EPA/600/R-01/093
October 2001

Capstone Report

on the Development of a Standard Test Method for VOC Emissions from Interior Latex and Alkyd Paints

by
John C. S. Chang

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
National Risk Management Laboratory
Air Pollution Prevention and Control Division
Indoor Environment Management Branch
Research Triangle Park, NC 27711

Abstract

This document provides a detailed report on the small-chamber test method developed by EPA/NRMRL for characterizing volatile organic compound (VOC) emissions from interior latex and alkyd paints. Current knowledge about VOC, including hazardous air pollutant, emissions from interior paints generated by tests based on this method are presented. Experimental data were analyzed to demonstrate the usefulness of the method and test results in terms of emission characterization, material selection, exposure assessment, and emission reduction by product reformulation. The conclusions drawn from the experimental results were used as input to develop a standard practice to be adopted by the American Society of Testing and Materials (ASTM). The draft standard practice is presented in Appendix A.

Table of Contents

Table of Contents (Continued)

Table of Contents (Continued)

List of Tables

List of Tables (Continued)

List of Figures

List of Figures (Continued)

Acknowledgments

The contents of this report are the results of a research program performed between 1995 and 1999. The author wishes to acknowledge the work of Mark Bero, Roy Fortmann, Huei-Chen Lao, Angelita Ng, and Nancy Roache of ARCADIS Geraghty & Miller, Inc. for collecting part of the experimental data. The author also wishes to acknowledge the assistance of Ray Merrill and David Berol of Eastern Research Group on literature survey, information compilation, and computer graphics.

Executive Summary and Conclusions

Americans spend about 90% of their time indoors, where concentrations of pollutants are often much higher than they are outdoors. It is not surprising, therefore, that risk assessment and risk management studies have shown that indoor environmental pollution poses significant risks to human health.

The U.S. Environmental Protection Agency (EPA) has evaluated a number of indoor materials and products as potential sources of indoor air pollution under the Indoor Air Source Characterization Project (IASCP). Interior architectural coatings, especially alkyd and latex paints, were identified as potentially high-risk indoor sources by the Source Ranking Database developed under the IASCP. EPA conducted a literature survey and found that there was a lack of reliable and consistent paint emission data for developing and evaluating risk management options. Further investigation showed that a standardized test method needed to be developed so that testing laboratories, researchers, and paint manufacturers could generate and report emission data that were complete, consistent, and comparable.

Between 1995 and 1999, EPA's National Risk Management Research Laboratory (NRMRL) conducted a paint emission characterization research program. The program was devoted to developing, verifying, and demonstrating a small chamber test method for the measurement of volatile organic compound (VOC) and hazardous air pollutant (HAP) emissions from alkyd and latex paints. The test method has been documented and submitted to the American Society for Testing and Materials (ASTM) for adoption as a standard practice.

This report summarizes the resulting test method, presents new findings, and describes the key results generated by NRMRL as it assessed emissions from alkyd and latex paints. The report is divided into four parts. After introducing the study and providing background information about existing literature on the subject paint emissions testing, the report describes the developed standard test method for characterizing organic compounds emitted from paint. It also describes the results of NRMRL's tests on alkyd and latex paints.

Standardized Test Method

The standardized test method addresses the following key issues:

- Storing and handling paint samples prior to analysis
- Analyzing paint in bulk (as a liquid)
- Selecting and preparing a paint substrate for testing
- Applying paint to a substrate to create a test specimen
- Establishing and controlling test conditions

- Sampling the VOC emissions from the painted specimen
- Analyzing the samples with chemical instruments
- Calculating emission rates/factors using experimental data
- Conducting quality assurance/quality control

The core experimental apparatus employed by the standardized test method is a device called a Small Environmental Test Chamber ("small chamber" for short). A test chamber is a hollow box that may range in size from a few liters to 5 m^3. The chamber used at NRMRL is 53 L (0.053 m^3) in volume. Chambers with volumes greater than 5 m^3 are defined as "large"—they may reach the scale of an entire room. The small chamber, on the other hand, is an apparatus suited to the spatial and financial constraints of a typical laboratory environment. It is also more convenient to operate than a large chamber. An environmental chamber test facility designed and operated to determine organic emission rates from paints should contain the following: test chambers, clean air generation system, monitoring and control systems, sample collection and analysis equipment, and standards generation and calibration systems. The purpose of these components is to provide a controlled environment for conducting emissions testing that can reflect common indoor air conditions.

The standardized test method includes a series of procedures and guidelines for preparing a painted test specimen. Procedures for handling and storing the paint to be tested were established to guard against the possibility of evaporative losses, stratification, and property changes. A modified version of EPA Method 311 (40 CFR, 1996) was adopted for the bulk analysis of paints, to facilitate the experimental design of the emissions test and the selection of sampling and analytical techniques. Instead of traditional test substrates such as glass, stainless steel, and aluminum, common indoor materials such as gypsum board and wood are recommended in the method for creating realistic and representative testing samples. Either a roller or a brush should be used to apply the paint to the substrate. A protocol was developed to quantify the amount of the paint applied so that the emission data can be consistent and comparable.

The "time zero" for the start of an emission test is established when the chamber door is closed (immediately after placing the test specimen inside the chamber). The small chamber should be operated to match the actual environmental conditions at which people paint the interiors of houses. The standardized method guides investigators in setting up their sampling protocols. The instructions help to ensure that investigators collect an adequate quantity of chamber air samples on the appropriate sampling media. The method describes several kinds of analytical instruments that can be used to determine the amounts and kinds of VOCs in the collected sample. Data reduction techniques and an example of an emission model are included in the method—it describes the mathematical procedures used to convert the analytical results into emission rates and emission factors. In addition, the method provides guidelines for reporting and quality assurance. These guidelines should help investigators compile their results in a consistent and complete fashion that allows for comparison or repeat emissions testing of similar or new architectural coatings.

Alkyd Paints

Alkyd paint continues to be used indoors because it has desirable properties such as durability, gloss, gloss retention, and fast drying. NRMRL has employed the developed standardized test method to conduct research that characterizes VOC emissions from alkyd paint. NRMRL used the results of its paint emissions tests to develop source emission models. These models, in turn, were used for the assessment of indoor exposure levels and risk management options.

The first test series that NRMRL performed on alkyd paints was integrated into the process of developing and validating its new standard practices for paint testing. The tests involved one primer and three alkyd paints. Bulk analysis indicated that the alkyd primer and two of the three paints tested contained more than 100 different VOCs, primarily straight-chain alkanes, with decane and undecane being the predominant compounds. The third paint had more branched alkanes. All four coatings contained low levels of aromatic compounds. The total VOC content of the liquid paints ranged from 32% to 42%. Measurements of the total VOC levels in the liquid coatings by gas chromatography/mass spectrometry (GC/MS) agreed well with manufacturers' data.

Mass balance calculations were conducted to compare the bulk analysis results and chamber emission data to evaluate the recovery. It was found that for total VOC, the majority (greater than 80%) of the mass in the applied paint could be accounted for in the subsequent air emissions. The data for the more abundant compounds (e.g., nonane, decane, and undecane) in the paint suggest that there was a margin of error of ± 20% in measuring these recoveries.

Due to the relatively high VOC content and fast emission pattern, peak concentrations of total VOC as high as 10,000 mg/m^3 were measured during small chamber emissions tests with a loading factor of 0.5 m^2/m^3 and an air exchange rate of 0.5 h^{-1}. Over 90% of the VOCs were emitted from the primer and paints during the first 10 hours following application.

A series of tests were performed to evaluate those factors that may affect emissions following application of the coatings. It was found that the type of substrate (glass, wallboard, or pine board) did not have a substantial effect on the emissions with respect to peak concentrations, the emissions profile, or the mass of VOCs emitted from the paint. The emissions from paint applied to bare pine board, a primed board, and a board previously painted with the same paint were quite similar. There were differences among the emissions from the three different paints, but the general patterns of these emissions were similar. The effect of other variables, including film thickness, air velocity at the surface, and air exchange rate, were consistent with theoretical predictions for gas-phase, mass-transfer-controlled emissions.

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

In addition to studying the effects of substrates and other environmental variables on total VOC emissions, small environmental chamber tests were conducted to characterize the emissions of a toxic chemical compound—methyl ethyl ketoxime (MEKO)—from three different alkyd paints. The data resulting from these tests facilitated the development of a set of risk management options for MEKO.

Methyl ethyl ketoxime, another name for 2-butanone oxime or ethyl methyl ketoxime [$CH_3C(NOH)C_2H_5$, CAS Registry No. 96-29-7], is often used by paint manufacturers as an additive to interior alkyd paints (Weismantel, 1981; Turner, 1988). MEKO has been found to be a moderate eye irritant (Krivanek, 1982). It was also the subject of a Section 4 test rule under the Toxic Substances Control Act (Fed. Regist., 1986). A number of toxicological endpoints have been evaluated by testing conducted under the test rule (Fed. Regist., 1989). MEKO demonstrated carcinogenic activity in long-term inhalation studies, causing liver tumors in both rats and mice.

MEKO acts as an anti-skinning agent (or anti-oxidant) that prevents oxidative drying or skinning of the alkyd paint to improve stability in the can. Usually, the MEKO content in a paint is less than 0.5% (Krivanek, 1982). Due to its relatively high volatility (its boiling point is only 152°C), the majority of the MEKO in the paint is expected to be released into the surrounding indoor air after painting to allow the paint to dry properly on the painted surfaces. The effects of MEKO emissions on indoor air quality (IAQ) and associated exposure risk depend on characteristics such as emission rates and patterns.

Bulk analysis showed that the MEKO content in alkyd paints can be as high as several mg/g. Material balance from the chamber tests indicated that the majority (greater than 68%) of the MEKO in the paint applied was emitted into the air. MEKO emissions occurred almost immediately after each alkyd paint was applied to a pine board. Due to the fast emission pattern, more than 90% of the MEKO emitted was released within 10 hours after painting. The peak concentrations of MEKO in chamber air correlated well with the MEKO content in the paint.

The chamber data were simulated by a first-order decay emission model that assumed that the MEKO emissions were mostly gas-phase mass-transfer-controlled. The first-order decay model was used as an input to the continuous-application source term of an IAQ model to predict indoor MEKO concentrations during and after the application of an alkyd paint in a test house. The predicted test house MEKO concentrations during and after the painting exceeded a suggested indoor exposure limit of 0.1 mg/m^3 for all three paints. The predicted MEKO concentrations also exceeded the lower limit of a suggested sensory irritation range of 4 to 18 mg/m^3 with two of the three paints tested. The elevated MEKO concentrations can last for more than 10 h after the painting is finished. The model was also used to evaluate and demonstrate the effectiveness of risk reduction options. These options involved selecting lower MEKO paints and establishing higher ventilation levels during painting. The higher ventilation should be maintained about 2 h after the painting is finished to avoid exposure to residual MEKO emissions.

In addition to total VOC and MEKO emissions, the unpleasant "after-odor" which can persist for weeks after application of alkyd paint has been a cause of IAQ concerns. Three different alkyd paints were tested in small environmental chambers to characterize the aldehyde emissions. Emission data indicated that significant amounts of odorous aldehydes (mainly hexanal) were emitted from alkyd paints during the air-drying period. Bulk analyses showed that the alkyd paint itself contained no aldehydes. Mass balance calculations indicated that any aldehydes emitted should have been produced after the paint was applied to a substrate. The aldehydes emission patterns were consistent with the theory that the aldehydes were formed as byproducts from spontaneous autoxidation of unsaturated fatty acids in the applied paint. Chamber data showed that the major volatile byproducts generated by the drying of the alkyd paints were hexanal, propanal, and pentanal. These results facilitated the development of an exposure assessment model for hexanal emissions from drying alkyd paint.

The hexanal emission rate was simulated by a model that assumed that the autoxidation process was controlled by a consecutive first-order reaction mechanism with an initial time lag. The time lag reflects an induction period after painting during which little oxygen is taken up by the alkyd coating. As the final byproduct of a series of consecutive first-order reactions, the hexanal emission rate increases from zero to reach a peak and is followed by a slow decay. This model was confirmed by chamber concentration data. The modeling results also showed that the hexanal emissions were controlled mostly by the chemical reactions that formed intermediates (i.e., the precursors to hexanal production).

An IAQ simulation that used the emission rate model indicated that the hexanal emissions can result in prolonged (several days long) exposure risk to occupants. IAQ simulation indicated that the hexanal concentration due to emissions from an alkyd paint in an indoor application could exceed the reported odor threshold for about 120 hours. The occupant exposure to aldehydes emitted from alkyd paint also could cause sensory irritation and other health concerns.

Latex Paints

The majority (over 85%) of the interior architectural coatings used in the United States are latex paints. Previous testing of latex paint emissions has focused on determining cumulative mass emissions of VOCs. The purpose of previous testing was to assess the effect of these paints on the ambient air and to determine how they contributed to photochemical smog (Brezinski, 1989). NRMRL's concern has been to estimate people's time-varying exposure to overall VOC levels and to specific VOCs from indoor latex paints.

The first test series that NRMRL performed on latex paints was integrated into the process of developing and validating its new standard practice for paint testing. NRMRL's small chamber tests indicated that the organic emission patterns of latex paints are very different from those of alkyd paints. Bulk analysis showed that the total VOC content of a commonly used latex paint is usually in the range of 2% to 5%, which is considerably lower than that of alkyd paints (32% to 42%). Instead of alkanes, alkenes, and aromatics, only several polar compounds such as glycols, alcohols, and aldehydes were found in the latex paints.

The chamber test results showed significant differences between the emissions of the same latex paint applied to two different substrates (a stainless steel plate and a gypsum board). The amount of VOCs emitted from the painted stainless steel was 2 to 10 times greater than the amount emitted from the painted gypsum board during the 2-week test period. After the first 2 weeks, over 90% of the VOCs were emitted from the paint on the stainless steel plate but less than 20% had left the gypsum board. The dominant species in the VOCs emitted also changed from ethylene glycol to 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate when stainless steel was replaced with gypsum board. Data analysis by a double-exponential model indicated that the majority of the VOC emissions from the painted stainless steel could be simulated by an evaporation-like phenomenon with fast VOC emissions controlled by gas-phase mass transfer. On the other hand, only a small fraction of the VOCs emitted from the painted gypsum board appeared to be controlled by the evaporation-like drying process. The majority of the VOCs were emitted after the painted gypsum board surface was relatively dry. They were probably dominated by a slow, solid-phase-diffusion-controlled mass transfer process. Long-term experimental data indicated that it may take as long as 3.5 years for all the VOCs to be released from the paint applied to the gypsum board.

The small chamber test results demonstrate that, when the objective of a test is to provide emissions data that are relevant to understanding a paint's emissions behavior in typical indoor environments, one should use "real" substrates such as wood and gypsum board instead of "ideal" substrates such as glass, aluminum, or stainless steel. Proper choice of substrate is therefore crucial for exposure and/or risk assessment studies involving indoor latex paints.

NRMRL also used the small chamber test method to evaluate a relatively new type of interior architectural coating, the so called "low-VOC" latex paint. Low-VOC paint has been used as a substitute for conventional latex paints to avoid indoor air pollution. Low-VOC latex paints are promoted for use in occupied hospitals, extended care facilities, nursing homes, medical facilities, schools, hotels, offices, and homes where extended evacuation of an entire building section for painting would be particularly difficult or undesirable.

Four commercially available low-VOC latex paints were evaluated as substitutes for conventional latex paints. They were evaluated by assessing both their emission characteristics and their performance as interior wall coatings. Bulk analysis indicated that the VOC contents of the four paints (which ranged from 0.01% to 0.3%) were considerably lower than those of conventional latex paints (3% to 5%). EPA Method 24 (40 CFR, 1994) for determining VOC content (commonly used by paint manufacturers) is not accurate enough to quantify the VOC contents of low-VOC latex paints for quality control and product ranking purposes. Other methods such as EPA Method 311 are more suitable, especially when individual VOC content data are needed.

The fact that "low-VOC" paint had relatively low VOC emissions was confirmed by small chamber emission tests. However, the experimental data also indicated that three of the four low-VOC latex paints tested either had some inferior coating properties or emitted hazardous air pollutants. Significant emissions of several aldehydes (especially formaldehyde, which is a HAP) were detected in emissions from two of the four paints. ASTM methods were used to evaluate the paints' coating performance including hiding power, scrub resistance, washability, drying time, and yellowing. The results indicated that one of the four low-VOC paints tested showed performance equivalent or superior to that of a conventional latex paint used as control. It was concluded that low-VOC latex paint can be a viable option to replace conventional latex paints for prevention of indoor air pollution. However, certain paints marketed as "low-VOC" may still emit significant quantities of air pollutants, including HAPs. In addition, some of these paints may not have performance characteristics matching those of conventional latex paints.

Due to the use pattern of low-VOC paints proposed by their manufacturers (i.e., partial occupancy during painting and immediate re-occupation after painting), the intimate exposure of sensitive occupants to the low-VOC latex paint emissions (especially to HAPs such as formaldehyde) is of special concern. Long-term environmental chamber tests were performed to characterize the formaldehyde emission profiles of a low-VOC latex paint. The formaldehyde emissions resulted in a sharp increase of formaldehyde concentrations within the chamber, rising to a peak followed by transition to a long-term slow decay. Environmental chamber data indicated that formaldehyde emissions from a low-VOC latex paint can cause very high (several ppm) peak concentrations in the chamber air. When the paint was applied to gypsum board, the formaldehyde emissions decayed very slowly after the initial peak, and the emission lasted for more than a month. The results of these tests allowed for the development of exposure assessment emissions models to facilitate pollution prevention efforts to reduce the amount of formaldehyde released by low-VOC paints.

A semi-empirical first-order decay in-series model was developed to interpret the chamber data. The model characterized the formaldehyde emissions from the paint in three stages: an initial "puff" of instant release, a fast decay, and a final stage of slow decay controlled by a solid-phase diffusion process that can last for more than a month. The semi-empirical model was used to estimate the amount of formaldehyde emitted or remaining in the paint. It also predicted the initial peak concentration of formaldehyde and the time necessary for the formaldehyde to become depleted from paint. Once the activity patterns of building occupants were defined, the model was used for exposure risk assessment.

Additional small chamber tests were performed to investigate the major sources of formaldehyde in the paint. Through comparing emission patterns and modeling outcomes of different paint formulations, a biocide used to preserve one of the paints was identified as a major source of the formaldehyde emissions. Chamber test results also demonstrated that paint reformulation by replacing the preservative with a different biocide for the particular paint tested resulted in an approximately 55% reduction of formaldehyde emissions. However, since other sources (e.g., additives and binders) of formaldehyde are present in the paint, biocide replacement can reduce only the long-term emissions. Short-term generation of high concentrations of formaldehyde remains a problem. Additional research is needed to identify other potential sources of formaldehyde to completely eliminate formaldehyde emissions from low-VOC paints.

Overall Conclusions

A standard test method was developed to characterize the VOC, including HAP, emissions from interior architectural coatings. The advantages of the developed method and the usefulness of the experimental data it can generate were demonstrated by extensive tests focused on two types of commercially available and commonly used interior architectural coatings: latex and alkyd paints. The experimental data generated by this test method can be used to estimate emission rates, to compare emissions from different products, to predict a paint's effects on IAQ and exposure levels, and to evaluate the effectiveness of risk management options. The test method can also be used as a pollution prevention tool to assist paint manufacturers in reducing or eliminating VOC emissions from their products.