, T. G.; Wilson, D. L.; Thompson, A. J.; Mason, M. A.; Bailey, S. N.; Nelms, L. H. *J. Air Poll. Control Assoc.* **1987**, *37*, 1320.
(23) Crump, D. R.; Yu, C. W. F.; Squire, R. W.; Atkinson, M. In *Characterizing Sources of Indoor Air Pollution and Related Sink Effects*; ASTM STP 1287, Tichenor, B., Ed.; American Society for Testing and Materials: Philadelphia, PA, 1996; pp 211−224.
(24) Liles, W. T.; Koontz, M. D.; Hoag, M. L. In *Characterizing Sources of Indoor Air Pollution and Related Sink Effects*; ASTM STP 1287, Tichenor, B., Ed.; American Society for Testing and Materials: Philadelphia, PA, 1996; pp 200−210.
(25) Nelms, L. H.; Mason, M. A.; Tichenor, B. A. In *Proceedings of IAQ 86*; American Society of Heating, Refrigeration, and Air Conditioning Engineers, Inc.: Atlanta, GA, 1986; pp 469−485.
(26) Black, M. S.; Bayer, C. W. In *Proceedings of IAQ 86*; American Society of Heating, Refrigeration, and Air Conditioning Engineers, Inc.: Atlanta, GA, 1986; pp 454−468.

Received for review June 9, 1998. Revised manuscript received September 28, 1998. Accepted October 15, 1998.

ES980592+