

# Characterization of Curing Emissions from Conversion Varnishes

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## ABSTRACT

Three commercially available conversion varnish coating "systems" (stain, sealer, and topcoat) were selected for an initial scoping study. The total volatile content of the catalyzed varnishes, as determined by U.S. Environmental Protection Agency (EPA) Method 24, ranged from 64 to 73 weight%. Uncombined (free) formaldehyde concentrations, determined by a sodium sulfite titration method, ranged from 0.15 to 0.58 weight% of the uncatalyzed varnishes. Each sealer and topcoat was also analyzed by gas chromatography (EPA Method 311). The primary volatile organic constituents included methyl ethyl ketone (MEK), isobutanol, n-butanol, methyl isobutyl ketone (MIBK), toluene, ethylbenzene, the xylenes, and 1,2,4-trimethylbenzene.

Dynamic small chamber tests were performed to identify and quantify emissions following application to coupons of typical kitchen cabinet wood substrates and during curing and aging. One of the objectives was to determine the relationship between the concentration

of solvents [hazardous air pollutants (HAPs) and volatile organic compounds (VOCs)] and formaldehyde measured in the coatings' formulations and the emissions released during curing, after the coatings were applied. The results to date have shown good mass balance (amount of a constituent applied versus amount emitted) for the individual HAPs (except formaldehyde) and VOCs identified in the sealers and topcoats. Formaldehyde emissions have shown six to seven times the emission compared to the free formaldehyde content in the formulation, indicating that formaldehyde is formed during the curing process. Results of the formulation analyses and emission tests completed to date are described in this paper.

## INTRODUCTION

Wood and wood-veneered kitchen cabinets present a unique finishing challenge, because the finish must not only be attractive but also resistant to water and the many different detergents and foods that may be spilled onto the cabinets during their lifetime. A typical finish involves application of three separate coatings: a stain, then a sealer, and finally a topcoat. The topcoat is always a conversion varnish, while the sealer may or may not be. Stains are typically not conversion varnishes. Conversion varnishes are widely used to provide a decorative and protective finish on kitchen cabinets. They form strong, water resistant, attractive coatings that cure by chemical reaction after they are applied. Also referred to as acid-catalyzed varnishes, these coatings consist of amino cross-linking agents, such as melamine formaldehyde or urea formaldehyde, that are "catalyzed" with a strong acid. Because these products may emit hazardous air pollutants (HAPs), including formaldehyde, the U.S. Environmental Protection Agency (EPA) is conducting scoping analyses to gain a better understanding of emissions during curing and aging.

## IMPLICATIONS

Conversion varnishes, also called catalyzed varnishes, are widely used finishes for kitchen cabinets. They contain amino cross-linking agents, such as melamine formaldehyde or urea formaldehyde, that are "catalyzed" with a strong acid. The bulk composition and curing emissions from three commercially available conversion varnish finishes, each consisting of a sealer and a topcoat, were measured. The bulk of the volatile organic components, such as xylene, were emitted within a few hours after application. The formaldehyde emission rate decayed much slower; 2,800 hr after application, the formaldehyde concentration from the exposure chamber operating at 0.5 air changes per hour was 0.3 mg/m<sup>3</sup>. This is cause for concern, since kitchen cabinets are typically installed in homes 30 days after manufacture.



Because these coatings cure by reaction (although most of the solvent is released by simple evaporation), they may release reaction byproducts during application and drying as well as during their use in the indoor environment. This contributes to chemical emissions from the manufacturing facilities as well as emissions into the household indoor air. Although several chemicals may be emitted from these coatings, the chemical of primary interest in this project is formaldehyde, because it is a HAP, a probable carcinogen, and an irritant. In addition, because the formaldehyde may be formed by the reaction that occurs after the coating is applied, its emissions cannot be estimated from formulation information alone.

## DISCUSSION

The overall objectives of this project are to:

- (1) develop methods to measure cure emissions from conversion varnishes;
- (2) measure cure emissions from several commonly used conversion varnishes to gain an understanding of their amount and composition;
- (3) investigate alternative, lower-emitting coatings that can provide the water and chemical resistance and appearance necessary for this application, including coatings currently in use commercially and promising emerging coatings; and
- (4) demonstrate the most promising alternatives, and measure emissions both in the manufacturing plant and in the household indoor environment to evaluate their emissions compared to those of the conversion varnishes.

This paper addresses objectives 1 and 2. Preliminary plans are being made to proceed, at least on a limited basis, with objective 3, and objective 4 is planned for the future.

### Objective 1: Emission Testing and Test Method Development

Although conversion varnishes cure by chemical reaction (rather than by simple evaporation of solvents), EPA Method 24 still provides a measure of the total volatile organic compound (VOC) content, including cure volatiles. Methods for speciation of cure volatiles were not readily available. Work on this project began with an investigation of existing methods and ways in which they could be modified to speciate cure volatiles from conversion varnishes.

**EPA Method 24 for VOCs.** EPA Method 24 is used to determine total VOC content of coatings.<sup>1</sup> A number of American Society for Testing and Materials (ASTM) standard methods are incorporated by reference. For total volatile content,<sup>2</sup> a 0.5-g sample of the coating, in 3 mL of solvent, is placed in an open aluminum weighing dish, heated to

110 °C for 60 min, then cooled and re-weighed. The volatile content of the sample, which includes VOCs, exempt solvents, and water, is determined by the difference between the beginning and ending weights. Then the water content is measured and subtracted from the total volatile content to yield the total volatile organic content, including any cure volatiles.<sup>3</sup> Exempt solvents are determined<sup>4</sup> and subtracted from the total volatile organic content to arrive at the VOC content. The solids content is determined from the manufacturer's formulation, and the VOC content is expressed as weight of VOCs per weight of solids.

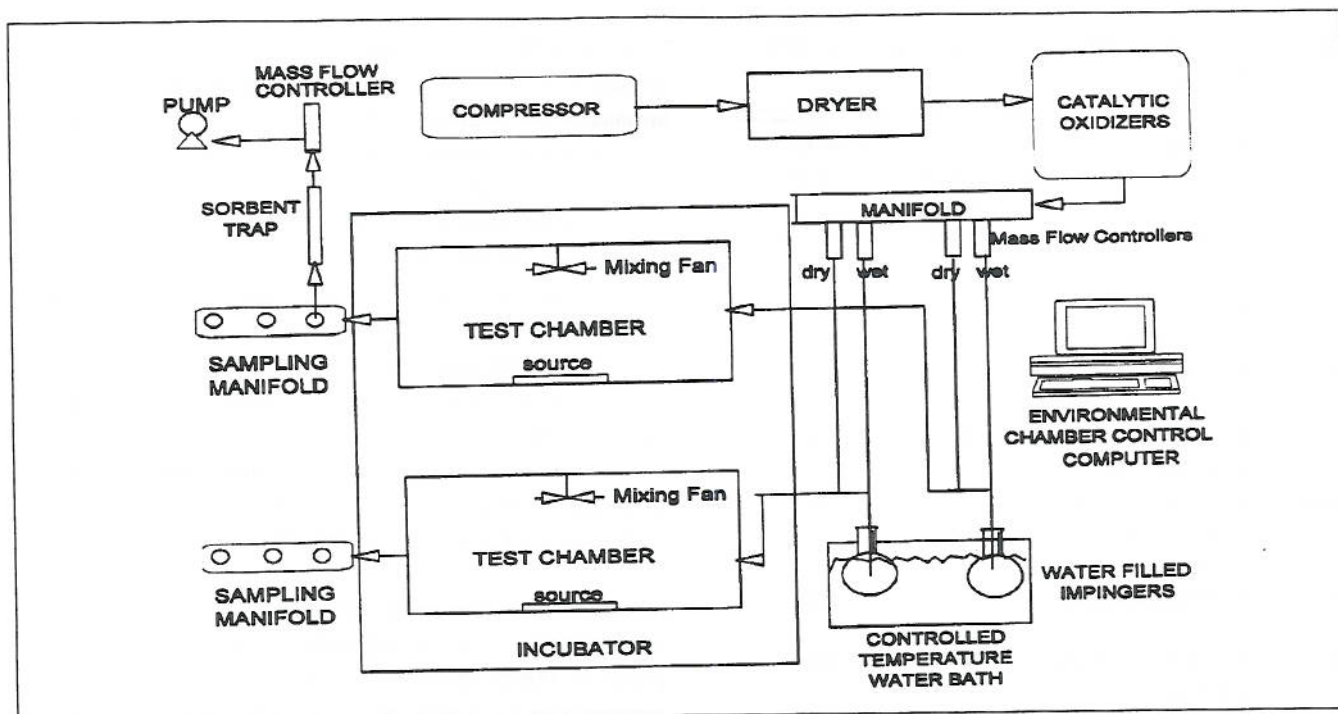
Recent changes to Method 24 (allowing an "induction period" at ambient temperature before placing the sample in the oven) now make it possible to obtain a reasonable measure of the volatile organic content (including cure volatiles) of reactive coatings such as conversion varnishes. Method 24 is based primarily on simple gravimetric methods so it does not provide for chemical speciation. Emissions of any particular compound (in this case, formaldehyde is of particular interest) cannot be measured.

**EPA Method 311 for HAPs.** Method 311 is a means of determining the HAPs in paints and coatings used in the wood furniture industry.<sup>5</sup> It is an analysis of the bulk product, so it measures only the organics contained in the product, not any that are formed during the curing process. In this method, the coating is mixed with an appropriate solvent, then injected into a gas chromatograph (GC). The GC results can be used to identify and quantify individual HAPs, but formaldehyde is not detectable by GC analysis. In this project, Method 311 is being used to obtain an analysis of the bulk varnish. Measurement of cure emissions is addressed below.

**Determination of free formaldehyde in the varnish formulation.** To find out if there is any relationship between the formaldehyde content of the varnish and the formaldehyde contained in the cure volatiles, a sodium sulfite titration method<sup>6</sup> was used to measure the formaldehyde in the as-received varnish at room temperature. The method used is based on the quantitative liberation of sodium hydroxide when formaldehyde reacts with sodium sulfite. Triplicate analyses of topcoat C showed an average of 0.211% free formaldehyde, with a relative standard deviation of 7.4%. A certified formaldehyde standard was used each day of analysis to verify that the analytical system met performance criteria.

**Small chamber tests—Curing in small environmental chambers.** To measure the cure volatiles under realistic, but controlled, conditions, small chamber tests are being conducted.<sup>7</sup> These





**Figure 1.** Schematic of small environmental test chambers.

tests are conducted using 53-L stainless steel chambers, which are commonly used for indoor air quality studies. A substrate (glass or wood in this case) is coated with a specified thickness of a coating, then placed in the chamber. Clean air, at a controlled temperature and humidity, flows through the chamber. Samples are taken on sorbent tubes and analyzed as appropriate, based on the compounds to be measured. The small chamber setup is shown schematically in Figure 1. These tests were designed to provide a good approximation of actual emissions from curing and aging of any coating, including conversion varnishes.

**Small chamber tests—Measurement of cure emissions.** The substrate coupon, measuring 29.5 × 9.2 cm, was coated using a slit applicator and then placed immediately into the environmental chamber. The air exiting the chamber was passed through adsorbent cartridges to collect the various compounds of interest. Hydrocarbons were collected on charcoal (high concentrations) or Tenax (low concentrations), while aldehydes were collected on silica gel impregnated with dinitrophenylhydrazine (DNPH).<sup>8</sup> The organics captured on the charcoal and Tenax cartridges were desorbed and then analyzed on a GC/mass selective detector (GC/MSD) and/or a GC/ion trap mass spectrometer (GC/ITMS). The DNPH-silica gel tubes were extracted, and the extract was analyzed on a high performance liquid chromatograph (HPLC).

### Objective 2: Test Series

Three commercially available conversion varnish coating systems (hereafter referred to as A, B, and C) were selected

for analysis. A coating system includes liquids used for each step in the coating process. For this project, short coating systems, consisting of stain, sealer, and topcoat, were investigated in this phase. Although all three systems selected included a stain step, it was decided to not include stains in this phase of the project. None of the stains were conversion varnishes, and thus contained other solvents, which would increase the complexity of the analysis without adding appreciably to our knowledge of conversion varnishes. The three coating systems (not including the stains) are described in Table 1.

**Results of scouting test.** An initial scouting test was run on topcoat C to determine the general conditions, flow rates, and sampling rates appropriate for use with conversion varnishes and identify the compounds emitted during cure so that calibration standards for those compounds could be purchased for use in the subsequent tests. The use of calibration standards allowed for good quantification of the amount of each chemical present. The VOCs for the scouting test were calculated as toluene, since the GC was calibrated to toluene. A glass panel was used as the substrate, with 72% of its surface area coated with a 100-μm wet film thickness of topcoat C. Glass was selected for this scouting test to eliminate the possibility of any confounding substrate effects.

Topcoat C was prepared by thinning it with xylene, as specified in the manufacturer's instructions. The standard chamber conditions used for this test (and the subsequent test series) are shown in Table 2.

Emission sample analyses yielded chamber concentration versus time curves for each compound. The total



**Table 1.** Description of three conversion varnish coatings systems (excluding stains) selected for evaluation.

System Code	Description	Free Formaldehyde <sup>a</sup> (% by wt)	Volatiles <sup>b</sup> (% by wt)
A sealer	Modified nitrocellulose (not a conversion varnish)	ND <sup>c</sup>	78.2
A topcoat	Acid cure alkyd urea	0.15	66.1
A catalyst	Added to topcoat 2% by volume immediately before application	ND	NA <sup>d</sup>
B sealer	Modified alkyd amino	0.49	73.0
B topcoat	Modified alkyd amino	0.53	64.0
B catalyst	Added to sealer and topcoat 3% by volume immediately before application	ND	NA
C sealer	C topcoat thinned with 25% xylol	0.17	64.9
C topcoat	Tall oil alkyd resin with urea formaldehyde resin as cross-linking agent	0.21	59.1
C catalyst	<i>p</i> -toluenesulfonic acid added 3% by volume to topcoat and sealer immediately before application	ND	NA

<sup>a</sup>As determined by sodium sulfite method described in the text.<sup>b</sup>As determined by EPA Method 24.<sup>c</sup>Not detected.<sup>d</sup>Not applicable.

mass of formaldehyde emitted during this test was 25.3 mg or 1% of the mass of topcoat C applied. Although the formaldehyde emissions did not fit a theoretically based mass transfer model, they did fit a second-order decay model fairly well.<sup>9</sup> The wellness of the fit was a little surprising, since the model was not developed to account for emissions arising from reactions within the coating. (Note that this model is not useful beyond the time frame of this test, because it allows for infinite emissions.) The model may be expressed as:

$$E(t) = E_0 / (1 + ktE_0) \quad (1)$$

where  $E(t)$  = the emission factor as a function of time;  $E_0$  =

**Table 2.** Environmental chamber standard parameters.

Air exchange rate:	0.5 hr <sup>-1</sup>
Temperature:	23 °C
Relative humidity:	50%
Air speed:	~10 cm/sec
Loading factor:	0.5 m <sup>2</sup> /m <sup>3</sup> (surface area of test coupon/ volume of chamber)

29.0 mg/m<sup>2</sup>/hr is the initial emission factor;  $k = 0.00361$  m<sup>2</sup>/mg is the second-order decay rate constant; and  $t$  = time after the beginning of the test.

The total mass of VOCs emitted during the test period (250 hr) was 41 mg or 44% of the mass of topcoat applied, calculated as toluene. The predominant VOC compounds were xylene, at 34%, and isobutanol, at 5% of the mass of varnish applied. These VOC emissions fit a mass transfer model<sup>10</sup> very well. In fact, the constants for the model could be calculated using physical constants for the formulation and xylene and mass transfer coefficients previously measured for this small chamber system.

Based on the results of this scouting test, formaldehyde, isobutanol, m,p,xylene, o-xylene, and ethylbenzene were selected for analysis during the main test series.

**Results to date from main test series.** To date, tests have been completed on coating system C, cured at room temperature. (Tests on systems A and B, requiring elevated temperature for a portion of the sealer and topcoat drying cycles, will be reported at a later date.) Tests on C have been completed on two substrates: solid oak and oak veneer on hardboard. Chamber conditions were the same as for the scouting test reported above. Test coupon dimensions were also the same. Prior to applying the coating, the test coupons were placed in chambers and background emissions measured over a period of two weeks. Results from the background tests (Tests 0, 1, 2, and 5) are summarized in Table 3.

The coupons were conditioned for 48 hours in a chamber under the conditions shown in Table 2 prior to coating. In Test 3, on solid oak substrate, the sealer was applied, and the coupon was placed in the chamber. The coupon was removed 23 hours later (a communication error transformed 1 hr into 1 day), and the topcoat was applied, then it was returned immediately to the chamber, where it remains. For Test 4, on oak veneer hardboard, the sealer was applied and allowed to dry in the chamber for 1 hr. The test coupon was removed, the topcoat was applied, and then the coupon was returned to the chamber, where it remains.

Following application of the sealers and topcoats to these coupons, emission samples were taken every 15 min during sealer cure (for the first hour only in Test 3) and every 15 min for the first hour after topcoat application. Sampling rate tapered off from that point, as the evolution rate of organics slowed, to the point that biweekly samples are now being taken. Results for the selected volatile organics from this test series are summarized in Tables 4 and 5.

One of the major objectives of this research was to measure the evolution of formaldehyde and look for a relationship to the free formaldehyde content of the varnish. As shown in Table 1, the topcoat in system C contained



**Table 3.** Summary of chamber and substrate background emission tests.

Condition	TVOC <sup>a</sup>	Hexanal	Decanal	Concentration, $\mu\text{g}/\text{m}^3$		Nonanal	C10 Branched Alkane
				Acetic Acid	2-Furaldehyde		
Empty chamber (Test 0)	11.0	0.4	0.4	0.8	0.2	ND <sup>b</sup>	ND
Solid oak (Test 1)	32.9	1.9	2.6	3.7	5.5	ND	ND
Oak veneer (Test 2)	15.8	2.3	2.5	1.0	ND	ND	ND
Solid oak (Test 5) <sup>c</sup>	NQ <sup>d</sup>	8.9	6.2	ND	ND	7.7	10.3

<sup>a</sup>Total volatile organic compounds, including any exempt solvents, found in the sample; reported as toluene.

<sup>b</sup>Not detected.

<sup>c</sup>Chamber temperature = 57.5 °C (Tests 0, 1, and 2 run at 23 °C).

<sup>d</sup>Not quantified.

0.21% free formaldehyde. Tables 4 and 5 show that emissions of formaldehyde were 700–800% of the amount of free formaldehyde applied in the coating. Figures 2 and 3 plot cumulative formaldehyde emissions (in milligrams) versus time for Tests 3 and 4, respectively. Figure 2, for example, illustrates that formaldehyde was still being emitted 3,300 hours (more than 19 weeks) after the coating was applied to the solid oak board. Typically, a kitchen cabinet will be placed in a home within 30 days after it is coated. Figure 4, a graph of chamber formaldehyde concentration as a function of time (since the coating was applied), illustrates that formaldehyde concentration was about 0.3 mg/m<sup>3</sup> at the 2,800-hr mark. One possible explanation for the continued evolution of formaldehyde is that the coating had not yet fully cured and polymerization was, therefore, not complete. Samples will continue to be taken periodically for several more months to determine if emissions continue to decrease or level off.

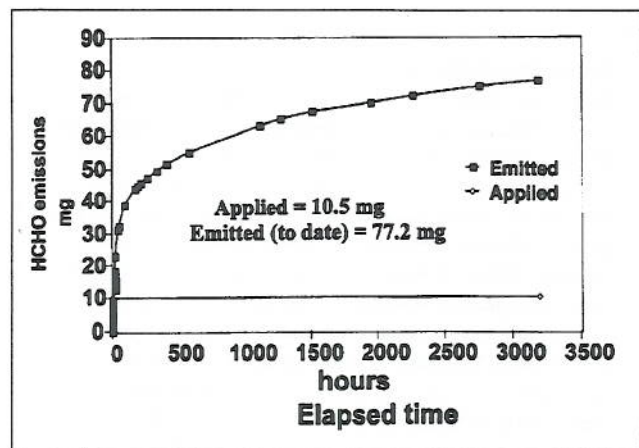
The manufacturer of topcoat C recommends drying at temperatures between 21 °C and 71 °C. The tests reported here were run at 23 °C. Drying (curing) at higher temperatures would accelerate the volatilization of the solvents, such as xylene. The effect on formation of

formaldehyde is more difficult to predict. Future tests planned include drying at elevated temperatures.

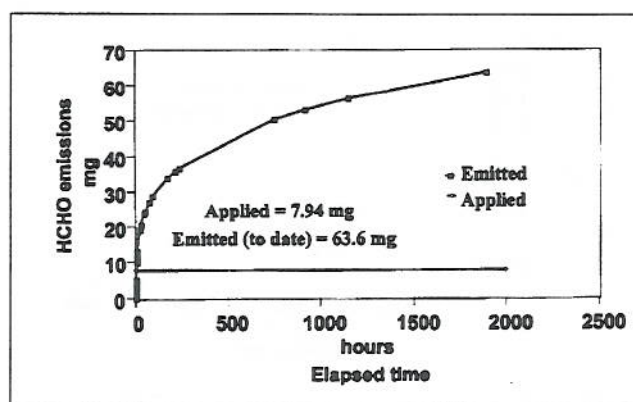
Another objective of the tests on coating system C was to determine the effect of substrate on emissions, especially the emissions decay rate. Figure 5 shows that, indeed, there is a substrate effect for m,p,xylene. A similar, but less pronounced, effect was also seen for isobutanol. A possible explanation is that the glue attaching the veneer to the hardboard acted as a barrier to the solvents. Thus they remained very close to the surface and could desorb and diffuse more readily. The substrate effect is, however, very minor when considered in terms of the mass applied compared to mass emitted during the test period (mass balance). For both substrates, virtually 100% of the m,p,xylene was emitted within the first few days after coating application.

### Objectives 3 and 4: Next Steps

The test series on the three-conversion varnish coating systems will be completed over the next few months. The plan is then to select one or more low-VOC/low-HAP coatings for testing in the chambers. The coatings selected would have to meet the Kitchen Cabinet Manufacturers Association (KCMA) criteria (i.e., KCMA A161.1). Beyond



**Figure 2.** Cumulative formaldehyde (HCHO) emissions in Test 3, conversion varnish C cured at room temperature.



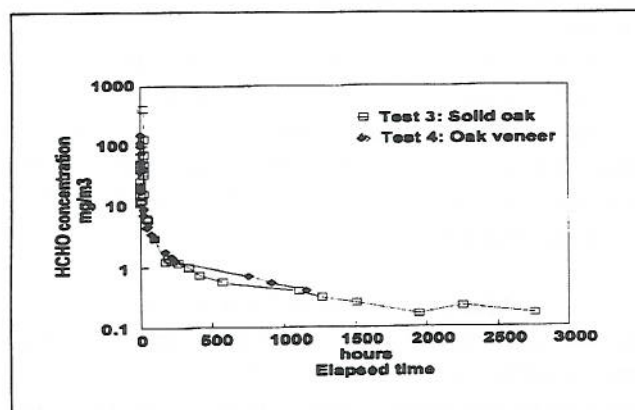
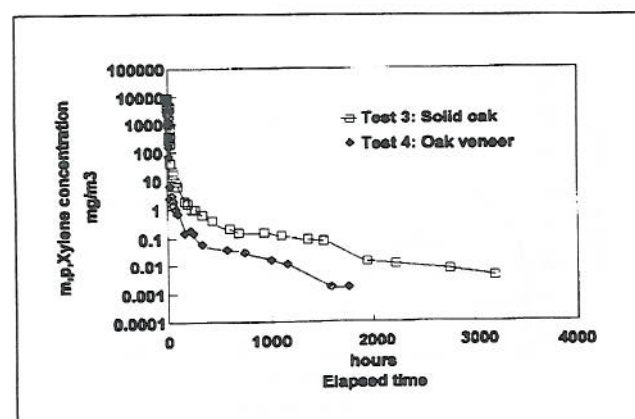
**Figure 3.** Cumulative formaldehyde (HCHO) emissions in Test 4, conversion varnish C cured at room temperature.

**Table 4.** Mass balance for selected volatile organics and formaldehyde for Test 3, 133 days after coating application (varnish C).

Compound	Emitted (mg)	Applied (mg)	Recovered (%)
Isobutanol	662	637	104
Ethylbenzene	255	317	80
m,p,xylene	994	1261	79
o-xylene	266	292	91
Formaldehyde	77.2	10.5	735

**Table 5.** Mass balance for selected volatile organics and formaldehyde for Test 4, 73 days after coating application (varnish C).

Compound	Emitted (mg)	Applied (mg)	Recovered (%)
Isobutanol	525	479	110
Ethylbenzene	193	243	79
m,p,xylene	800	971	82
o-xylene	175	226	77
Formaldehyde	63.6	7.94	801

**Figure 4.** Comparison of formaldehyde concentrations in chamber exhaust for conversion varnish system C, room temperature drying.**Figure 5.** Comparison between m,p,xylene concentrations in chamber exhaust over time, conversion varnish C, room temperature drying.

this, the long-range plan includes working with furniture manufacturers to switch over to one of the low-VOC/low-HAP coating systems.

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