Indoor Emissions from Conversion Varnishes

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ABSTRACT

Conversion varnishes are two-component, acid-catalyzed varnishes that are commonly used to finish cabinets. They are valued for their water and stain resistance, as well as their appearance. They have been found, however, to contribute to indoor emissions of organic compounds. For this project, three commercially available conversion varnish systems were selected. A U.S. Environmental Protection Agency (EPA) Method 24 analysis was performed to determine total volatile content, and a sodium sulfite titration method was used to determine uncombined (free) formaldehyde content of the varnish components. The resin component was also analyzed by gas chromatography/mass spectroscopy (GC/MS) (EPA Method 311 with an MS detector) to identify individual organic compounds. Dynamic small chamber tests were then performed to identify and quantify emissions following application to coupons of typical kitchen cabinet wood substrates, during both curing and aging. Because conversion varnishes cure by chemical reaction, the compounds emitted during curing and aging are not necessarily the same as those in the formulation. Results of small chamber tests showed that the amount of formaldehyde emitted from these coatings was 2.3–8.1 times the amount of free formaldehyde applied in the coatings. A long-term test showed a formaldehyde emission rate of 0.17 mg/m²/hr after 115 days.

INTRODUCTION

Wood and wood-veneered kitchen cabinets present a unique finishing challenge. The finish must be not only attractive, but also resistant to water and the many different detergents and foods that may be spilled onto it during use. Conversion varnishes, widely used to provide a decorative and protective finish on kitchen cabinets, form strong, water-resistant, attractive coatings. Also referred to as acid-catalyzed varnishes, these coatings contain amino cross-linking agents, such as melamine formaldehyde or urea formaldehyde. The cross-linking reaction is catalyzed with a strong acid, such as para-toluene sulfonic acid.

Because conversion varnishes cure by chemical reaction, they may release reaction byproducts during application and curing, as well as during their use in the indoor environment. These byproducts contribute to chemical emissions from the manufacturing facilities as well as into the household indoor air. Although many chemicals may be emitted, formaldehyde is of particular interest. It is a hazardous air pollutant (HAP),[1] a probable carcinogen, and an irritant.[2] In addition, because formaldehyde may be formed by the reaction that occurs after the coating is applied, its emissions cannot be estimated from formulation information.

In response to questions about the amount of these emissions, both to the ambient air and to the indoor environment, the U.S. Environmental Protection Agency's (EPA) Indoor Environment Management Branch (IEMB) has undertaken a research project. Its purpose is to try to understand the amount of chemical emissions from these varnishes, and the duration of their release. The overall objectives of this project were to:

(1) develop methods to measure cure and aging emissions from conversion varnishes;

(2) measure emissions from several commonly used

IMPLICATIONS
Results of small chamber tests confirmed that the amount of free formaldehyde contained in three conversion varnishes was just a fraction of the total amount of formaldehyde emitted from the varnished surfaces, implying that formaldehyde is formed as a result of the curing reaction. Nonetheless, formaldehyde emissions make up only a small portion of total organic emissions. The remainder result from solvent evaporation. A long-term test showed a formaldehyde emission rate of 0.17 mg/m²/hr at 115 days, which has the potential to create elevated concentrations in indoor environments.

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conversion varnishes to gain an understanding of their amount, duration, and composition; and

(3) compare these emissions to the coating systems' formulations to determine to what extent the composition of a coating system might be useful for estimating total emissions to the indoor and outdoor atmospheres.

VARNISHES TESTED

Three commercially available conversion varnish coating systems (hereafter referred to as A, B, and C) were selected for evaluation. A coating system includes all the products used for every step in the coating process. For this project, short coating systems, which consist of stain, sealer, and topcoat, were investigated. Although all three systems selected included a stain, the stain was not evaluated in this 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. It is not uncommon for a manufacturer to use one of these coating systems without a stain, for a light-colored (natural) wood finish. The three coating systems are described, using manufacturer-supplied data, in Table 1.

EXPERIMENTAL METHODS

Because conversion varnishes cure by chemical reaction, no existing standard test method will provide a measure of their cure volatiles. However, several test methods are 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. Note that the emissions measured during this project include both those that would occur within the manufacturing facility and those that would occur during use in the consumer's home.

Volatile Organic Compound (VOC) Content of Coating, Before Mixing and Application

EPA Method 24 for VOCs. EPA Standard Method 24,[3] used to evaluate compliance with ambient air pollution standards, is a method for measuring volatile emissions from coatings. This test was included in this project because of its use as a measurement of organic emissions to the ambient air, and because one of the goals of this research was to gain an understanding of the ambient air emissions from conversion varnishes. It provides a point of comparison for understanding the contribution of any formaldehyde emitted to the total regulated VOC emissions.

For total volatile content,[4] a 0.5-gram sample of the coating, in 3 mL of solvent, is placed in an open aluminum weighing dish with a magnetic stirring bar, heated to 110 °C for 60 min, then cooled and reweighed. The weight gives the amount of non-volatile matter. The volatile content of the sample, which includes VOCs that are regulated under U.S. Ambient Air Quality Standards, exempt solvents, and water, is determined by difference. Then the water content is measured[5] and subtracted from the total volatile matter to yield the total volatile organic content. Exempt solvents are determined[6] and subtracted from the total volatile organic content to arrive at the regulated VOC content. The solids content is determined from the manufacturer's formulation, and the regulated VOC content is expressed as weight of VOCs per weight of solids. Each varnish was analyzed in duplicate. This method measures only the VOC content of the varnish components, and does not account for any emissions created by chemical reaction during cure.

Table 1. Manufacturers' data on the three coating systems.

Coating System	Type	Volatile	Reduction (dilution)	Recommended Film Thickness	Drying
A-Sealer	modified nitrocellulose	78.63% by volume	N/A	3-4 mils (wet)	5 min air dry + 15 min @ 125 °F (52 °C) + 10 min ambient cool
A-Topcoat	acid-cure alkyd urea	71.14% by volume	N/A	4-6 mils (wet)	20 min air dry + 20 min @ 150 °F (66 °C)
B-Sealer	modified alkyd amino, acid-cure	71.75% by volume	N/A	3-4 mils (wet)	15 min air dry +15 min @ 1 135 °F (57 °C)
B-Topcoat	modified alkyd amino, acid-cure	63.18% by volume	N/A	3-4 mils (wet)	15 min air dry + 15 min @ 135 °F (57 °C)
C-Sealer	acid-cure, resin unspecified	501 g/L	up to 50% by volume w/toluene or xylene	3-4 mils (wet); 0.75-1 mil (dry)	30-60 min @ 77 °F (25 °C) + 50% RH
C-Topcoat (same as sealer)	acid-cure, resin unspecified	501 g/L	up to 25% w/toluene, xylene, or high flush naphtha	3-4 mils (wet); 1-1.3 mils (dry)	30-60 min @ 77 °F (25 °C) + 50% RH

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) are not measured.

EPA Method 311 for HAPs.[7] Method 311 is a method for identifying and quantifying the HAPs in paints and coatings used in the wood furniture industry. 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 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 was used with an MS detector to obtain an analysis of the bulk varnish (resin component). The acid catalyst was not analyzed.

Determination of free formaldehyde in the varnish formulation. In order to ascertain any relationship between the formaldehyde content of the varnish and the formaldehyde emitted in the cure volatiles, a sodium sulfite titration method[8] was used to measure the formaldehyde in the as-received varnish (resin component only). This method is based on the quantitative liberation of sodium hydroxide when formaldehyde reacts with sodium sulfite:

$$HCHO + Na_2SO_3 + H_2O \longrightarrow NaOH + HOCH_2SO_3Na$$

$$(1)$$
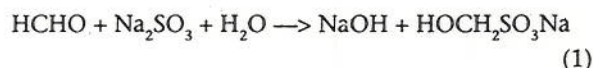
Small Chamber Tests

To measure the cure volatiles under realistic, but controlled, conditions, small chamber tests were conducted.[9] These tests, commonly used for indoor air quality studies, were conducted in 53-L stainless steel chambers. For the experiments in this study, a substrate, measuring 29.5×9.2 cm, was coated with the sealer (using a slit applicator) and then placed immediately into the chamber. The amount of each coating applied is shown in Table 2. The substrates used in these tests were glass, oak-veneered hardboard, and solid oak board. Clean air, at a controlled temperature and humidity, flowed through the chamber at a controlled rate. Samples of the air exiting the chamber were collected on sorbent cartridges for analysis of the various compounds of interest. After the sealer cured, the coupon was removed from the chamber and coated with the topcoat, then returned to the chamber. All

Table 2. Amounts of coating applied for each test.

Varnish System	Test Name	Amount of Sealer Applied (g)	Amount of Topcoat Applied (g)
A	—	4.2	3.8
B	—	2.0	1.7
C	test 1	3.2	2.5
C	test 2	2.6	1.7

cure times and temperatures followed manufacturers' recommendations, shown in Table 1.

Two of the three conversion varnish systems required an elevated temperature drying period for both the sealer and topcoat. In order to simulate the manufacturers' recommended curing conditions, one chamber was outfitted with a heating jacket. Three thermocouples were strategically placed inside the chamber to monitor the temperature of the chamber air, the substrate surface, and the internal temperature of the substrate. The chamber air temperature was monitored in the center of the chamber directly below the mixing fan. Five air exchanges per hour (ACH) of fresh air were passed through the elevated temperature curing chamber to simulate the higher-than-residential air exchange expected in the cure oven of a manufacturer. After the cure period, the substrate was removed from the heated chamber and placed in a chamber operated at room temperature. See Table 1 for the cure temperature regime used for each coating.

Hydrocarbons were collected on charcoal (high concentrations)[10] or Tenax (low concentrations),[11] while aldehydes were collected on silica gel impregnated with dinitrophenylhydrazine (DNPH).[12] The organics collected on the Tenax cartridges were thermally desorbed, preconcentrated, and analyzed by GC. Individual VOCs were quantified with GC/FID (Flame Ionization Detector), using a compound-specific response factor. Individual compounds were identified using calibration retention times and verified with a model 5970 Hewlett Packard mass selective detector (MSD). The samples collected on charcoal were extracted according to the Activated Charcoal Tube Adsorption Method[10] using a 1% isopropanol/carbon disulfide eluent, and analyzed on a Varian Saturn 3 GC/MS ion trap. The DNPH-silica gel tubes were extracted and the extract analyzed on a high-performance liquid chromatograph (HPLC).

A set of tests was run using varnish C on three different substrates to determine whether there was a significant effect of substrate on varnish emissions. Because emissions from all three tests were very similar, oak was used for the remaining tests. The oak board provided a realistic substrate with fewer potentially confounding

emissions than the veneered hardboard. The edges of the board were coated with sodium silicate before use.

RESULTS

VOC Content of Coating, Before Mixing and Application

EPA Method 24 for VOCs. The volatile matter content of the three coating systems, as stated by the coating manufacturers in their Material Safety Data Sheets (MSDSs) and as measured by EPA Method 24, is shown in Table 3. The volatile content ranged from 59.1 to 78.2% by weight. Note that volatile content would increase if the cabinetmaker reduced (diluted) the coating by adding solvent, as suggested for varnish C. The amount of solvent added varies between manufacturers to achieve the optimum viscosity for each manufacturer's application equipment. The Method 24 results agreed well with data provided by the coating manufacturers on the MSDSs.

EPA Method 311 for HAPs. The speciated VOC content of the three varnish systems, determined using EPA Method 311 (proposed), is shown in Table 4.

Determination of free formaldehyde in the varnish formulation. The free formaldehyde content of the uncatalyzed varnishes ranged from 0.15 to 0.54% by weight (Table 5). The sealer for Varnish A contained no free formaldehyde because it is not a conversion varnish. It is a nitrocellulose-based product.

Effect of Substrate

Varnish C was applied to three different substrates: glass, oak board, and oak-veneered hardboard. The data for the glass substrate are from an initial test, in which a different lot of Varnish C was used. One lot was used for all the other tests. No significant substrate effect was observed for formaldehyde emissions (Figures 1 and 2). The effect of substrate on emissions of total xylenes is shown in Figures 3 and 4. There may be a small effect of substrate over the long term (100 hr and longer), but the effect is of little significance for

Table 4. Varnish VOC content by Method 311 with MS detector (in mg/g coating).

| | Varnish A | | Varnish B | | Varnish C |
	Sealer	Topcoat	Sealer	Topcoat	Sealer/Topcoat
methyl ethyl ketone	–	37.6	0.04	26.7	0.48
isobutanol	62.2	44.2	169	367	127
n-butanol	26.4	191	1.43	11.6	2.69
methyl isobutyl ketone	–	69.8	–	0.72	4.26
toluene	50.8	9.82	203	38.0	3.60
ethyl benzene	3.29	29.7	13.0	14.2	44.6
m-xylene	–	138	41.2	43.0	–
o-xylene	2.73	29.3	10.4	12.2	34.0
p-xylene	8.52	–	–	–	177
1,2,4-trimethylbenzene	–	0.03	0.08	0.24	0.34
isobutyl acetate	248	–	–	–	–
nonane	8.31	–	–	–	0.86
decane	–	–	–	–	0.13
other (as toluene)	–	64.7	75.0	316	–
TVOC	410	614	513	830	39

solvent VOCs, as the majority are emitted within 24 hr of varnish application.

Formaldehyde Emissions

Cumulative emissions of formaldehyde from the three varnishes are shown in Figure 5. Note that the early emissions are generated within the manufacturing plant, and would not be a part of the residential indoor emissions. According to a cabinet manufacturer and the Kitchen Cabinet Manufacturers' Association, the product would likely be installed in a residence about one month (720 hr) after coating. Emissions from that point onward would be into the residential environment.

A comparison of the amount of formaldehyde emitted from the coatings to the amount of formaldehyde applied in the varnish is shown in Table 6. It is apparent that the amount of formaldehyde emitted exceeds the amount applied, implying that formaldehyde is formed as a result of chemical reaction. The ratio of formaldehyde emitted to

Table 3. Volatile matter content (weight %) determined with Method 24.

Product	Mean, Method 24	Material Safety Data Sheet
Varnish A/Sealer	78.2	78.6
Varnish A/Topcoat	66.1	63.3
Varnish B/Sealer	73.0	71.0
Varnish B/Topcoat	64.0	62.3
Varnish C	59.1	51.7

Table 5. Free formaldehyde content in uncatalyzed varnish (weight %).

Product	% Free HCHO	Manufacturer's Estimate (%)
Varnish A/Sealer	a	a
Varnish A/Topcoat	0.146	< 0.2
Varnish B/Sealer	0.491	0.101
Varnish B/Topcoat	0.535	0.125
Varnish C	0.211	< 1

[a]Varnish A/Sealer does not contain any free formaldehyde because it is a nitrocellulose-based product.
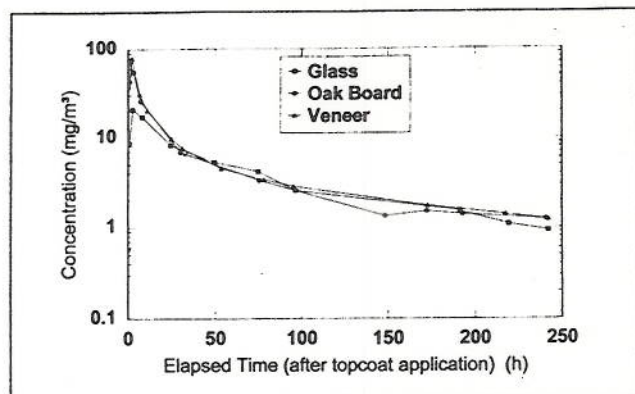
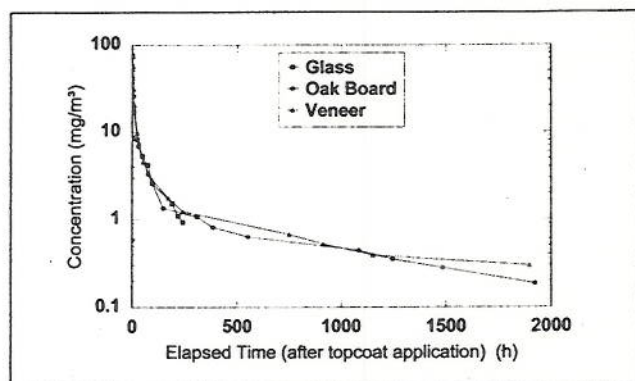**Figure 1.** Effect of substrate on formaldehyde emissions (short term).

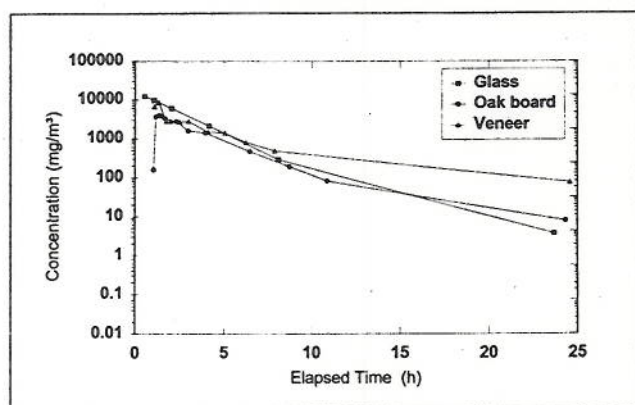**Figure 2.** Effect of substrate on formaldehyde emissions (long term).

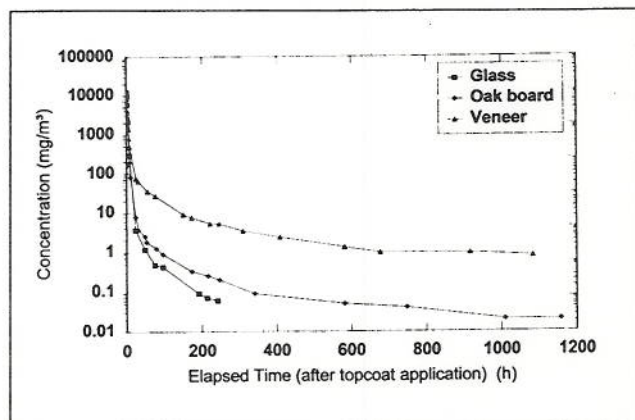**Figure 3.** Effect of substrate on xylene emissions (short term).

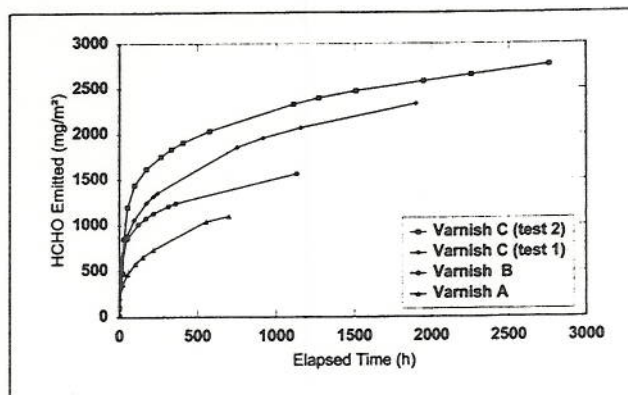**Figure 4.** Effect of substrate on xylene emissions (long term).

Figure 5. Cumulative emissions of formaldehyde.

formaldehyde applied was between 2.3 and 8.1. There was no indication that the total amount of formaldehyde emitted had any direct relationship to the amount of free formaldehyde in the formulation.

The three varnishes follow a very similar formaldehyde emission pattern (Figures 6 and 7). Figure 7 shows that the emission rate drops quickly in the first couple hundred hours (about eight days), then declines much more slowly over the longer term. Even 2,762 hr (about 115 days) after application, the formaldehyde emission rate from Varnish C is still 0.17 mg/m²/hr. For comparison purposes, the emission rate (0.13 mg/m²/hr) corresponding to the concentration-based standard (0.2 ppm) in Section 308 of the U.S. Department of Housing and Urban Development (HUD) standard[13] for plywood (0.2 ppm) is shown on Figure 7. The standard's chamber concentration was converted into an emission rate according to the emission rate equation and chamber conditions provided in American Society for Testing and Materials (ASTM) E1333-96,[14] with product loading as specified in the section 406 of the HUD standard.

These long-lasting formaldehyde emissions may cause elevated concentrations in indoor environments. To assess this, an exposure model[15,16] was used. The hypothetical scenario that was modeled is: A set of kitchen cabinets with an HCHO emission rate of 0.5 mg/m²/hr, the approximate rate 42 days after conversion varnish application, are installed in a typical house (300 m³ volume). The predicted indoor concentrations as a function of air-exchange rate (AER) are shown in Figure 8. At 0.5 ACH, the indoor HCHO concentrations resulting from emissions from this source were predicted to be 16 µg/m³ (12 ppb) for a source area of 5 m², and 67 µg/m³ (50 ppb) for a source area of 20 m². For comparison, the irritation threshold used in the EPA's risk assessment for formaldehyde is 100 ppb[2]. The projected concentrations in the hypothetical house are below, but very close to, the irritation threshold. If other sources of formaldehyde emissions are present, such as composite wood products, or if a house has lower air exchange or higher cabinet loading, the concentration might be even higher.
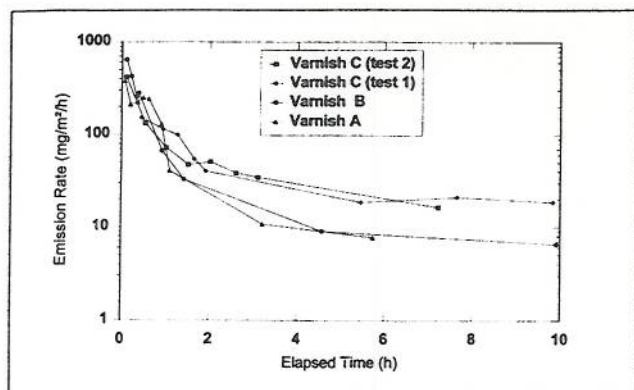
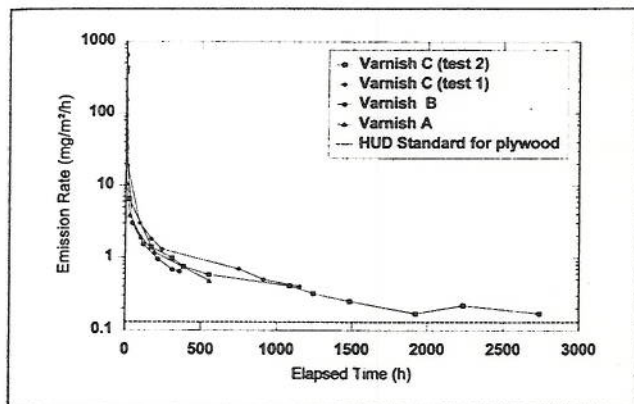**Figure 6.** Short-term formaldehyde emission rates.

Figure 8. Predicted formaldehyde concentration in a 300 m³ house.

Figure 7. Long-term formaldehyde emission rates.
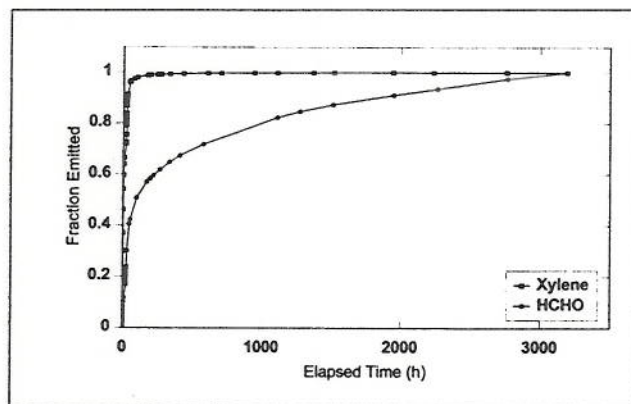
Figure 9. Relative cumulative emissions of formaldehyde and xylene.

Comparison of Emissions Between Formaldehyde and Other VOCs

Emissions of solvents from coatings usually occur by a fast process. In the case of the conversion varnishes in this study, more than 90% of solvent VOCs are released in the first several hours. For formaldehyde, however, the emission rate declines much more slowly. As an illustration, Figure 9 compares the relative cumulative emissions (i.e., the total amount emitted is normalized to 1 for each compound) for xylene and formaldehyde for one test.

Table 6 shows the total amount of formaldehyde applied and emitted during testing, as well as the amount of total VOC applied. It is obvious from the table that the formaldehyde emissions constitute only a minor portion of the total organic emissions from these products.

CONCLUSION

Methods and protocols were developed for measuring emissions from conversion varnish coatings. A small chamber method was developed for measuring emissions from the varnishes during elevated temperature curing. The system provided reasonable temperature control and may be useful for testing with other products.

No mechanistic model was investigated for predicting formaldehyde emissions from conversion varnishes.
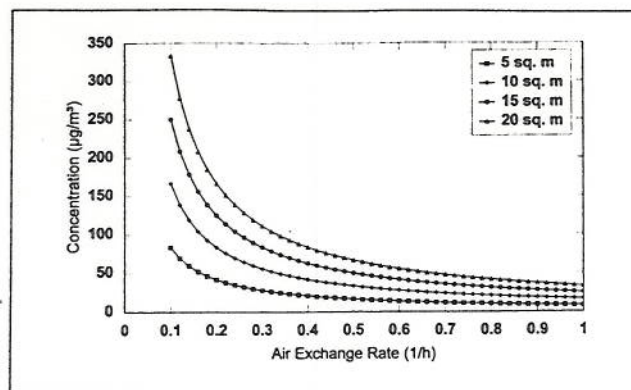
Since the underlying reaction mechanisms have not been worked out, it is not possible to determine the time course of emissions after the test period, or to predict when emissions will either cease or fall below some specified level.

This project has provided a better understanding of the characteristics of emissions from conversion varnishes including the types of compounds emitted, the magnitude of their emissions, and the profile of the emissions.

Table 6. Amount of formaldehyde emitted versus amount of formaldehyde and VOC applied.

Varnish	A	B	C (Test 1)	C (Test 2)
Free HCHO applied (mg)	5.59	18.8	7.9	10.5
HCHO emitted (mg)	30.0	42.6	63.6	77.2
Ratio of HCHO emitted to applied	5.4	2.3	8.1	7.4
Amount of VOC applied (Method 24) (mg)	5790	2550	2540	3250
Ratio of HCHO emitted to VOC applied (Method 24)	0.005	0.017	0.025	0.024
Amount of VOC applied (Method 311)	4050	2450	1919	2250
Ratio of HCHO emitted to VOC applied (Method 311)	0.007	0.017	0.033	0.034
Duration of test (hr)	697	1128	1755	3194

The only relationship that was found between the free formaldehyde content of the varnish and the total amount emitted was that the total amount emitted was greater than the formaldehyde content of the varnish. The amount of formaldehyde generated is most likely a function of the product formulation and, possibly, cure conditions, and can be expected to vary from product to product.

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