

Characterization of 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. Total volatile content of the catalyzed varnishes, as determined by 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 resin. Each resin was also analyzed by gas chromatography/mass spectrometry (EPA Method 311) to identify the volatile components that may be emitted. The primary volatile organic constituents identified in the resin formulations included 2-butanone, n-butanol, 4-methyl-2-pentanone, toluene, ethylbenzene, 1,2,4-trimethylbenzene, and the xylenes.

Dynamic small chamber (53L stainless steel) 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 is to determine the relationship between the concentration of hazardous air pollutants (HAPs), volatile organic compounds (VOCs), and formaldehyde in the resins and emissions from the catalyzed varnish. The results to date show good mass balance for the HAPs and VOCs. Formaldehyde emissions show 6-7 times the emission compared to the free formaldehyde content, 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 must also be resistant to water and the many different detergents and foods which may be spilled onto the cabinets during their lifetime. Conversion varnishes are widely used to provide a decorative and protective finish on kitchen cabinets. They form strong, water resistant, attractive coatings 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 is conducting scoping analyses to gain a better understanding of emissions during curing and aging.

Because these coatings are reactive, they may release reaction byproducts during application and curing, 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 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.

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 which 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 steps 1 and 2; preliminary plans are being made to proceed, at least on a limited basis, with step 3; and step 4 is planned for the future.

Emission Testing and Test Method Development

Because conversion varnishes cure by chemical reaction, no existing standard test method provides a measure of their cure volatiles. There are, however, several test methods available for testing volatile emissions from coatings. Work on this project began with an investigation of these existing methods, and ways in which they could be modified to measure cure volatiles from conversion varnishes.

EPA Method 24 for VOCs. EPA Method 24 is used to determine VOC content of coatings¹. A number of American Society for Testing and Materials (ASTM) standard methods are incorporated by reference. For total volatile content², 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 minutes, 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 measured³ and subtracted from the total volatile matter to yield the total volatile organic content. Exempt solvents are determined⁴ 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 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 method for determining the HAPs in paints and coatings used in the wood furniture industry⁵. 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. In order 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 method⁶ was used to measure the formaldehyde in the as-received varnish.

Small Chamber Tests -- Curing in small environmental chambers. To measure the cure volatiles under realistic, but controlled conditions, small chamber tests are being conducted⁷. These tests are conducted using 53L 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 varnish, 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 are 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 x 9.2 cm, is coated using a slit applicator and then placed immediately into the environmental chamber. The air exiting the chamber is passed through adsorbent cartridges to collect the various compounds of interest. Hydrocarbons are collected on charcoal (high concentrations) or Tenax® (low concentrations), while aldehydes are collected on silica gel impregnated with dinitrophenylhydrazine (DNPH)⁸. The organics caught on the charcoal and Tenax® cartridges are desorbed and analyzed on a gas chromatograph/mass selective detector (GC/MSD) and/or a gas chromatograph/ion trap mass spectrometer. The DNPH-silica gel tubes are extracted and the extract analyzed on a high performance liquid chromatograph (HPLC).

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, are being investigated in this phase. Although all three systems selected included a stain step, it was decided to not include it in the project, at least not at this time. 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 allows 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 varnish. Glass was selected for this scouting test to eliminate the possibility of any confounding substrate effects.

The varnish 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 mass of formaldehyde emitted during this test was 25.3 mg, or 1% of the mass of varnish applied. Although the formaldehyde emissions did not fit a theoretically based mass transfer model, they did fit a second order decay model⁹ fairly well. (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:

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

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

E_0 = 29.0 $\text{mg}/\text{m}^2/\text{hr}$ is the initial emission factor;

k = 0.00361 m^2/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 varnish 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 model¹⁰ 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, the following five compounds were selected for analysis during the main test series: formaldehyde, isobutanol, m,p-xylene, o-xylene, and ethylbenzene.

Results to date from main test series. To date, tests have been completed on Coating System C, cured at room temperature. Systems A and B require elevated temperature for a portion of the sealer and topcoat drying cycles. 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 2 weeks. Results from the background tests (Tests 0, 1, and 2) 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 then the coupon was placed in the chamber. The coupon was removed 23 hours later 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 hour. The test coupon was removed, the topcoat was applied, 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 minutes during sealer cure (for the first hour only in Test 3) and every 15 minutes 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 first test series on Coating System C are summarized in Tables 4 and 5.

One of the major objectives of this research is 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 0.21 % free formaldehyde. Tables 4 and 5 show that emissions of formaldehyde are 6-700 % of the amount of free formaldehyde applied in the coating. Plots of cumulative formaldehyde emissions (in mg) versus time (Figures 2 and 3) show that formaldehyde is still being emitted 1500 hours (about 9 weeks) after the coating was applied. Typically, a kitchen cabinet will be placed in a home within 4 weeks after it is coated. Figure 4, a graph of chamber formaldehyde concentration as a function of time (since the coating was applied), shows that formaldehyde concentration is about 0.3 mg/m³ at the 1500 hour mark. One possible explanation for the continued evolution of formaldehyde is that the coating has not yet fully cured; polymerization is not complete. Biweekly samples will continue to be taken for several more weeks.

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).

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 several low-VOC/low-HAP coatings for testing in the chambers. The coatings selected would have to meet the Kitchen Cabinet Manufacturers Association criteria. Beyond this, the plan includes working with one or more furniture manufacturers to switch over to one of the low-VOC/low-HAP coating systems.

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

| <u>System Code</u> | <u>Description</u> | <u>Formaldehyde (%wt)</u> | <u>Free Volatiles (%wt)</u> |
|--------------------|---|-------------------------------|-------------------------------------|
| A sealer | Modified nitrocellulose (not a conversion varnish). | ND | 78.2 |
| A topcoat | Acid cure alkyd urea. | 0.15 | 66.1 |
| A catalyst | Added to topcoat 2% by volume immediately before application. | | NA |
| 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. | | 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. | | NA |

Table 2. Environmental chamber standard parameters.

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

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

| <u>Condition</u> | <u>Concentration, $\mu\text{g}/\text{m}^3$</u> | | | | |
|------------------|---|----------------|----------------|--------------------|----------------------|
| | <u>TVOC^a</u> | <u>Hexanal</u> | <u>Decanal</u> | <u>Acetic acid</u> | <u>2-Furaldehyde</u> |
| Empty chamber | 11.0 | 0.4 | 0.4 | 0.8 | 0.2 |
| Solid oak | 32.9 | 1.9 | 2.6 | 3.7 | 5.5 |
| Oak veneer | 15.8 | 2.3 | 2.5 | 1.0 | ND ^b |

a = total volatile organic compounds, including any exempt solvents, found in the sample; reported as toluene.

b = not detected.

Table 4. Mass balance for selected volatile organics and formaldehyde for Test 3, 1514 hours after coating application.

| <u>Compound</u> | <u>Emitted (mg)</u> | <u>Applied (mg)</u> | <u>Recovered (%)</u> |
|-----------------|---------------------|---------------------|----------------------|
| Isobutanol | 645 | 637 | 101 |
| Ethylbenzene | 253 | 317 | 80 |
| m,p-Xylene | 990 | 1261 | 78 |
| o-Xylene | 265 | 292 | 91 |
| All Xylenes | 1254 | 1553 | 81 |
| Formaldehyde | 67.4 | 10.5 | 642 |

Table 5. Mass balance for selected volatile organics and formaldehyde for Test 4, 1157 hours after coating application.

| <u>Compound</u> | <u>Emitted (mg)</u> | <u>Applied (mg)</u> | <u>Recovered (%)</u> |
|-----------------|---------------------|---------------------|----------------------|
| Isobutanol | 523 | 479 | 109 |
| Ethylbenzene | 193 | 243 | 79 |
| m,p-Xylene | 800 | 971 | 82 |
| o-Xylene | 175 | 226 | 77 |
| All Xylenes | 977 | 1197 | 81 |
| Formaldehyde | 56 | 7.9 | 709 |

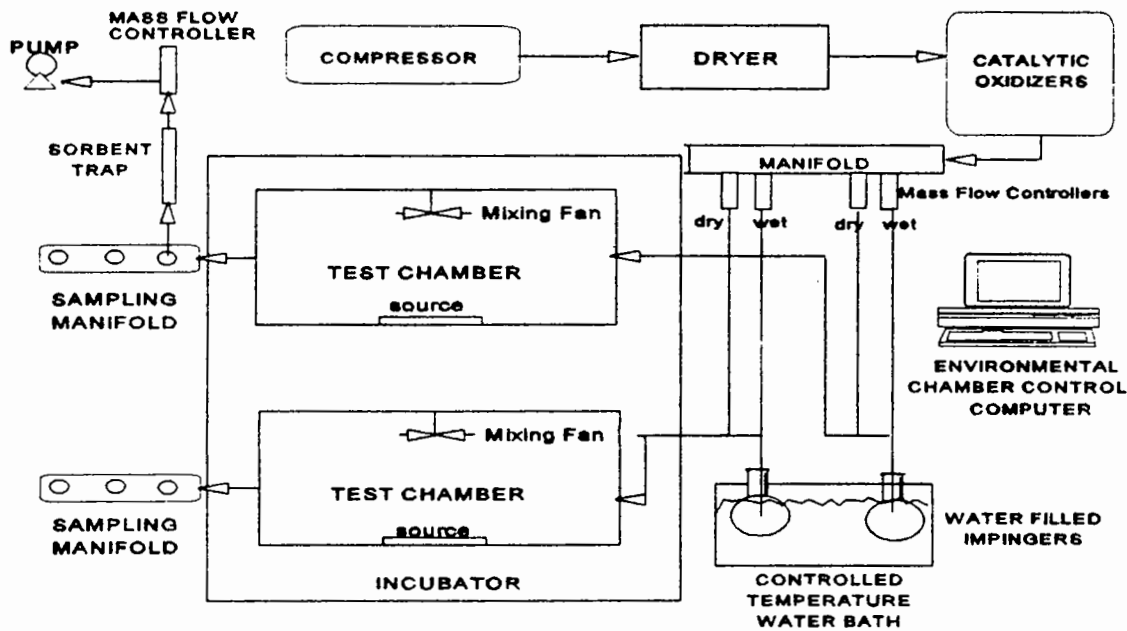


Figure 1. Schematic of small environmental test chambers.

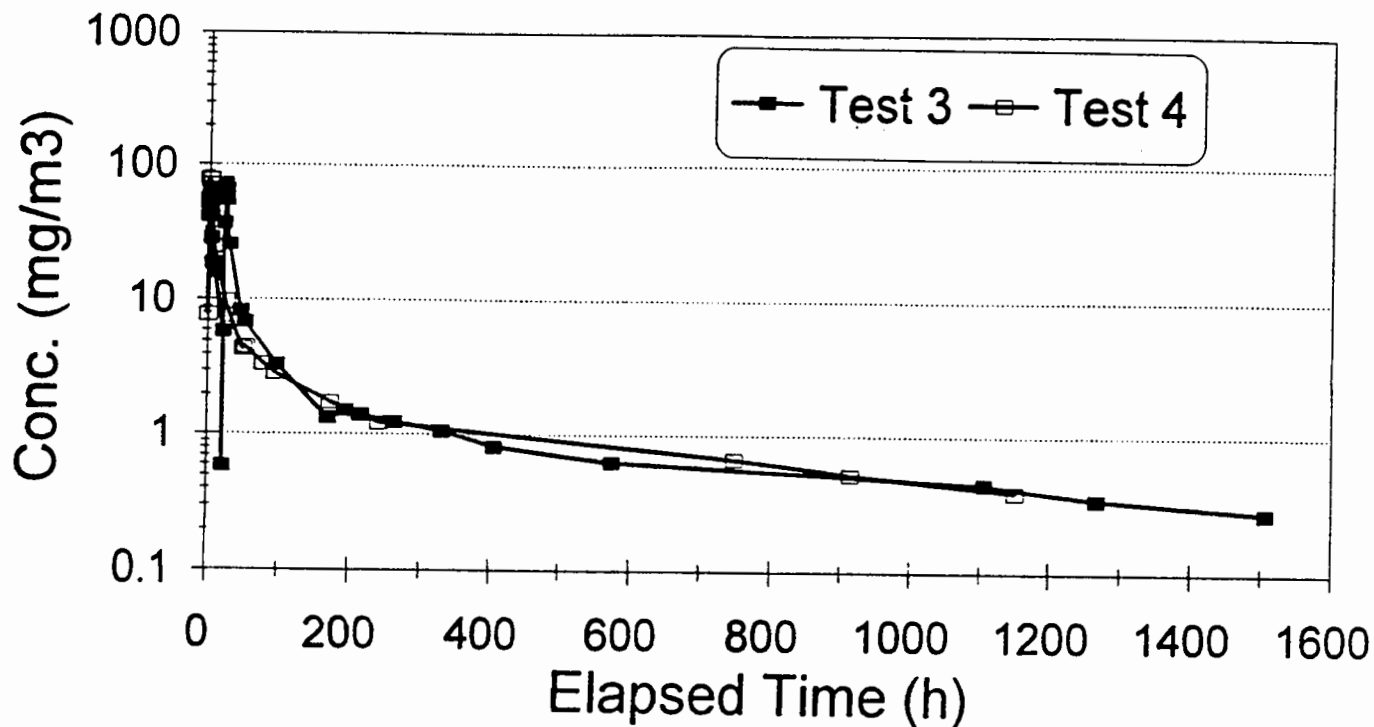


Figure 4. Comparison of formaldehyde concentrations in chamber exhaust for conversion varnish system C, room temperature drying. Test 3 = solid oak, Test 4 = oak veneer on hardboard.

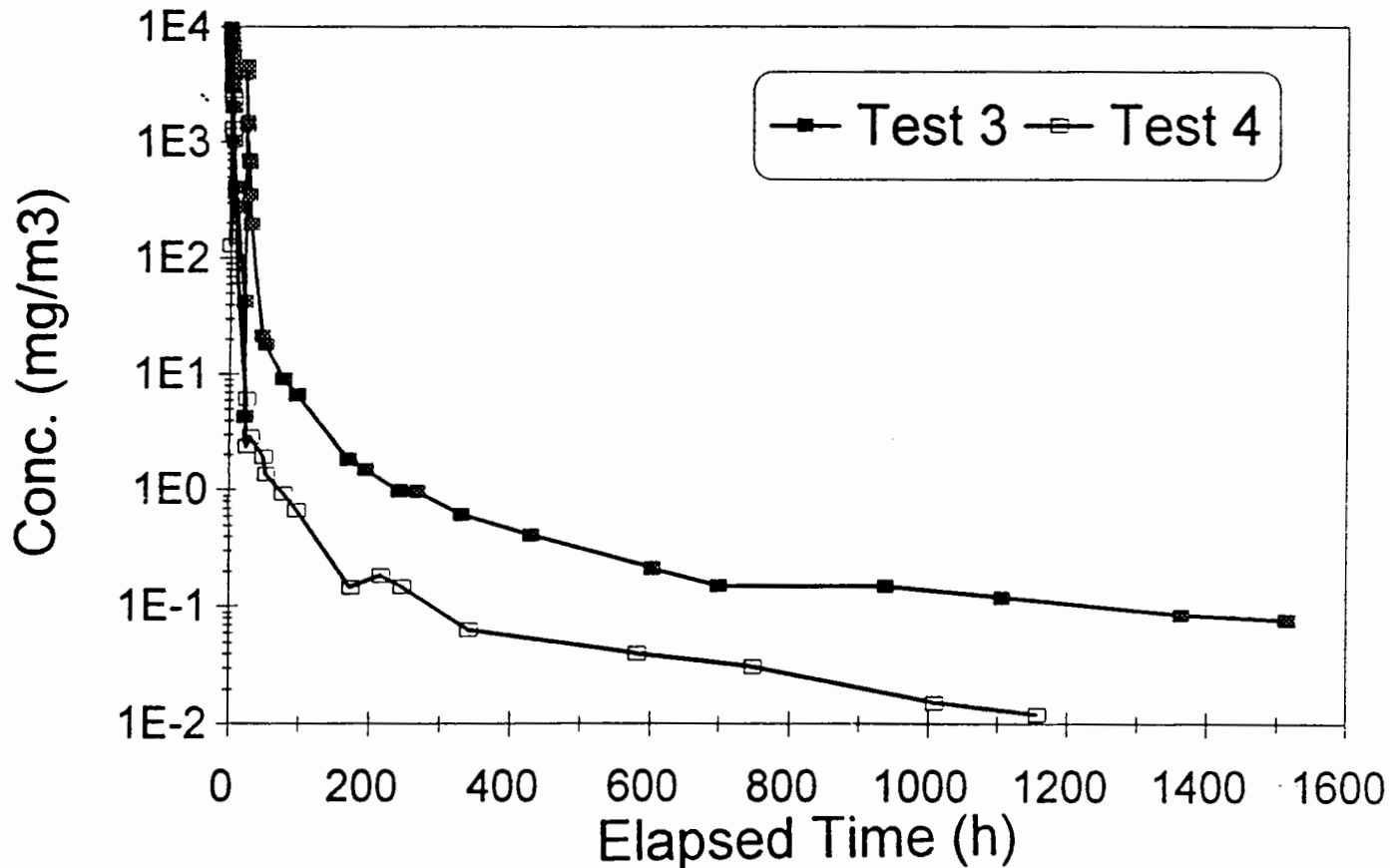


Figure 5. Comparison between m-p-Xylene concentrations in chamber exhaust over time, room temperature drying. Test 3 = solid oak substrate, Test 4 = oak veneer on hardboard substrate.

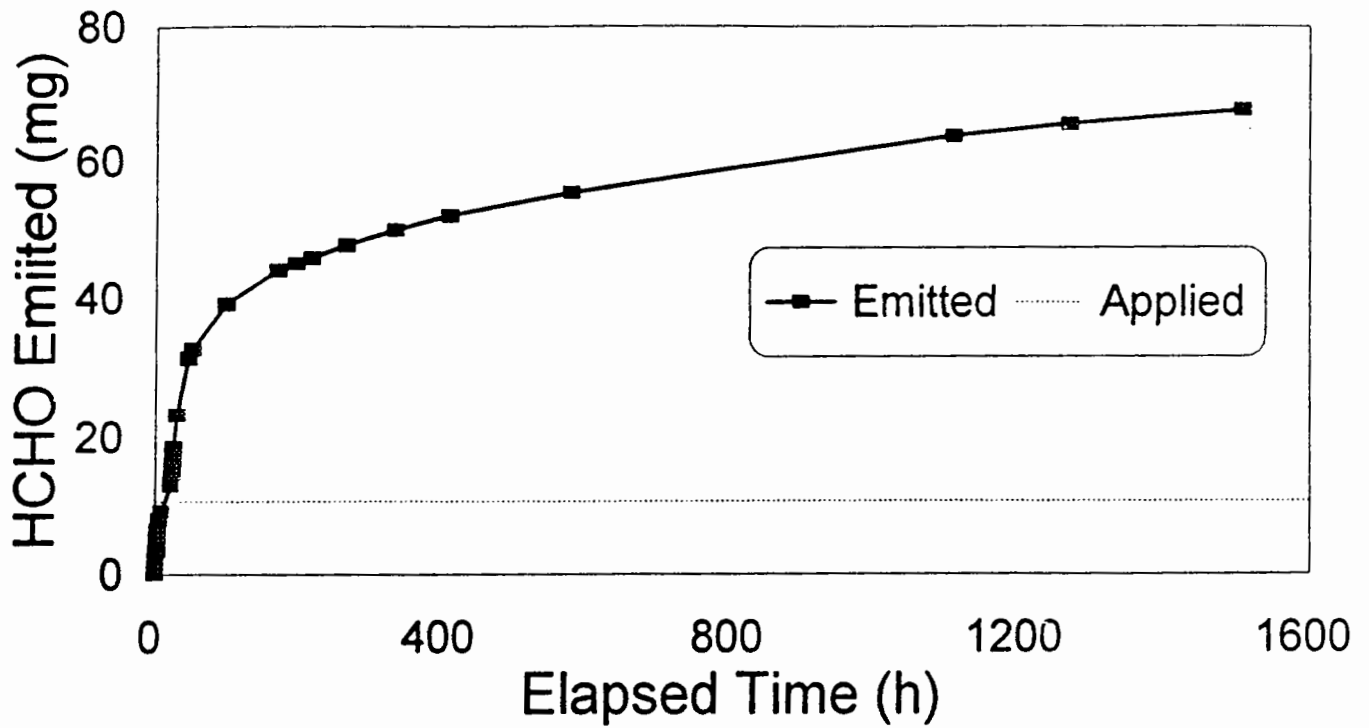


Figure 2. Cumulative formaldehyde (HCHO) emissions in Test 3, conversion varnish system C, room temperature drying. Total HCHO applied = 10.5 mg, total emitted = 67.4 mg.

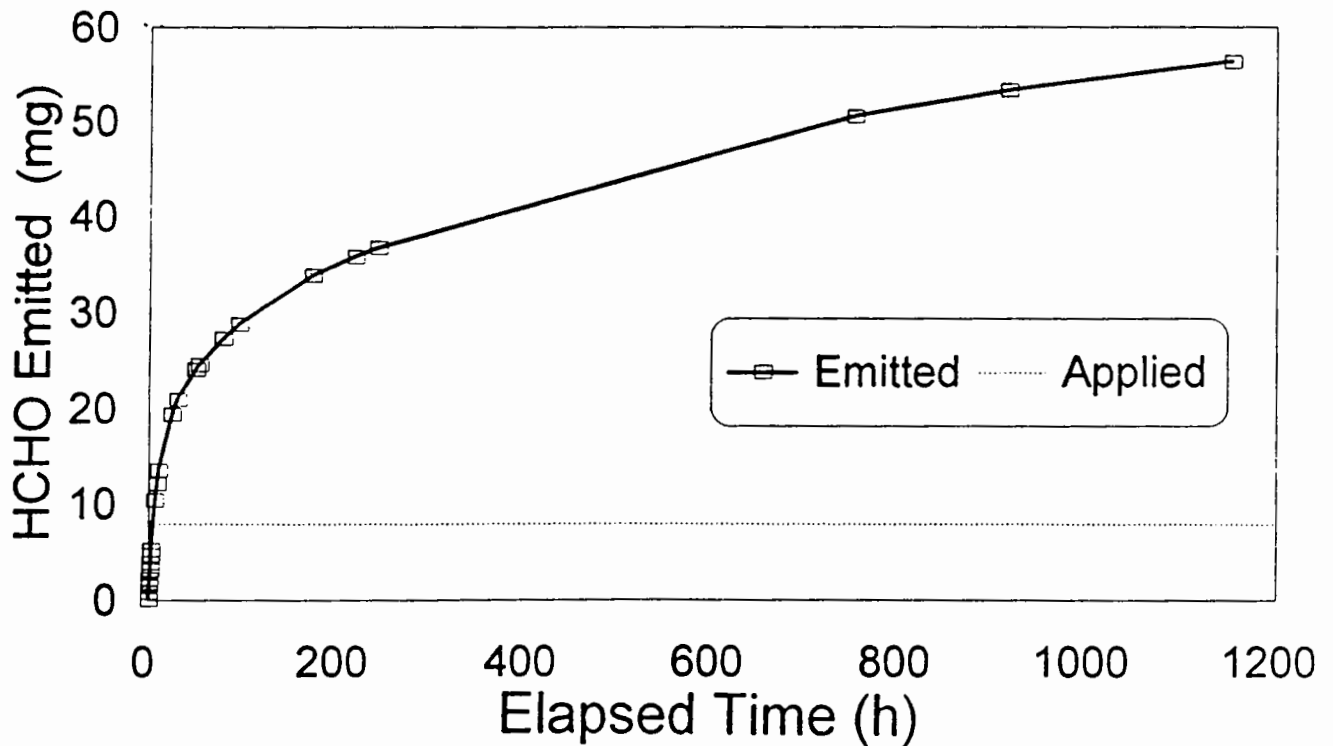


Figure 3. Cumulative formaldehyde (HCHO) emissions in Test 4, conversion varnish system C, room temperature drying. Total HCHO applied = 7.9 mg, total emitted = 56.0 mg.

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