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Characterization of Emissions of Volatile Organic Compounds from Interior Alkyd Paint

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ABSTRACT

Alkyd paint continues to be used indoors for application to wood trim, cabinet surfaces, and some kitchen and bathroom walls. Alkyd paint may represent a significant source of volatile organic compounds (VOCs) indoors because of the frequency of use and amount of surface painted. The U.S. Environmental Protection Agency (EPA) is conducting research to characterize VOC emissions from paint and to develop source emission models that can be used for exposure assessment and risk management. The technical approach for this research involves both analysis of the liquid paint to identify and quantify the VOC contents and dynamic small chamber emissions tests to characterize the VOC emissions after application. The predominant constituents of the primer and two alkyd paints selected for testing were straight-chain alkanes (C9–C12); C8–C9 aromatics were minor constituents. Branched chain alkanes were the predominant VOCs in a third paint. A series of tests were performed to evaluate factors that may affect emissions following application of the coatings. The type of substrate (glass, wallboard, or pine board) did not have a substantial impact on the emissions with respect to peak concentrations, the emissions profile, or the amount of VOC mass emitted from the paint. Peak concentrations of total volatile organic compounds (TVOCs) as high as 10,000 mg/m^3 were measured during small chamber emissions tests at 0.5 air exchanges per hour (ACH). Over 90% of the VOCs were emitted from the primer and paints during the first 10 hr following application. Emissions were similar from paint applied to bare pine board, a primed board, or a board previously painted with the same paint. The impact of other variables, including film thickness, air velocity at the surface, and air-exchange rate (AER) were consistent with theoretical predictions for gas-phase, mass transfer-controlled emissions. In addition to the alkanes and aromatics, aldehydes were detected in the emissions during paint drying. Hexanal, the predominant aldehyde in the emissions, was not detected in the liquid paint and was apparently an oxidation product formed during drying. This paper summarizes the results of the product analyses and a series of small chamber emissions tests. It also describes the use of a mass balance approach to evaluate the impact of test variables and to assess the quality of the emissions data.

IMPLICATIONS

This research demonstrates that alkyd paints, which typically contain over 30% by weight of predominantly hydrocarbon solvents, can be significant sources of VOCs in indoor environments, but that the exposures to these compounds are predicted to be of relatively short-term duration. The data show that over 90% of the VOCs in alkyd paint are emitted during the first 10 hr following application and that nearly all of the VOCs are recovered during a two-week emissions test. The effects of gypsum board and wood substrates on VOC emissions from alkyd paints are shown to be negligible. This is in sharp contrast to previously reported emissions test results that showed that during a two-week period following application of a latex paint to gypsum board only approximately 20% of the oxygenated solvents in the water-based paint were recovered, indicating that exposures would occur over extended durations. The results of this research project also demonstrate the application of mass balance calculations to evaluate and validate small chamber emissions test results.

INTRODUCTION

Building materials are recognized as important sources of indoor air contaminants.[1] Although some building materials are relatively minor sources, paint may represent a significant source of indoor air contaminants because of the volume of paint used and the frequency of re-application

during the life of a building. Despite a trend toward increased use of water-based architectural coatings, alkyd paints are still used for some applications. The U.S. Environmental Protection Agency (EPA) has evaluated wall paint as a source of indoor air pollution under the Indoor Air Source Characterization Project (IASCP).[2] Alkyd paint, which usually contains greater than 30% by weight of organic solvents, has been identified in the Source Ranking Database (SRD) developed under the IASCP as a potentially significant source of indoor air pollution.

Emissions of VOCs have been determined for a number of different coatings. Wolkoff[3] cited 13 references on emissions of VOCs from lacquer, paint, and varnish in his review of sources and emissions of VOCs. Tichenor[4] reported major organic compounds in a variety of building materials, including polyurethane finish, latex paint, and wood stain. Products with petroleum-based solvents contained alkanes (nonane, decane, undecane), substituted alkanes, and aromatics. Emissions data have been reported for wood stain,[5] varnish,[6] latex paints,[7] and alkyd paints.[8] Data from these studies have been used to develop methods and models for predicting VOC emissions from coatings used indoors.[9,10]

Alkyd paint was selected for testing because of the potential exposure of painters and building occupants to high VOC concentrations following application. Alkyd paint continues to be used indoors because of desirable properties such as durability, gloss, gloss retention, and fast drying. The volatile portion of alkyd paints consists of aliphatic and aromatic hydrocarbons that serve as the solvents. The solvents function to dissolve the film-former, reduce the solution or emulsion to proper solids content and proper viscosity, and control the rate of film formation by their evaporation rate. The solvents are generally straight-chain petroleum fractions and may contain some aromatics.

This paper describes the technical approach for characterizing emissions from interior alkyd paints, results of analyses of the liquid product, and VOC emissions following application. Results are presented for a series of tests performed to evaluate factors that may impact emissions of VOCs from paints. The paper also describes the use of a mass balance approach to evaluate emissions test results.

TECHNICAL APPROACH AND TEST METHODS

Technical Approach

The technical approach used in this project for characterizing emissions from alkyd paints involved both the analyses of the liquid coatings and measurement of the emissions following application to a substrate. The concentrations of the predominant VOCs in the liquid product are not generally reported as part of emissions characterization projects. However, use of this approach allows the researcher to evaluate the emissions test results using a mass balance approach, as described in a following section. The analyses of the liquid product were performed using gas chromatography/mass spectrometry (GC/MS) to identify the VOCs in the paint that were most likely to be emitted following application. The GC/MS measurement results were used to develop the final design of the small chamber emissions tests, including selection of sampling methods, and to develop the test protocols (e.g., sampling frequency and sample volume).

Product Analysis by GC/MS

One alkyd primer and three alkyd enamel paints were purchased at local retail outlets for the research program. All four products were commercially available and typical of products that would be purchased by homeowners for application to walls or woodwork in residences. The liquid products were analyzed by GC/MS to identify and quantify VOCs in the liquid product. The extraction and analysis method was based on EPA Method 311,[11] but the analysis was not limited to quantification of only the hazardous air pollutants (HAPs) regulated under the Clean Air Act. The method was used to quantify predominant VOCs in the product with a boiling point of approximately 35–250 °C. The coatings were extracted by diluting 1 g of paint with 10 mL of methylene chloride. The sample was shaken for several min, then centrifuged for 5 min to remove the solids. The supernatant was analyzed by GC/MS. Compound identification was performed by matching spectra using the National Institute of Standards and Technology (NIST) mass spectra library. Following identification of the predominant peaks and calibration of the GC/MS, triplicate aliquots of each coating were analyzed to quantify the concentration of 15–20 of the predominant VOCs. Blanks (solvent) and spiked controls were analyzed as part of the quality assurance program.

Small Chamber Emissions Test Methods

Small chamber emissions tests were performed to measure the emission rates of the selected VOCs from the primer and paints following application to test substrates. Small chamber test methods are described in the American Society for Testing and Materials (ASTM) *Standard Guide for Small-Scale Environmental Chamber Determination of Organic Emissions From Indoor Materials/Products*, ASTM D5116.[12] The emissions tests were performed using 53-L stainless steel chambers housed in a temperature-controlled incubator. A clean air system with particle filters and catalytic oxidizers supplies VOC-free air to the chambers. Relative humidity (RH) is controlled by blending dry air and humidified air. All airflows are controlled by mass flow controllers. A data acquisition system continuously logs airflow rates, temperature and RH in the chamber, and RH in the inlet air. The emissions chamber operating

conditions for the 15 tests conducted for this project were as follows:

- Temperature: 23 ± 0.5 °C ;
- Relative humidity: 50 ± 5% (chamber inlet air);
- Air-exchange rate: 0.5 ± 0.5 hr^{-1}, for a nominal ventilation rate of 0.442 L/min; and
- Air speed: 10 cm/sec (nominal) at 1 cm above the surface of the test substrate.

The substrates for the tests were glass, new gypsum board, or white pine board. The gypsum board and pine board were cut to a size of 16 × 16 cm for a total area of 0.0256 m^2, which gave a loading factor of approximately 0.5 m^2/m^3 in the 53-L chamber. The edges of the test specimens were sealed with sodium silicate. The bottom of the substrates were not sealed; the substrate was placed on the floor of the chamber during the test. The substrates were conditioned in a chamber at 23 °C and 50% RH for at least 24 hr prior to application of the primer. The primer and paint were applied to the top surface of the gypsum board or pine board substrates with paint rollers purchased at a local retail outlet. The average mass applied was 2.8± 03 g/256 cm^2 (89-µm wet film thickness) for the primer and 2.3±0.3 g/256 cm^2 (68-µm wet film thickness) for the paint. The application rates were slightly lower than the manufacturer's recommended rates for wet film thickness of 100 mm for the primer and 76 mm for the paint, but were realistic based on application method and visual observation. Paint was applied to the glass with a slit applicator. The slit applicator does not work well with substrates whose edges are sealed with sodium silicate because of the rough edge. The paint roller method has been demonstrated to provide reproducible film applications on realistic substrates and it allows scale-up with the same application method for tests in large chambers or full-scale test rooms or houses. Standardized methods were followed for gravimetric determination of the mass applied to the substrate by weighing the paint container, roller, paint tray, and test substrate before and after application. The test specimen was placed on the floor of the chamber for testing.

For most tests, the protocol involved application of the primer followed by application of the paint after the primer was dry. During the first three tests of the project, the drying time for the primer was only 1 hr, after which the test specimen was removed from the chamber and the paint applied. In subsequent tests, the drying time was extended to 48 hr to obtain additional information on the emissions from the primer alone and to simplify the modeling. Comparison of the recovery of VOCs during the first three tests with recovery during the other 11 tests did not indicate an impact of drying time on the recovery of VOCs during the tests. Most tests were two weeks in duration and involved application of primer and paint to the pine board substrate.

Sampling and Analysis Methods

During small chamber emissions tests with alkyd paint, air samples were collected from the chamber outlet on four types of sampling media. All air sampling was performed with sorbents to collect integrated samples that were subsequently analyzed by GC/MS or high-performance liquid chromatography (HPLC). During the first 10–20 hr after application of an alkyd primer or paint, air samples for determination of VOCs were collected on activated charcoal cartridges. This was necessary because the very high concentrations of the VOCs in the emissions precluded use of Tenax and thermal desorption methods due to the potential for breakthrough on the sorbent media and overloading of the GC column during analysis. After the initial drying period, the concentrations of VOCs decreased to levels amenable to collection on Tenax and analysis by thermal desorption/GC/MS.

In addition to the charcoal and Tenax samples, air samples were collected on silica gel for the determination of methyl ethyl ketoxime (MEKO, 2-butanone oxime), a chemical of concern in alkyd paint for health effects, including developmental toxicity, blood effects, and cancer risk.[13] Initial testing demonstrated that MEKO could not be quantitatively recovered from air samples collected on charcoal, necessitating use of the alternative sampling method.

The fourth sampling method was collection of aldehydes on silica gel coated with acidified 2,4-dinitrophenylhydrazine (DNPH).

Samples were collected at a relatively high frequency in order to obtain sufficient resolution of the emission profile and to obtain the best estimate of the peak concentration of VOCs in the emissions for the purposes of model development. Each test with primer and paint involved collection of 30 charcoal samples, 21 Tenax samples, 37 DNPH-silica gel samples, and 12 silica gel samples for MEKO during the two-week test period.

Charcoal sorbent samples. The sampling and analysis method for collection of air samples on charcoal sorbents was based on ASTM Standard Practice D3686[14] and National Institute for Occupational Safety and Health (NIOSH) Method 1500.[15] Samples were collected on commercial sorbent tubes 6-mm OD × 70-mm long containing two sections (50/100 mg) of coconut shell charcoal. Air sample volumes of 0.5–3.0 L were collected at a flow rate of 200 cm^3/min. After collection of air samples, the contents of both sections were combined and extracted with 1% 2-propanol in carbon disulfide. A surrogate (d_{10} xylene) standard was added to determine the extraction efficiency. Analysis was performed with a Varian Star

3400CX GC/Varian Saturn Ion Trap MS system. Quantification was performed using an internal standard method. Performance of the instrument was verified by analyzing daily calibration check samples prior to starting analysis of the samples.

Silica gel sorbent samples for MEKO. Air samples were collected on silica gel cartridges, 8-mm OD × 70-mm long, consisting of two sections (150 and 75 mg) of activated silica gel (20/40 mesh). The sampling and analysis method was a modification of NIOSH Method 2010.[16] The samples were extracted with methanol and analyzed by GC/MS.

Tenax sorbent method. Air samples were collected on Tenax for quantification of VOCs after the concentrations in the chamber decreased to levels that permitted use of the thermal desorption method. The Tenax tubes used in this project were 203-mm long × 6-mm OD containing 250 mg of 60/80 mesh Tenax TA. Sample volumes of 0.5–8.0 L were collected at flow rates of 50–200 cm^3/min. The samples were analyzed by thermal desorption/GC/MS. The method was based on the EPA TO-1 method.[17]

DNPH-Silica gel samples. Air samples were collected on commercially available silica gel coated with acidified DNPH. Sample volumes of 2–30 L were collected at flow rates of 200–400 cm^3/min. Analysis was performed by HPLC. The sampling and analysis method was based on EPA Method TO-11.[17] The HPLC was calibrated for nine carbonyl compounds: formaldehyde, acetaldehyde, propanal, benzaldehyde, pentanal, m-tolualdehyde, methyl isobutyl ketone, hexanal, and heptanal.

RESULTS AND DISCUSSION

One interior-grade alkyd primer and three interior semi-gloss enamel paints were used to characterize emissions from alkyd paint. All four coatings were commercially-available products purchased at local retail outlets and were typical of products used in residences. The substrates, glass, wallboard (gypsum board), and white pine board, were also purchased at local retail outlets.

VOC Content Determined by GC/MS

GC/MS analysis was performed to identify and quantify the predominant VOCs in the coatings (Table 1). Decane, nonane, and octane were the three most abundant VOCs in the primer. Decane, at a concentration of 30.7 mg/g, constituted approximately 10% of the total volatile content of the primer. Undecane, o-ethyltoluene, decane, and dodecane were the most abundant VOCs in Paint A, the paint used in most tests. The four compounds constituted 20% of the total volatile organic compounds (TVOCs) of Paint A. Paint B, with undecane, decane, o-ethyltoluene, and dodecane as the predominant compounds, was very similar to Paint A. Paint C differed from Paints A and B. The concentrations of the straight chain C8–C12 alkanes were substantially lower in Paint C and it contained more branched alkanes. There were number of aromatics present in the products, but at lower concentrations. MEKO was not detected in the primer, but was present in all three paints at concentrations ranging from 0.92 to 2.93 mg/g. Hexanal, although detected in the emissions from the primer and paints, was not detected in the liquid primer or the three paints above the method detection limit of 0.03 mg/g.

TVOC concentration, calculated by integration of all peaks in the chromatogram between toluene and tetradecane and using the response factor for toluene, was 316 mg/g for the primer and ranged from 347 to 421 mg/g for the paints. Total volatile matter content was also

Table 1. Concentrations of the predominant VOCs in the liquid primer and three interior alkyd enamel paints.

ID	Compound	mg/g[a] Primer	Paint A	Paint B	Paint C
0	TVOC	316	347	350	421
1	toluene	0.35	0.27	0.83	0.06
2	octane	15.6	0.08	0.62	0.06
3	methyl ethyl ketoxime	BDL[b]	0.92	2.93	1.34
4	ethylbenzene	0.29	1.10	1.54	2.05
5	p-xylene	1.39	4.91	5.48	6.92
6	nonane	18.4	3.49	7.55	0.79
7	o-xylene	0.23	0.73	1.45	1.36
8	propylcyclohexane	4.06	2.22	5.00	BDL
9	isopropylbenzene	BDL	BDL	0.18	0.08
10	n-propylbenzene	0.03	0.22	0.42	0.07
11	p-ethyltoluene	0.21	0.63	1.54	0.30
12	1,3,5-trimethylbenzene	0.02	0.28	0.62	0.16
13	decane	30.7	13.2	23.4	4.89
	branched decane a	—	—	—	11.3
	branched decane b	—	—	—	0.04
14	o-ethyltoluene	—	15.1	27.6	7.26
15	1,2,4- trimethylbenzene	0.14	0.89	1.01	0.44
16	1,2,3- trimethylbenzene	—	0.29	0.41	0.22
17	2-methyldecane	2.19	3.74	BDL	BDL
18	trans-decalin	2.28	3.96	4.54	BDL
19	undecane	6.68	31.2	32.6	7.87
	branched undecane a	—	—	—	12.0
	branched undecane b	—	—	—	8.47
	branched undecane c	—	—	—	13.6
	branched undecane d	—	—	—	13.0
	branched undecane e	—	—	—	11.7
	branched undecane f	—	—	—	11.2
20	dodecane	0.063	10.5	8.57	1.13

[a] Mean concentration of analyses of triplicate aliquots.

[b] BDL = below method detection limit.

determined for the primer and Paint A by EPA Method 24,[18] a gravimetric method. The results were 333 mg/g for the primer and 331 mg/g for Paint A, results consistent with the manufacturer's reported volatile content of 332 and 328 mg/g for the primer and Paint A, respectively. The TVOC concentrations estimated for the primer (316 mg/g) and Paint A (347 mg/g) based on the GC/MS analyses were remarkably similar to both the Method 24 results and the manufacturer's data considering the potential magnitude of the errors associated with the integration method and the use of toluene (only) as the response factor for TVOC.

Emission Tests—Mass Balance Calculations

A series of 14 small chamber emissions tests were performed to characterize emissions from alkyd paint. The tests are summarized in Table 2, and included evaluation of the effect of substrate, primer, paint, previous coat, film thickness, air-exchange rate (AER), and air speed at the substrate surface.

For each test, the total mass of the individual VOCs and TVOCs emitted during the two-week duration tests was calculated from the concentrations in the air samples. These results were used with the data from the analysis of the liquid product by GC/MS to calculate a mass balance for each test. The mass balance can be used to evaluate the test results to determine if they are reasonable and can be used to compare results from tests performed under different conditions (e.g., AER) or with different test parameters (e.g., film thickness, substrate).

The mass balance was calculated as the total amount (in mg) of the TVOCs or individual VOCs emitted during the test versus the amount (in mg) of the TVOCs or individual VOCs applied. The total mass of primer or paint applied was determined gravimetrically at the time of application. Concentration data for TVOCs and individual VOCs measured in the paint formulation by GC/MS were used with the mass applied to calculate the mass of each VOC applied to the substrate. The mass of TVOCs and individual VOCs emitted was calculated as

$$\text{Amount emitted (mg)} = A_c \times Q \qquad (1)$$

where A_c = the area under the time/concentration curve and Q = the chamber AER.

The mass balance, reported as the percent of the applied VOCs or TVOCs recovered in the emissions, was calculated for the entire test and included the emissions from both the primer and paint. Emissions were measured over a two-week test period. The results of the mass balance calculations are summarized in Table 3. The average percent TVOCs recovered in the 14 tests was 111±20%. The median recovered was 103%. The recovery of TVOCs ranged from 84 to 146%, but was 84–110% in nine of those tests. The reason for the high recoveries in five of the tests could not be determined. Due to resource and time constraints, the tests could not be repeated.

There are no criteria for determining what is an acceptable mass balance. The error in the mass balance calculation will be a function of the analytical errors associated with analysis of both the liquid product and the air samples. Because greater than 90% of the VOCs are emitted during the first 10 hr, the data for the samples collected on the charcoal sorbents have the greatest impact on the mass balance. Analyses of duplicate samples collected on charcoal during each test gave an average percent relative standard deviation (%RSD) ranging from 2 to 19%. The median %RSD was below 10% for all but one of the 20 VOCs. The ASTM Standard Practice D3687 for analysis of VOCs collected with the charcoal tube method states that a relative precision of ±15% can be expected for the method.[19] For TVOCs, therefore, recoveries of 85–115% would be very good because the error associated with estimating TVOCs would be expected to be substantially greater than the error for individual VOCs. TVOC concentrations are estimated by integration of all peaks in the chromatogram in the retention time window between toluene and tetradecane and use of only the toluene response factor for quantitation.

The percent recoveries for individual VOCs were highly variable. As shown in Table 3, the median percent recovered ranged from 30% for toluene to 190% for 1,3,5-trimethylbenzene. Eleven of the 20 VOCs had median recoveries between 74

Table 2. Matrix of tests performed in the program.

Test No.	Substrate	Primer	Paint	Notes	Test for Impact of
1	, Glass	Yes[a]	A		Substrate
2	Gypsum	Yes[a]	A		Substrate
3	Pine	Yes[a]	A		Substrate
4	Glass	Yes	None		Substrate
5	Gypsum	Yes	None		Substrate
6	Pine	Yes	A		Substrate
7	Pine	Yes	A	Replicate-Test 6	Precision
8	Pine	None	A		Primer
9	Pine-Test 3	None	A	Apply second coat	Two coats
10	Pine	Yes	B		Paint
11	Pine	Yes	C		Paint
12	Pine	Yes	A	Velocity-3cm/sec	Air velocity
13	Pine	Yes	A	AER=1.12	AER
14	Pine	Yes	A	Heavier application	Thickness

[a] Primer dried for 1 hr before application of paint in Tests 1–3; dried for 48 hr in all other tests.

Table 3. Percent of the applied VOC mass recovered in emissions during 14 two-week small chamber tests with alkyd primer and paints.

Compound	Amt.[a]	% of Applied Mass Recovered Minimum	Maximum	Average	Std. Dev.	Median
TVOC		84	146	111	20	10
toluene	16	2	138	35	36	30
octane	4	17	121	50	28	43
n-propylbenzene	19	8	385	100	107	61
m,p-xylene	9	27	202	80	42	70
ethylbenzene	11	48	191	87	47	74
nonane	3	55	112	82	14	79
o-xylene	13	51	209	115	55	83
methyl ethyl ketoxime	14	63	105	84	13	89
propyl-cyclohexane	7	71	455	127	93	96
decane	1	83	126	101	11	100
trans-decahydranaphthalene	8	92	172	115	21	105
undecane	2	80	136	113	16	111
dodecane	6	86	500	146	101	114
2-methyldecane	10	36	314	127	68	119
p-ethyltoluene	15	65	345	138	71	120
1,2,4-trimethylbenzene	12	88	1712	346	470	160
1,3,5-trimethylbenzene	17	38	2069	448	615	190
o-ethyltoluene[b]	5	—	—	—	—	—
1,2,3-trimethylbenzene[c]	18	—	—	—	—	—
isopropylbenzene[d]	—	—	—	—	—	—

[a]Amt. = Relative amount in primer/Paint A system listed in order, with 1 being the most abundant VOC.
[b]Mass balance not calculated due to analytical problems with this compound.
[c]Most air concentrations below practical quantification limit; mass balance not calculated.
[d]Present only in Paints B and C; mass balance not calculated.

and 120%. The average percent recovery was between 80 and 127% for 11 of the 20 VOCs. Data are presented in Table 3 for individual VOCs in ascending order for the median percent recovered (last column) in order to evaluate which compounds fall into an "acceptable" range for recovery. The column labeled "Amt." is the relative abundance of the VOC in the primer/Paint A coating system. Decane, listed as "1," is the most abundant VOC in the coating, followed by undecane (2), and nonane (3). The trimethylbenzenes were present in the coatings at much lower concentrations (Table 1). The mass balances were not calculated for 1,2,3-trimethylbenzene because the concentrations in most air samples were below the practical quantification limit (PQL) of the method in many of the tests. Due to analytical problems with o-ethyltoluene, the mass balances were not calculated.

Recoveries of VOCs in the emissions were low for the more volatile compounds (e.g., toluene, octane, ethyl benzene, *m,p*-xylene). The low recovery of the more volatile compounds is likely to be an artifact of the small chamber emissions test method, which requires application of the coating to the substrate outside of the chamber. Substantial losses of the most volatile compounds in the paint may occur during the 3–4 min required to prepare and weigh the test specimen.

The mass balances were very good for the most abundant compounds in the primer and Paint A system. For decane, the most abundant compound, the average and median recoveries were near 100% and the range for the 14 tests was from 83 to 126%. The results were also very good for undecane and dodecane. The one test in which the mass recovery of dodecane was 500% was a test with primer only. Because the primer contained a low concentration of dodecane, concentrations of dodecane in the air samples were low. Two of the 14 tests involved application of only the primer to glass or a pine board. Because of the low concentrations of aromatic compounds in the primer, the mass balances were poor. The maximum mass recoveries for n-propylbenzene, p-ethyltoluene, 1,3,5-trimethylbenzene, and 1,2,4-trimethylbenzene occurred in the tests with the primer only.

The data presented in Table 3 demonstrate that the error of the mass balance can be significant if calculations are made for VOCs present at low concentrations in the coatings. However, the data suggest that for the more abundant compounds, an error in the mass balance of less than ±20% is probably reasonable. This assumes that all of the VOCs are emitted from the test specimen and the duration of the small chamber emissions test is sufficient to collect most of the emissions. The mass balance data are useful for evaluating the performance of the test method for solvent-based liquid coatings when there are no substrate effects. The data may be more difficult to interpret for some products, including water-based products that emit less volatile and more polar compounds, because the compounds may be emitted over long time periods (weeks to months) and substrate effects may affect the emission rates. However, experience with a number of coatings suggests that the mass balance approach provides a valuable "reality check" of the data and is useful for evaluating emissions test results.

Emission Test Results

Effect of substrate. Previous research has demonstrated that there can be a substantial effect of the substrate on emissions of VOCs from coatings. Gehrig et al.[20] reported that compounds with polar oxygen-containing functional

groups showed reduced emissions from a low-VOC paint applied to gypsum board or wallpaper as compared to applications to glass plate. They did not observe any significant effect for less polar alkanes and aromatics. Guo et al.[10] reported similar results for latex paint applied to gypsum board. They observed a significant effect of the gypsum board substrate on emissions of ethylene glycol and propylene glycol from latex paint. Therefore, the first tests for this project were performed with the primer and one paint (Paint A) applied to glass, gypsum board, or a white pine board to assess substrate effects.

There were no substantial differences in the emissions of TVOCs or any of the individual VOCs measured during tests with the primer and Paint A applied to glass, gypsum board, or pine board. Emissions of decane, the most abundant VOC in the primer/Paint A coating system, are depicted in Figure 1 and are representative of the emissions profiles for TVOCs and individual VOCs. Decane emissions were not substantially different for the three substrates. The highest concentrations of decane measured from the application of the primer were 1,060, 926, and 1,450 mg/m^3 for glass, gypsum board, and pine board, respectively. Following application of the paint, the highest concentrations of decane were 370, 394, and 569 mg/m^3 for the three substrates. There were slight differences in the application rates during the three tests. If the peak concentrations of decane were normalized for the amount of primer and paint applied, the difference between the glass and gypsum board was less than 4%, but the peak concentration of decane in the test with the pine board was nearly 40% higher than in the test with the glass. The reason for the difference in peak concentrations was not determined. But, despite the differences in peak concentrations, the concentrations of decane in the emissions after 4 hr were very similar for the three substrates. Air samples collected from the chamber with only the pine board, prior to application of the primer and paint, did not show detectable levels of decane emissions from the board.

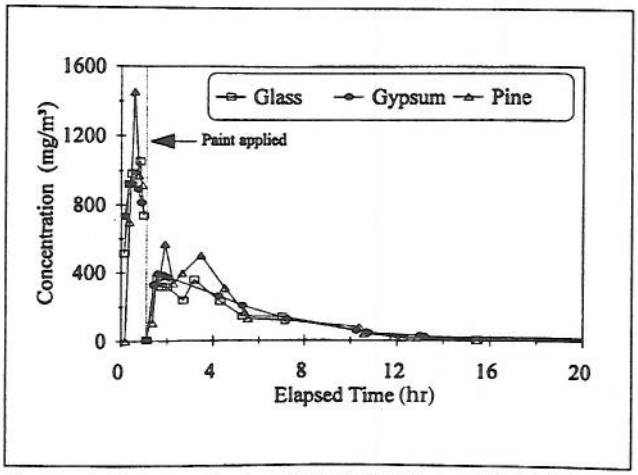

Figure 1. Decane emissions from alkyd primer and Paint A for first 20 hr after application to glass, gypsum board, or pine board substrates.

The high cost of performing small chamber emissions tests precludes extensive replication of tests. Therefore, the statistical significance of differences between the three tests cannot be determined. Comparing peak concentrations of the emissions is not the best approach for assessing the significance of the differences between tests. Although air samples are collected frequently, they cannot be collected continuously and the peak concentration may be missed. As discussed in the previous section, the mass balance approach is useful for evaluating chamber test data. For the tests with the three different substrates, the percent of the applied TVOCs recovered in the emissions was 84, 97, and 133% for glass, gypsum board, and pine board, respectively. Recoveries can be greater than 100% if there are substantial background emissions from the substrate or due to the imprecision of the sampling and analysis methods. Background air samples collected from the test chambers prior to the tests with gypsum board and pine board demonstrated that background emissions from the substrates were very low, generally below the method detection limit. The variation in recovery, ranging from 84 to 133% in these tests, therefore, is likely related to the errors associated with estimating TVOCs in the product and in the emissions, as was discussed in the previous section. For decane, the most abundant VOC in the primer/Paint A coating system, the recovery was 83, 99, and 126% of the applied amount in the three tests. Because it was the predominant VOC, the variation in the decane measurements would have a substantial effect on the calculated recoveries of TVOC.

In spite of the low recoveries of TVOCs from the glass and high recovery from the pine board, the differences in emissions between the substrates was not substantial when compared to the differences observed in previous tests with latex paint.[7] In that study, emissions from latex paint applied to gypsum board were compared to the same paint applied to a stainless steel plate. During a two-week period following application of the paint, only 20% of the TVOCs were recovered from the gypsum board substrate compared to 97% from the stainless steel substrate. Nine percent of the ethylene glycol applied to the gypsum board was recovered compared to 103% from the stainless steel.

Effect of primer or a previous paint coating. The effect of the primer on emissions of VOCs was determined by applying Paint A to a pine board without application of the primer and comparing the results to a standard test involving application of the primer followed 48 hr later by application of Paint A. Results of the comparison for decane emissions are depicted in Figure 2. The peak concentrations and the

rate of emissions during the first 20 hr were not substantially different in the two tests. In the test without the primer, the recovery in the air emissions was 102% for decane and 101% of the applied TVOC. This compared to recoveries of 110% for decane and 104% for TVOCs in the test with the primer.

A similar test was performed to determine if emissions from Paint A differed due to application over a previous coat of the same paint. The results were similar to that of the primer. The previous coat did not affect the peak concentrations or the rate of emissions. The total mass recovered was 104% for Paint A applied over the primer and 102% for Paint A applied to a pine board coated with primer and Paint A three months prior to application of the second coat of Paint A.

Comparison of three paints. Emissions from three alkyd paints purchased from major U.S. manufacturers were compared during the study. The predominant VOCs (straight-chain alkanes) and the TVOC concentration were similar in the liquid Paints A and B (Table 1). Paint C had a different formulation; the TVOC concentration was higher and the predominant VOCs in the coating were branched alkanes. A major difference between the three paints was the concentration of methyl ethyl ketoxime (MEKO), which ranged from 0.92 to 2.93 mg/g. Figure 3 depicts the emissions of TVOCs for the three paints (the emissions from the primer applied 48 hr prior are not depicted in the figure). The TVOC emission profile was similar for Paints B and C. The emissions from Paint A were somewhat lower during the initial 4 hr following application, but approximately 10% less paint was applied to the substrate. There was little difference in the total mass of emissions recovered during the two-week tests. TVOC recoveries were 104, 110, and 94% for Paints A, B, and C, respectively. For decane, the recoveries were 110, 119, and 100%.

The emission profile depicted in Figure 3 was typical for the tests with the alkyd paints. The peak concentration of TVOCs occurred within an hour after application. Calculated cumulative emissions showed that approximately 90% of the TVOCs were emitted during the first 10 hr following application of either the primer or paint. Within 100 hr after application, concentrations of VOCs in the test chamber dropped by three orders of magnitude.

Emissions profiles for individual VOCs were similar for the alkanes, branched alkanes, and the aromatics. For all compounds, including methyl ethyl ketoxime, but excluding the aldehydes, peak concentrations occurred within 2 hr following application of the primer or paint and the concentrations then decreased rapidly (e.g., Figure 3).

Effect of film thickness. The effect of film thickness on emissions has not been studied in detail.[3] Clausen[21] reported that for a waterborne paint, the initial emission rate was not affected by film thickness and that the first-order decay constant was inversely proportional to film thickness. The effect of film thickness on VOC emissions from the solvent-based paint A was evaluated by comparing an application with a paint film thickness of 59 mm with a film thickness of Paint A of 82 mm, both on previously primed pine boards. The effect of wet film thickness on emissions of decane is depicted in Figure 4. With the increased film thickness, the peak concentration of individual and total VOCs was higher and the peak concentration occurred later. The total emissions were higher, consistent with the increased amount of VOC mass applied.

Effect of AER. The emission rates of VOCs from wet coatings, which may be controlled by evaporation, have been

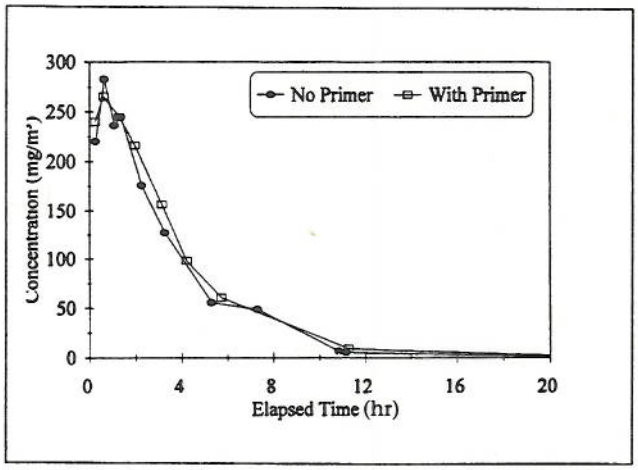

Figure 2. Effect of primer on short-term decane emissions from Paint A applied to pine board; data presented for first 20 hr after paint application.

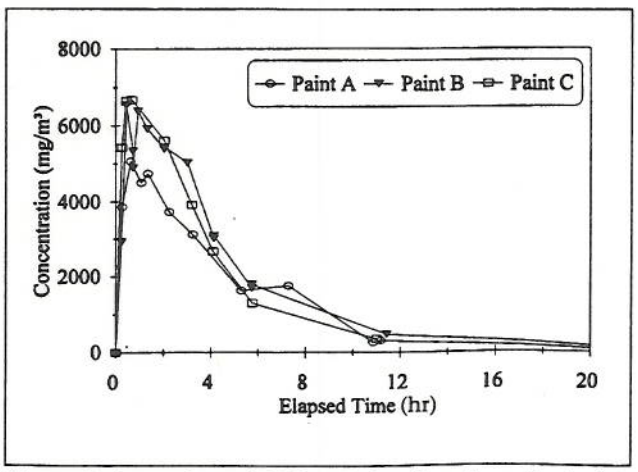

Figure 3. Comparison of TVOC emissions from three alkyd paints for first 20 hr after application to a pine board previously coated with primer.

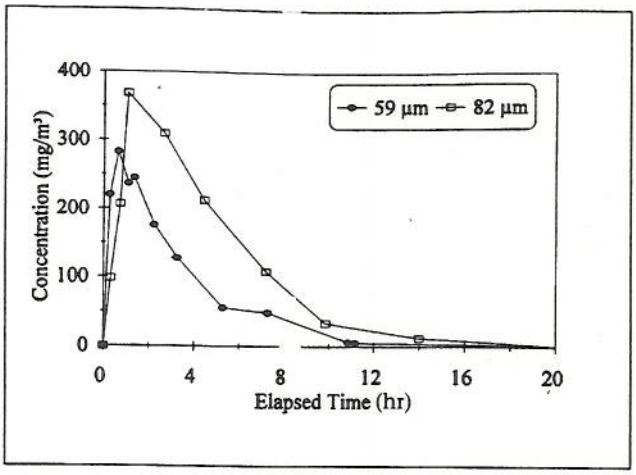

Figure 4. Impact of wet film thickness on short-term decane emissions from Paint A during first 20 hr following application to pine board previously coated with primer.

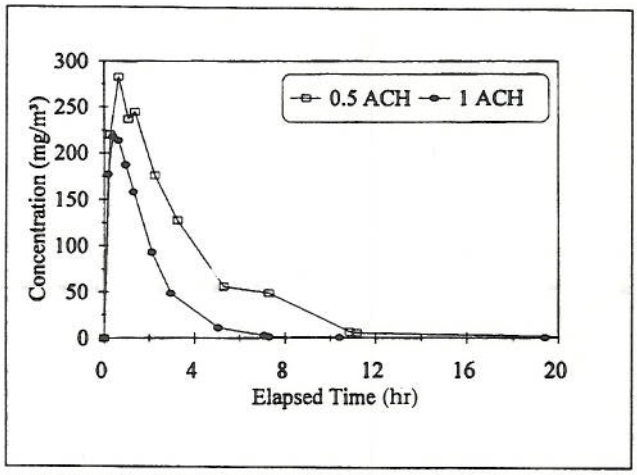

Figure 5. Effect of AER on short-term decane emissions during small chamber tests with Paint A applied to pine board previously coated with primer.

shown to be impacted by the AER.[5,22,23] For evaporative emissions, increased AERs (i.e., increased ventilation) can be expected to result in lower peak VOC concentrations in the test chamber and occurrence of the peak concentration earlier. Results of the test with Paint A in tests with AERs of 0.5 and 1.0 hr^{-1} were consistent with these predictions, as depicted in Figure 5 for decane.

Effect of air velocity at the surface. To evaluate the impact of air velocity at the surface on emissions, one test was conducted at 0.5 air changes per hour (ACH) with a mixing fan in the chamber. With the fan, the air speed at the surface is approximately 10 cm/sec. In a second test, the chamber was operated at 0.5 ACH without a mixing fan. Measurements have shown that without the mixing fan, the air speed at the surface is less than 3 cm/sec, the minimum speed that can be measured with the hot-wire anemometer. Based on theoretical predictions for gas-phase mass transfer-controlled emissions,[22] the peak VOC concentrations should be lower and occur later at lower air speeds. Results of the tests were consistent with theoretical predictions. In the chamber test with the fan operating, the peak concentration of decane from the primer was 814 mg/m^3 at 1.29 hr after application and the peak concentration of decane from the paint was 245 mg/m^3 at 1.36 hr after application. But in the test without the fan, the peak decane concentrations were 523 mg/m^3 at 2.44 hr after primer application and 164 mg/m^3 at 2.23 hr after paint application.

Emissions of aldehydes. In addition to the solvent VOCs, aldehydes were detected in the emissions from the primer and paint. Formaldehyde, acetaldehyde, propanal, pentanal, and hexanal were detected in the emissions. The concentrations of formaldehyde were low and generally below the practical quantification limit of the method. The predominant aldehyde in the emissions from the alkyd paints was hexanal, a compound that was not detected in the liquid primer or paint by GC/MS analysis. Background samples collected from chambers containing the unpainted pine boards had hexanal concentrations ranging from non-detectable to 0.02 mg/m^3, which was at least two orders of magnitude lower than the peak hexanal concentrations during the tests. The hexanal was apparently formed by oxidation.[24,25] An example of the hexanal emissions for the primer and three paints is presented in Figure 6. The following observations were made during the project: (1) the emissions of hexanal were lower from the primer than from the paints; (2) peak concentrations differed, but the total mass emitted during the two week test periods was similar for the three paints; and (3) unlike the VOCs, hexanal emissions were not significant until about 10 hr after paint application and peaked at about 20–24 hr for Paint A. Figure 6 is included in this paper for illustrative purposes only. Results of the aldehyde emissions are not presented in detail in this paper, but will be published in a separate technical paper.

CONCLUSIONS

The alkyd primer and two of the three paints tested in this project contained primarily straight-chain alkanes, with decane and undecane being the predominant compounds. The third paint contained more branched alkanes. All four coatings contained low levels of aromatic compounds. The three paints contained methyl ethyl ketoxime, but the primer did not. The total VOC content of the liquid paints ranged from 32 to 42%. Measurements of the VOCs in the liquid coatings by GC/MS agreed well with Method 24 measurements and manufacturer's data.

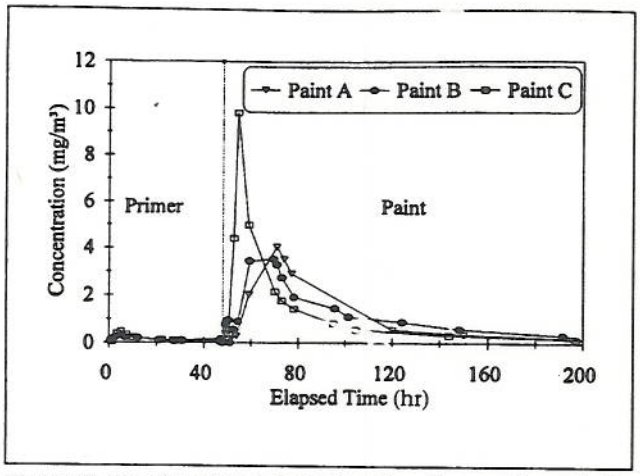

Figure 6. Long-term hexanal emissions from three paints applied to pine board coated 48 hr earlier with alkyd primer.

Small chamber emission test conducted by coating glass, gypsum board, or pine board with primer, followed 1 hr later by application of the paint, demonstrated that the substrate did not have a substantial impact on the peak VOC concentrations, the emission rates, or the total mass of VOCs emitted. Over 90% of the VOCs were emitted within the first 10 hr following application of the primer or paint. There were differences in emissions of individual VOCs from the three paints, but the general patterns of the emissions were similar. The impact of other variables, including air velocity, AER, and film thickness, were consistent with theoretical predictions.

Mass balance calculations showed that for the most abundant compounds, the entire mass of VOCs applied to the substrate could be accounted for in the air samples of emissions collected during the test, that is, there was 100% recovery. The data for the most abundant compounds in the paint suggest errors of ±20% can be expected for this type of product. The mass balance approach was useful for evaluating differences between tests and for assessing the reasonableness of the test results.

Results from the testing performed in this study are being used to develop computational methods for estimating the emission rate of VOCs from solvent-based coating products used indoors; the methods will be reported in a separate paper currently in preparation. The database on VOC emission from alkyd paint should also be useful for others involved in model development and validation.

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